



Influence of a thin aluminum hydroxide coating layer on the suspension stability and reductive reactivity of nanoscale zero-valent iron

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ABSTRACT

A novel structured material, aluminum hydroxide-coated nanoscale zero-valent iron (NZVI@Al(OH)₃), was synthesized to improve the applicability of NZVI in environmental remediation. Using a rate-control precipitation method, the surface of NZVI was covered with a thin shell of amorphous Al(OH)₃. ζ-potential of NZVI under a weak alkaline condition became positive after coating with the Al(OH)₃ shell. NZVI@Al(OH)₃ performed remarkably higher suspension stability in aqueous phase than bare NZVI, owing to the increased electrostatic repulsion and the reduction of magnetic attraction between the NZVI@Al(OH)₃ particles. Results of H₂ generation test indicated that the pH buffering capacity of the Al(OH)₃ shell and the enlarged surface area benefitted the reductive reactivity of NZVI@Al(OH)₃. Additionally, the adsorption capability of the positive Al(OH)₃ shell facilitated the reduction and detoxification of contaminants on the NZVI surface. Consequently, the core-shell structure dependent modification with a thin inorganic shell with multiple functions is a promising design for environmental nanomaterials, and the NZVI@Al(OH)₃ synthesized in this study is a feasible and environmentally benign material for environmental remediation.

1. Introduction

The high reactive surface area (10–100 m²/g) of nanoscale zero-valent iron (NZVI) makes it an attractive material for various environmental applications, including the removal of contaminants such as hexavalent chromium [1,2], arsenic [3], chlorinated aliphatics [4], or nitro-aromatics [5] from the subsurface environment. However, strong magnetic attraction between the NZVI nanoparticles causes them to agglomerate into larger clusters, or aggregates, in aqueous solution [6]. The increased size of these clusters diminishes their effective surface area, and makes it difficult for NZVI particles to migrate through water-saturated porous media for much-needed *in-situ* remediation [7]. The precipitation of iron oxidation products on the NZVI surface during application also rapidly decreases the reactivity of the NZVI [8].

To prevent the aggregation of NZVI dispersions, a wide array of polyelectrolytes have been used to stabilize NZVI in laboratory and field studies [9,10]. Adsorption of polymers on the NZVI surface can introduce a large negative charge, thereby increasing the electrostatic repulsion between particles to prevent aggregation. An improvement in colloidal stability makes more of the surface area available for chemical reactions. Another way to increase the reactivity is to dope NZVI with noble metals to form bimetallic or trimetallic nanoparticles [11,12]. Doped noble metals can accelerate electron transfer from the Fe⁰ anode

to the noble metals, and thus improve the formation of atomic hydrogen for chemical reactions [11].

However, concerns have been raised over the environmental compatibility and toxicity of the polymers and noble metals involved in the NZVI synthesis and application [10]. Therefore, using environmentally benign modifications for NZVI seems to be a more attractive and practical approach. Mg-aminoclay [13], pillared bentonite [14] and porous carbon [15] can be applied to support NZVI, which can prevent the NZVI particles from aggregating and induce the mass transfer of contaminants from the solution onto the NZVI surface. Electromagnetic induction has been used to accelerate dichlorination with NZVI [16,17]. However, these approaches always require large amounts of the modification materials (several times the quantity of NZVI by weight) or sophisticated techniques, which increases the technical difficulty and the cost of NZVI modification and application.

Aluminum hydroxide (Al(OH)₃) is a safe and environmentally abundant material that has been widely used as a low-cost, environmentally friendly adsorbent [18]. Al(OH)₃ nanoparticles have their zero point of charge from around 9–11.5 [19,20], and normally they are positively charged in water or in the subsurface environment (pH 6.5–8). Therefore, negatively charged solutes such as phosphate [21], arsenate [22], or fluoride ions [23] can be effectively adsorbed and removed from the aqueous environment by Al(OH)₃. Zhao et al.

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(2010) used Fe_3O_4 as a magnetic core to support $\text{Al}(\text{OH})_3$ for quicker adsorption and separation of contaminants from water [23]. With a covering of non-magnetic $\text{Al}(\text{OH})_3$ on the Fe_3O_4 surface, the magnetic attraction between particles can be greatly weakened.

The surface properties and non-magnetic features of $\text{Al}(\text{OH})_3$ make it a promising material for improving the stability and chemical reactivity of NZVI. However, no techniques involving the coating of NZVI particles with such an inorganic substance have yet been reported, and the results of such coating have not been determined. In theory, the core-shell structures can be more effective than composites and/or supportive structures for modifying the surface properties and the intrinsic reactivity of the core materials [24,25]. In this study, we developed a new technique to synthesize NZVI with a thin $\text{Al}(\text{OH})_3$ coating shell, thereby forming novel $\text{Al}(\text{OH})_3$ -coated NZVI (NZVI@ $\text{Al}(\text{OH})_3$) nanoparticles. The stability of these nanoparticles in suspension was evaluated, and their reactivity was systematically studied with H_2 generation and 4-nitrophenol (4-NP) reduction. The coating of NZVI particles with a proper amount of $\text{Al}(\text{OH})_3$ was found to be highly effective for improving the suspension stability, chemical reactivity and longevity of NZVI. The core-shell structure and material properties of NZVI@ $\text{Al}(\text{OH})_3$ were also characterized to study multiple mechanisms influencing the improvements.

2. Materials and methods

2.1. Materials

FeCl_3 , NaOH ($\geq 99\%$), and HCl (37%) were obtained from VWR International; NaBH_4 (98%) and 4-NP (99%) were purchased from Acros; ethanol and methanol (ACS, ISO, Reag. Ph. Eur.) were obtained from Merck; and anhydrous AlCl_3 (99%) and NaHCO_3 (99.5%) were purchased from Sigma-Aldrich and UNI-CHEM, respectively.

2.2. Synthesis of BNZVI and NZVI@ $\text{Al}(\text{OH})_3$

Bare NZVI (BNZVI) was prepared by chemical reduction of FeCl_3 with NaBH_4 , following the borohydride reduction method described previously by others [26,27]. In brief, a 0.4 M NaBH_4 aqueous solution was added into 71.5 mL of a 0.01 M FeCl_3 aqueous solution at a rate of 4.5 mL/min as controlled by a peristaltic pump (Longer Pump BT100-2J) and then mixed with mechanical stirring. After a 10-min injection and reaction period, the BNZVI particles that formed in the solution were separated by a magnet, and washed three times with water and three times with ethanol in a nitrogen gas atmosphere. The ethanol washing was assisted with sonication (40 kHz, 100 W) to completely remove impurities.

A rate-control precipitation method was applied to coat $\text{Al}(\text{OH})_3$ onto the NZVI surface, thereby synthesizing $\text{Al}(\text{OH})_3$ -coated NZVI particles, or NZVI@ $\text{Al}(\text{OH})_3$. The coating was conducted in a 100-mL flask reactor, sealed with a cap with needles inserted for chemical injection and atmospheric control. To protect the NZVI from oxidation, the coating process was performed in an N_2 atmosphere in the flask, at room temperature ($23 \pm 1^\circ\text{C}$). First, 20 mg of BNZVI in 40 mL of ethanol was sonicated for 5 min. An ethanol solution of AlCl_3 with an Al concentration of 1 g/L was then injected into the BNZVI slurry in the flask. To bring about different thicknesses of coating, the Al dose in relation to the Fe content ($m_{\text{Al}}/m_{\text{Fe}}$) was varied from 3 to 10 wt%; this corresponded to the AlCl_3 concentration varying from 0.55 to 1.76 mM in the BNZVI slurry. Lastly, 3 mL of NaOH ethanol solution was introduced into the BNZVI slurry via a syringe pump (Longer Pump TJ-3A) at an injection rate of 1 mL/min. The overall molar ratio of OH to Al was controlled at 3. Sonication was used to keep the NZVI particles well separated during the whole coating process. Upon completion, the particles were thoroughly washed with methanol and ethanol to remove NaCl . The synthesized BNZVI and NZVI@ $\text{Al}(\text{OH})_3$ were both stored in ethanol and used within one day to prevent oxidation. The

NZVI stock suspension was washed with deoxygenated DI water or blow-dried with N_2 gas, when needed, before use. For comparative tests, particles of iron oxides and pure $\text{Al}(\text{OH})_3$ were also synthesized, following the methods described in Supporting Information (SI).

2.3. Characterizations

The morphology and structural details of the obtained BNZVI and NZVI@ $\text{Al}(\text{OH})_3$ particles were examined by using a scanning electron microscope (SEM, Hitachi S-4800 FEG) and a transmission electron microscope (TEM, FEI Tecnai G2 20 S-TWIN). The BNZVI and NZVI@ $\text{Al}(\text{OH})_3$ were further characterized by X-ray diffraction (XRD, D8 Advance diffractometer) for their crystalline features, by X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5600) for their surface compositions, by vibrating sample magnetometer (VSM, Lake Shore 7037) for the magnetism saturation values (M_s), and by a BET surface area analyzer (Beckman Coulter SA3100) for their specific surface areas. An acid digestion was also used to determine the resulting coating mass of $\text{Al}(\text{OH})_3$ (Al/Fe, wt%) for different Al coating doses by digesting nanoparticles in a 2% HCl aqueous solution. Concentrations of dissolved Fe and Al ions were measured by an inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 8300). A Delsa Nano C Particle Analyzer (Beckman Coulter) was used to measure the particle size (diameter, D) distributions and ζ -potentials of both the BNZVI and NZVI@ $\text{Al}(\text{OH})_3$. NZVI particles were suspended in a 1.0 mM deoxygenated NaHCO_3 aqueous solution (pH = 8.3 ± 0.1) and then sonicated for 20 s before taking the measurements.

2.4. Sedimentation test

The sedimentation test was conducted to evaluate the stability of the BNZVI and NZVI@ $\text{Al}(\text{OH})_3$ in suspension [6]. This test was conducted in a 1-cm optical cuvette, which was also used for indication of particle concentrations by UV-vis spectrophotometry (Biochrom Libra S12). Typically, a BNZVI or NZVI@ $\text{Al}(\text{OH})_3$ particles with a NZVI concentration of 0.1 g/L were suspended in a deoxygenated 1.0 mM NaHCO_3 solution. The cuvette was filled with 2 mL of the solution, so that the UV-vis light could illuminate the top region of the dispersion in the cuvette during the sedimentation test. The optical absorbance of a colloidal suspension can be well correlated with the colloidal concentration [6]. For a sedimentation test on the NZVI particles in suspension, after a 20-s sonication, the dispersion was monitored at 508 nm to record the change in its optical absorbance (I_t) over time.

2.5. Reactivity test – H_2 generation

The batch H_2 evolution test was conducted under an anaerobic condition in 126-mL serum bottles to evaluate the reactivity of NZVI with different masses of $\text{Al}(\text{OH})_3$ coating following the approach previously described [28]. Typically, a serum bottle was filled with 80 mL of deoxygenated dispersion containing 0.1 g/L NZVI and 1.0 mM NaHCO_3 . Operated in a glove box filled with pure N_2 gas, the bottle was capped with a rubber stopper and an aluminum flip-off cap, and thereby the headspace of the serum bottle was initially filled with pure N_2 . The test bottles were then placed on a shaker at room temperature ($23 \pm 1^\circ\text{C}$). A 200 rpm rate of shaking was applied to induce the reaction and perform the test. During the reaction, H^+ in water was reduced by the NZVI to produce H_2 . Gas samples of 50 μL were taken from the headspace at various time intervals to quantify the H_2 production. After the test, a deoxygenated 37% HCl aqueous solution was injected into the bottles to digest all Fe^0 . Assuming that the stoichiometry molar ratio of Fe^0 and produced H_2 is 1:1, the total H_2 production in the headspace was measured to indicate the total amount of Fe^0 involved in the reaction [29,30]. The concentration of H_2 produced in the headspace of the test vial was measured in term of the volume fraction (vol

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