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Reduction of nitrobenzene in aqueous and soil phases using carboxymethyl cellulose stabilized zero-valent iron nanoparticles

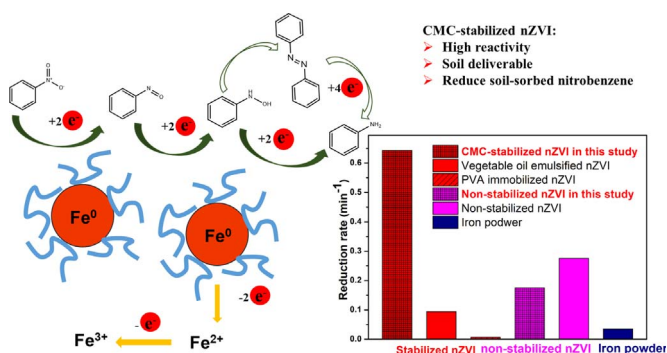Zhengqing Cai[a,b], Jie Fu[b], Penghui Du[c], Xiao Zhao[a], Xiaodi Hao[d], Wen Liu[a,c,*], Dongye Zhao[d,a,*]

[a] Environmental Engineering Program, Department of Civil Engineering, Auburn University, Auburn, AL 36849, USA
[b] Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, PR China
[c] College of Environmental Sciences and Engineering, Peking University, The Key Laboratory of Water and Sediment Sciences, Ministry of Education, Beijing 100871, PR China
[d] Beijing University of Civil Engineering and Architecture, Beijing 100044, PR China

GRAPHICAL ABSTRACT

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ABSTRACT

Zero valent iron (ZVI) has been extensively studied for reductive degradation of a host of organic pollutants including nitrobenzene (NB) in the water phase. However, little is known about the effectiveness for degrading soil-adsorbed NB, for which stabilized ZVI nanoparticles are often required to facilitate delivery of the reactive materials into contaminated soil. In this study, stabilized ZVI nanoparticles were prepared using a food-grade and low-cost polysugar, carboxymethyl cellulose (CMC), as a stabilizer; and the nanoparticles were tested for reductive degradation of NB in both water and soil phases. Compared to non-stabilized ZVI, CMC-stabilized ZVI nanoparticles degraded NB 3.7 times faster based on the apparent pseudo-first order reaction rate constant (0.643 min^{-1} for stabilized ZVI). Nearly 90% of electrons donated by ZVI were effectively used for NB reduction according to the reaction stoichiometry. Dissolved organic matter at 10–50 mg/L as TOC had little effect on NB conversion into nitrosobenzene, but decreased aniline formation rate by 30–58%; and higher pH (> 8) favored the NB reduction. Based on the reduction intermediates and computational chemistry analysis, the reaction pathway was determined, showing that CMC-stabilized ZVI nanoparticles rapidly converted NB to nitrosobenzene, but the subsequent conversion of the intermediates (nitrosobenzene → phenylhydroxylamine → aniline) was relatively slower. When tested for reductive degradation of NB pre-sorbed on a model soil, CMC-stabilized ZVI nanoparticles could completely reduce the soil-sorbed NB (0.01 mmol/g) at a ZVI dosage of 0.6 g/L, and the reaction was limited by available electrons rather than desorption. The findings indicate that CMC-

stabilized ZVI nanoparticles hold the potential to facilitate *in-situ* remediation of NB-contaminated soil and groundwater.

1. Introduction

Nitrobenzene (NB) has been widely used in herbicides, insecticides, explosives, pharmaceuticals, and dyes [1]. Consequently, NB has been widely detected in surface waters as well as in soil and groundwater [2,3]. According to a U.S. EPA survey on NB levels in the effluents from 4000 publicly owned treatment works and industrial sites, the maximum NB concentrations can be 190 mg/L, and higher NB concentrations were associated with wastewaters from organic chemicals and plastics industries [4,5]. In addition, chemical accidents are also a major source of NB release. For instance, in 2005, an explosion of petrochemical plant in Jilin, China, discharged approximately 100 tons of toxic chemicals (mainly NB) into Songhua River [6,7], and the NB concentration was found as high as 0.581 mg/L in the river even after dilution for 12 days after the accident [6].

Exposure to high concentrations of NB can harm aquatic and terrestrial organisms. The LC_{50} (50% lethal concentration) for freshwater organisms ranges from 2 to 156 mg/L [3]. NB is classified as *a likely human carcinogen by any route of human exposure* according to the U.S. EPA [8]. NB has been listed as a priority pollutant by U.S. EPA [9], and the maximum allowable concentration is 1 mg/L for wastewater discharge in the U.S. [10], and the maximum contaminant level is set at 17 μg/L in drinking water in both U.S. [11,12] and China [13].

To mitigate human exposure, researchers have studied numerous engineered technologies to degrade NB in water, such as photocatalysis [14], supercritical oxidation [14,15], combined Fenton and photochemical oxidation [16], and ultrasound-enhanced zero-valent iron (ZVI) reduction [17]. Although NB can be either oxidized or reduced, reductive degradation is more favorable than the oxidation process either biotically or abiotically due to the electron-deficient character of the nitro-group (NO_2^-) [18]. In addition, when subjected to reduction, e.g. by ZVI [19], or photocatalytic reduction [20], the primary product (aniline) is more prone to further biodegradation [2].

Reductive degradation of NB using ZVI powder or synthesized non-stabilized ZVI particles has been extensively investigated for more than 70 years [21,22]. In 1944, Hazlet and Dornfeld [22] used a HCl activated granulate iron (40 mesh) to reduce NB and other aromatic nitro compounds dissolved in benzene, the aniline hydrochloride was identified as the final product of NB reduction. Agrawal and Tratnyek [23] used 18–20 mesh acid-washed iron at a fairly high dosage of 33.3 g/L to reduce NB under anaerobic conditions, and found the reduction of both NB and nitrosobenzene (an intermediate) followed the first-order rate law (with a pseudo-first-order rate constant of $k_{app} = 0.035$ and $0.034\,min^{-1}$, respectively). Their study also showed that the reduction rate increased linearly with iron surface area concentration, giving a specific reaction rate constant of $3.9 \times 10^{-2}\,min^{-1}\,m^{-2}\,L$ [23]. Huang and Zhang [24] found that a stratified iron corrosion coating (lepidocrocite) was formed on the ZVI particle during the reduction of NB, which blocked active surface sites and thus limited further reduction of NB. Therefore, the reduction rate of NB by ZVI powder is primarily limited by the effective surface area of iron and the surface mass/electron transfer.

To our knowledge, most relevant studies so far have been focused on testing non-stabilized ZVI nanoparticles for reduction of NB in the water phase [25–27]. However, due to the strong van der Waals and magnetic interactions, non-stabilized ZVI particles aggregate rapidly into micro-millimeter scale aggregates, which not only reduces their specific surface area, but also renders the particles undeliverable in soil or other porous media due to elevated filtration effects [28]. As a result, non-stabilized ZVI particles are not only less reactive, but also non-

dispersible in contaminated aquifers to facilitate *in situ* remediation of contaminated soil and groundwater. To prevent particle aggregation and maximize the reactivity, various stabilization techniques have been developed. For instances, Tong et al. [2] immobilized ZVI nanoparticles on a nylon membrane to treat NB in groundwater, and found that the supported ZVI exhibited a higher reactivity ($k_{app} = 2.28\,h^{-1}$) toward NB at an iron dosage of 32.5 mg/L. Others loaded ZVI nanoparticles on PVA microspheres [29], organobentonite [30] and montmorillonite [31] to prevent aggregation and maximize reactivity. However, these supported materials are only suitable for treating contaminants in water, but hardly deliverable into contaminated soil.

To facilitate soil delivery of ZVI nanoparticles for *in situ* degradation of soil-sorbed contaminants, He et al. [32,33] developed a pre-aggregation stabilization technique using carboxymethyl cellulose (CMC) as a "green" and low-cost stabilizer. CMC is a modified polysaccharide carrying dense carboxymethyl groups with a p*K*a value of 4.3. Due to its strong interactions with the ZVI surface and highly negative charges, CMC can effectively stabilize ZVI nanoparticles through concurrent steric and electrostatic repulsion mechanisms. Bench- and field-scale studies have demonstrated that CMC-stabilized ZVI nanoparticles are not only more reactive than the non-stabilized counterparts, but also more deliverable in soil [34–36]. For instance, the TCE degradation rate by CMC-stabilized ZVI nanoparticles (doped with 0.1% of palladium) was reported to be 17 times faster than the non-stabilized counterparts in the aqueous phase, and column tests showed that the CMC-stabilized nanoparticles are readily transportable in a loamy sand soil [32]. Moreover, field push-pull tests confirmed that CMC-stabilized ZVI nanoparticles were mobile in saturated sediments, but appeared to lose mobility with time due to the interactions with sediments [37]. In a pilot-scale field experiment [34], CMC-stabilized ZVI nanoparticles were tested for *in situ* destruction of various chlorinated solvents in the subsurface. The results showed that CMC-stabilized ZVI can be delivered into contaminated source zone under a minimal hydrostatic pressure (< 5 psi), and the nanoparticles showed nearly the same transport pattern as the tracer when monitored at 10 ft down-stream. While CMC-stabilized ZVI nanoparticles have been widely studied for reductive dechlorination in groundwater; the effectives for reduction of NB, especially for soil-sorbed NB, has not been investigated. In fact, very little information is available on the use of stabilizer-modified ZVI for NB degradation. Dong et al. [27] modified ZVI nanoparticles by coating emulsified vegetable oil membrane on the surface for NB degradation. Although the materials were claimed as oil-phase dispersible, the reactivity was decreased by a factor of 3 compared with the non-stabilized ZVI.

Environmental factors, such as dissolved organic matter (DOM) and pH, can affect the effectiveness of ZVI nanoparticles. For instance, Tong et al. [2] observed that the NB reduction by ZVI supported on PEG/nylon membrane was more effective at lower pH (pH = 3) and the formation of iron hydroxide precipitates at higher pH impedes the reactivity. DOM is known to interact with ZVI particles and inhibit TCE degradation [38]. While such effects are expected to be lower for CMC-stabilized ZVI nanoparticles, the relevant information is limited.

NB has moderate adsorption potential to soil (log $K_{ow} = 1.85$) [39]. Consequently, NB in the environment is subject to soil adsorption, yet the soil-sorbed NB may be slowly released back into groundwater, posing a long-term threat to the environmental and human health. From a remediation standpoint, the desorption and/or diffusion rates of soil-sorbed NB may affect the availability of NB for reacting with the reactive media (e.g., ZVI). Moreover, the soil matrix can hinder the mass transfer of ZVI nanoparticles to the target contaminants. In