



Optimal design and characterization of sulfide-modified nanoscale zerovalent iron for diclofenac removal



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ABSTRACT

Noble metal catalyzed nanoscale zerovalent iron (nZVI) has shown some promise in degrading pharmaceuticals, but it still suffers from inactivation caused by common anions. In this study, sulfidation was adopted to enhance diclofenac (DCF, an emerging groundwater pollutant) removal under aerobic conditions in the presence of common anions. X-ray adsorption near edge structure (XANES) analysis shows that dithionite is not only able to sulfurize nZVI, but also stimulates the crystal growth of Fe(0) and restrains FeOOH formation to some degree. Except in CaCl₂ solution, certain extent of sulfidation can inhibit the aggregation and sedimentation of nZVI in aqueous media with common ions and anions. While pristine nZVI achieves only 21.2% DCF removal, the optimal sulfide-modified nZVI (S-nZVI) shows 73.5% DCF removal under near neutral condition (pH ~6.5), and the maximum removal could reach 85.9% at pH 4.5. Mechanism study shows that a heterogeneous layer composed of iron sulfide and iron oxide restricts the direct reaction between oxygen and Fe(0), but facilitates electron transfer from Fe(0) core to Fe(III), producing considerable amount of surface bound Fe(II). Electron Paramagnetic Resonance spectroscopy (EPR) analysis and quenching experiments further demonstrate that sulfidation catalyzes dissolved molecular oxygen activation through one-electron transfer. Moreover, sulfidation can lower the negative impact of common anions and humic acid on DCF removal, and S-nZVI is capable of removing DCF in simulated groundwater efficiently. This study provides fundamental understanding on the sulfur catalyzed oxidation of DCF under aerobic conditions.

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1. Introduction

Diclofenac (DCF) is a synthetic non-steroidal anti-inflammatory drug, which is widely used as a pain killer. Due to its widespread use and poor treatability in conventional sewage treatment plants (STPs) [1], DCF has been found in a wide range of environmental circumstances including drinking water, surface water, and groundwater [2–4]. The European Union recently included DCF in the “watch list” of emerging aquatic pollutants, and required its

environmental monitoring in member states [5]. Therefore, efficient technologies for DCF removal are needed.

Nanoscale zerovalent iron (nZVI), a green in-situ nanomaterials for both organic [6–8] and inorganic [9–11] contaminants removal, has been shown to degrade organic contaminants such as chloramphenicol [12], ibuprofen [13], 4-chlorophenol [14], under aeration conditions effectively. Mechanistic studies show that nZVI can react with molecular oxygen (O₂) to produce reactive oxygen species (ROS) [15–19], but the low yield of ROS production in nZVI/O₂ system restricts its further application. To catalyze ROS generation, organic (such as oxalate, nitrilotriacetic acid, and ethylenediaminetetraacetic acid) [20,21] and inorganic ligands (such as polyoxometalate and polyphosphate) [22–24] have been used. However, these are not stable in the presence of ROS. Modifying electron transfer on the core-shell surface of nZVI is another strategy to enhance ROS generation. Ai et al. [25] synthesized core-

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shell Fe@Fe₂O₃ nanowires, which provided more surface bound ferrous ions to catalyze O₂. Lee et al. [26] a nickel modified nZVI, and found that it yielded more oxidants compared to nZVI by restricting the direct reaction between hydrogen peroxide and the nickel-iron surface, and by catalyzing the reaction between hydrogen peroxide and dissolved Fe(II). Nie et al. [27] introduced cobalt to iron to create a bimetallic catalyst; this enhanced interfacial electron transfer due to the presence of two redox couples (Fe³⁺/Fe²⁺ and Co²⁺/Co³⁺).

Although doped noble metals can boost free radical production, catalyst poisoning is often observed when sulfide or humic acid is present in the reaction system [28]. Sulfidation of nZVI may be a better alternative to noble metal doping due to its electron conductivity [29]. In recent studies, a one-pot sulfidation method to synthesize sulfide-modified nZVI (S-nZVI) was developed and the derived nanoparticles were successfully used for metal removal [30] and rapid dechlorination of trichloroethylene (TCE) [31]. However, the atomic and molecular structure of the nanoparticles, especially the iron-sulfur cluster structure was not elucidated. For O₂ reduction catalysis, not only is the particle composition importance, but also the particle surface and size [32]. Additionally, for the application of nanomaterials in groundwater remediation, the stability of the particles need to be understood as their aggregation and sedimentation behavior may affect their pollutant removal efficiency [33,34]. However, despite a steady growth in the publications demonstrating successful lab-scale application of S-nZVI [29–31,35], systematic studies on surface chemistry, aggregation, and sedimentation behavior of the nanoparticles have not been done.

In this study, we synthesized and characterized S-nZVI nanoparticles with different iron-sulfide ratios, and investigated their reactivity towards DCF under aeration condition. Experiments were conducted over a range of pH conditions (3.5–8.5), in the presence of different anions, and in a simulated groundwater to determine potential applicable conditions for in-situ remediation. This study improves our understanding of the mechanism of O₂ activation by S-nZVI.

2. Materials and methods

2.1. Chemical reagents

Sodium borohydride (NaBH₄, 98%), dithionite (Na₂S₂O₄, 85%), anhydrous ferric chloride (FeCl₃, 99.9%), sodium hydroxide (NaOH, 99.99%), sodium chloride (NaCl, 99%), sodium nitrate (NaNO₃, 99%), sodium sulfate (Na₂SO₄, 99%), sodium bicarbonate (NaHCO₃, 99.7%), nickel sulfate heptahydrate (NiSO₄·7H₂O, 99%), disodium hydrogen phosphate (Na₂HPO₄, 99%), humic acid (HA, technical), hydrochloric acid (HCl, 37%), 5,5-Dimethyl-1-pyrrolidine *N*-oxide (DMPO, 97%), methanol (HPLC grade, 99.9%), acetic acid (HPLC grade, 99.99%) were purchased from Sigma-Aldrich. Diclofenac sodium (98% purity), was purchased from J&K Chemical Co. Ltd. (Beijing, China). All chemicals were used without further purification. Ultrapure water (18.2 MΩ·cm, Barnstead) was used to prepare all reagents and particle suspensions.

2.2. nZVI, Ni-coated nZVI and S-nZVI synthesis

nZVI, S-nZVI and Ni-coated nZVI were synthesized using methods described previously [26,30]. Briefly, 200 ml containing 7.6 g sodium borohydride and different amounts of dithionite (0, 0.25, 0.5, 0.75, 1.0 g for samples hereafter referred as nZVI, 0.25 S-nZVI, 0.5 S-nZVI, 0.75 S-nZVI and 1.0 S-nZVI, whose S/Fe molar ratio were approximate 0, 0.1, 0.2, 0.3 and 0.4, respectively) were added in a dropwise manner to 200 ml FeCl₃ (4.9 g) solution. For Ni-coated nZVI, nZVI suspension was firstly prepared, followed by addition of

nickel sulfate solution, setting Ni/Fe molar ratio to 0.5. The particles obtained were washed three times using deoxygenated water, and then separated from the aqueous phase using a magnet. Notably, at dosage of 1.0 g dithionite, part of the final material became flocculent, and we collected the magnetic part for this study. Fresh nZVI and S-nZVI nanoparticles were stored in deoxygenated water at 4 °C and used within three days.

2.3. Stability experiments

Stability of particles in natural waters and different salt solutions was investigated via time-resolved aggregation and sedimentation kinetics studies [36,37]. 400 mg/L nanoparticle stock suspensions were bath-sonicated (Branson 2510) for 30 min to disperse the particles. Measured aliquots of nanoparticle stock suspensions, salt (NaCl, NaNO₃, Na₂SO₄, Na₂CO₃, or CaCl₂), and buffer were pipetted into a cuvette, and diluted with DI water (Barnstead NANO pure Diamond, 18.2 MΩ·cm). Final concentration of nanoparticle, salt and buffer for each condition was 50 mg/L, 5 mM, and 5 mM, respectively. For studies in simulated groundwater, no further addition of buffer was performed, and the concentration of nanoparticles was 50 mg/L. Mixing was done via 5 s probe sonication with a Misonix Sonicator S-4000 (QSonica LLC). Aggregation was studied via dynamic light scattering (DLS) using Zetasizer Nano-ZS90 (Malvern, UK). Data were collected in triplicates at 30 s intervals for 1 h. Attachment efficiencies (α) were calculated by normalizing the measured initial aggregation rate constant (k) of particles in a given condition by the diffusion-limited aggregation rate constant, k_{fav} [37]. k_{fav} was determined with nZVI or S-nZVI in the presence of 5 mM CaCl₂. Sedimentation was studied via time-resolved optical absorbency (Shimadzu 1601 UV-vis spectrophotometer).

2.4. Aerobic DCF degradation experiments

The aerobic DCF degradation experiments were carried out at room temperature (25 °C) in 250 ml three-necked flask with bubbling air (800 ml/L). Typically, 6 ml of S-nZVI stock suspension (concentration ~100 g/L) were added to 194 ml solution with 10 mg/L DCF to initiate reaction. ORP and pH were monitored in real time. In experiments to determine the role of pH, solution pH was kept constant by 0.1 mM HCl or NaOH. Aliquots were collected at time intervals using syringes, and immediately filtered with 0.22 μm nylon syringe filters for high performance liquid chromatography (HPLC, Agilent 1200, Japan) analysis. In order to determine the effectiveness of aeration alone in DCF degradation, control experiments were set up in a similar manner but with no addition of S-nZVI. All the degradation experiments were conducted in triplicates.

2.5. Quenching experiments

In these experiments, various amount of quenching reagents were selectively used to quench different types of ROS. *tert*-butanol was used to scavenge all the hydroxyl radical (\cdot OH) produced in the reaction system [38], and iodide ion was used to scavenge surface-bounded \cdot OH. Sulfate radical (\cdot SO₄⁻) formation was probed using ethanol, which is a well-known quenching agent for both \cdot OH and (\cdot SO₄⁻) [39]. Superoxide radical (\cdot O₂⁻) was scavenged by 1,4-benzoquinone (BQ).

2.6. DCF removal tests in simulated groundwater

In this part, the initial concentration of DCF was set to 2 mg/L, anion concentration was set to 1 mM, and 5 mg/L humic acid was added to simulate naturally-occurring groundwater situation [40]. For better comparison, the simulated groundwater recipe is

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