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Rapid removal of selenate in a zero-valent iron/Fe_3O_4/Fe^{2+} synergetic system

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ABSTRACT

Batch experiments were conducted to investigate selenate reduction in a hybridized zero-valent iron (ZVI or Fe^0) system that was easily created by mixing magnetite and Fe^{2+} with ZVI particle (20 mesh) and preconditioning for 24 h prior to selenate addition. The performance of the hybrid ZVI/Fe_3O_4/Fe^{2+} system (hZVI) were compared with those of non-hybrid (ZVI, Fe^{2+} and Fe_3O_4 alone) or partial-hybrid systems (ZVI/Fe^{2+}, Fe_3O_4/Fe^{2+} and ZVI/Fe_3O_4). The results showed that precondition of 24 h significantly increased the reactivity of hZVI towards selenate reduction possible due to the formation of reactive interface between ZVI and magnetite. hZVI achieved the most effective selenate removal than any of other systems. ZVI/Fe_3O_4/Fe^{2+} was a synergetic system, in which any constituent was indispensable for rapid removal of selenate. ZVI was the primary electron donor for selenate reduction. Fe^{2+} instead of acidic pH (H^+) participated in selenate reduction together with ZVI. Moreover, Fe^{2+} rejuvenated the passivaed surface of ZVI and magnetite, and thus sustained the reactivity of hZVI for rapid removal of selenate. Magnetite served as the primary reaction sites for selenate removal. Se speciation extraction and X-ray photoelectron spectroscopy evidences indicated stepwise reduction of Se^{VI} to Se^{IV} and then to Se^0 or Se^{-II} in the hZVI system. Findings of this study could help develop an hZVI technology suitable for treating various selenium-contaminated wastewaters.

1. Introduction

Selenium (Se), an essential trace nutrient for many living organisms including humans, is toxic at elevated level [1]. Anthropogenic activities such as mining, smelting, oil refineries, coal-fired power plants, and agriculture runoff are the predominant sources in the natural aquatic environment [2,3]. For the common pH and redox conditions of most soil and aquatic environments, Se^{IV} and Se^{VI} are the dominant forms [4]. Selenite tends to adsorb onto soil minerals, particularly onto iron/aluminum-containing minerals [5,6], both of which are very abundant in the Earth. Selenate; however, a highly soluble and chemically stable compound with higher bioavailability, exhibits only a weak adsorption affinity to most solid surfaces and attenuates slowly in the environment [2,7].

Multiple technologies have been explored for the remediation of Se-contaminated water and wastewater. Adsorption, coagulation, membrane filtration, ion exchange, biological and chemical reduction are all the methods currently used [1,3]. But high operating and maintenance costs for adsorption, coagulation, ion exchange and membrane filtration limit their wide application. Biological technology is a promising technology for Se contamination remediation, but its potential formation of highly toxic organic Se from biological treatment remains a concern [8].

Among the various chemical reduction technologies, zero-valent iron (ZVI) based technology is a promising approach due to its relatively low cost and toxicity [9,10]. It has been widely used for *in-situ* and *ex-situ* remediation of various organic and inorganic

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contaminants [11,12]. ZVI was capable of removing selenate from water via reduction, co-precipitation and adsorption [10]. However, the practicability of the process is markedly diminished by the iron surface passivation problem, and then fast loses its reactivity. In order to reduce or inhibit ZVI surface passivation and thus enhance ZVI reactivity and longevity, some additives were added to form a combined system, for example bicomponent system such as ZVI/sand [13], ZVI/Fe_2O_3 [14], ZVI/activated carbon [15], ZVI/MnO_2 [16] and ZVI/Fe_3O_4 [17,18], triple component system such as ZVI/Fe_2O_3/Fe^{2+} [19] and ZVI/Fe_3O_4/graphene [20]. All of these additives could enhance ZVI reactivity in some degree towards specific contaminant removal. Among all the additives, Fe_3O_4, a semiconductor with special electrical property, and Fe^{2+} are corrosive products from ZVI, both of which are reactive species in ZVI system [21]. Magnetite (Fe_3O_4) alone has a limited capacity for selenate adsorption [22] or for selenite redox reduction [23]. Surface-bound Fe^{II} was found to be effective for reductive removal of selenite [24], but it is not reactive for selenate reduction.

The strategy of augmenting a ZVI system with externally-supplied Fe^{2+} to overcome ZVI surface passivation was highly effective for trichloroethylene degradation [25], nitrate [26] and selenate reduction [27] by ZVI. The primary role of Fe^{2+} was to facilitate ferric (hydr) oxides, the passive corrosion products, transformation to magnetite, and thus enhanced selenate reduction by ZVI [27]. Similar to Fe^{2+}, other transition metals such as Mn^{2+} and Co^{2+} also enhanced selenate removal by ZVI [28]. As an electron-conducting iron oxide, magnetite can mediate redox reactions between ZVI and pollutants [18]. The previous study concluded that both Fe^{2+} and Fe_3O_4 are very important for pollutants degradation by ZVI [26], but they did not demonstrate ZVI/Fe_3O_4/Fe^{2+} as an integral system by strictly controlled experiments. Moreover, our studies showed ZVI/Fe_3O_4/Fe^{2+} hybrid system exhibited highly effective performance for heavy metals and nitrate reduction [29,30].

Based on the understanding of the important roles of Fe^{2+} and magnetite in overcoming ZVI surface passivation and sustaining ZVI system's reactivity for contaminants reduction, we hypothesized that introducing a separate magnetite phase into a ZVI/Fe^{2+} system to form a hybridized ZVI/Fe_3O_4/Fe^{2+} system could further enhance the system reactivity for contaminant degradation such as selenate reduction. The objectives of this study were (1) to evaluate the efficiency of the hZVI system for selenate removal in comparison with non-hybrid systems; and (2) to provide some basic understandings on the roles of magnetite and Fe^{2+} as well as selenate reduction mechanisms in the hZVI system through carefully controlled batch tests and spectroscopic evidences.

2. Materials and methods

2.1. Materials

All chemicals used were analytical reagent grade. All reagent solutions were prepared with deoxygenated deionized (DDI) water (E-pure D4641, USA) and stored in an anaerobic chamber containing an atmosphere of 95% N_2/5% H_2 with catalytic oxygen gas removal system (Coy Laboratory, USA). The DDI water was made by N_2 (>99.99%) bubbling for 1 h to remove dissolved oxygen, followed by stabilizing 72 h in the anaerobic chamber before use to remove DO completely. Stock solutions of $SeO_4{}^{2-}$ and Fe^{2+} were prepared with Na_2SeO_4 (>99.8%, Johnson Matthew) and $FeCl_2{\cdot}4H_2O$ (J.T. Baker), respectively. Zero-valent iron grains of 20 mesh (>99.2%, Johnson Matthey) had a specific surface area of 0.073 m^2/g, which was measured by BET nitrogen absorption analysis (Autosorb-6, Quantachrome, USA). Magnetite powder (>95%) with a particle size range of 0.1–0.5 μm and a specific surface area of 2.53 m^2/g was purchased from Strem Chemicals, USA.

2.2. Batch experiments

During the preliminary experiment, unintentionally, we found that the precondition of ZVI–Fe_3O_4–Fe^{2+} hybrid system prior to selenate addition could significantly increased hZVI reactivity towards selenate removal. Longer time duration precondition resulted in higher reactivity of hZVI. Thus, the effect of incubation duration on the reactivity of hZVI was investigated firstly.

Batch experiments were conducted using 12-mL serum bottles as reactors in the anaerobic chamber. In the preliminary test, the reactors, each pre-filled with 0.100 ± 0.001 g ZVI grain and 0.100 ± 0.001 g magnetite powder, were transferred into the anaerobic chamber, followed by adding with designed volumes of ferrous stock solution and DDI water up to 10 mL in total with a concentration of 0.5 mM Fe^{2+}, and then sealed with rubber stoppers and aluminum crimps. The reactors were then placed in a rotary tumbler for complete mixing at 30 rpm and room temperature ($21 \pm 2\,^{\circ}C$) in the dark for precondition. After preconditioning the hZVI system for 0, 2, 6, 12, 24 and 48 h, respectively, 50 μL selenate stock solutions was added into each reactor using a micro-syringe, resulting in 0.253 mM selenate (or 20 mg/L as Se) in 10.05 mL reactive mixture. At designed time interval, three reactors were withdrawn as triplicate for pH, dissolved selenate, selenite and Fe^{2+} determination after filtration through 0.2 μm membranes. The result of preliminary test showed that 24 h precondition duration was enough to activate the hZVI system. Thus, 24 h pretreatment time was chosen for further experiment to probe the effect of other parameters.

Same process as above was performed but just added various amount of Fe^{2+} and only pretreated 24 h prior to selenate addition. Moreover, six control experiments were conducted separately on non- or partial-hybrid systems of ZVI-only, Fe_3O_4-only, Fe^{2+}-only, ZVI/Fe_3O_4, ZVI/Fe^{2+}, and Fe_3O_4/Fe^{2+} to compare with the hZVI system. All test results were reported as an average with a standard deviation bar from triplicate reactors.

To characterize the effect of precondition duration on the hZVI, the Fe^{II}/Fe^{III} ratio of the suspended solid in the hZVI after precondition with different time was determined by chemical analysis because XRD could not distinguish the difference of microstructure of hZVI after preconditioning different time duration. Described as in the preliminary experiment mentioned above, a serial of reactors containing 10 g/L ZVI, 10 g/L Fe_3O_4, and 0.5 mM Fe^{2+} were incubated 0, 2, 6, 12, 24 and 48 h. After pretreatment, three reactors as triplicate were transferred to the anaerobic chamber before open the cover. After settling 2–3 min, a small amount of surface suspension (~0.5 mL) was gently collected by syringe to avoid collecting iron particles. Only some small size of corrosion products and magnetite were suspending after settling 2–3 min. They settled very slowly. The solid was retained on a filter membrane by filtration and rinsed with 5 mL 0.2 M acetic acid to remove surface-bound Fe^{2+}, followed by rinsing three times with DDI to remove residual acetic acid. Then the membrane together with the solid was placed in a new reactor and transferred to the anaerobic chamber quickly, followed by adding 10 mL 3 M deoxygenated HCl to dissolve the solid for Fe^{2+} and total iron determination after filtration.

Sequential dosing tests were performed to assess the role of dissolved Fe^{2+} in the hZVI system and the reusability of hZVI for selenate removal. Some procedure was described in previous study [27]. Another dose of selenate and Fe^{2+} were added once they were exhausted. When dissolved Fe^{2+} was exhausted, the reactors were split into three groups for three parallel tests: (1) the first group was augmented with 0.50 mM Fe^{2+}; (2) the second group with 1.0 mM