Simultaneous Oxidation and Reduction of Arsenic by Zero-Valent Iron Nanoparticles: Understanding the Significance of the Core—Shell Structure

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Increasing evidence suggests that nanoscale zerovalent iron (nZVI) is effective for the removal of arsenic from contaminated water, but the immobilization mechanism is unclear. In particular, the existence of As(0) on the nanoparticle surface has been proposed but not substantiated in prior studies. By using high-resolution X-ray photoelectron spectroscopy (HR-XPS), we report clear evidence of As(0) species on nZVI surfaces after reactions with As(III) or As(V) species in solutions. These results prove that reduction to elemental arsenic by nZVI is an important mechanism for arsenic immobilization. Furthermore, reactions of nZVI with As(III) generated As(0), As(III), and As(V) on the nanoparticle surfaces, indicating both reduction and oxidation of As(III) take place with nZVI treatment. The dual redox functions exhibited by nZVI are enabled by its core—shell structure containing a metallic core with a highly reducing characteristic and a thin amorphous iron (oxy)hydroxide layer promoting As(III) coordination and oxidation. Results demonstrated here shed light on the underlying mechanisms of arsenic reactions with nZVI and suggest nZVI as a potential multifaceted agent for arsenic remediation.

Introduction

Arsenic is a well-known carcinogen, and arsenic contaminated groundwater is prevalent around the world, particularly in South Asia. In the United States, groundwater supplies about one-third of the country’s drinking water. However, there are many locations in the southwestern states where groundwater contains arsenic concentrations in excess of the World Health Organization (WHO) guidelines and the U.S. Environmental Protection Agency (USEPA) drinking water standard of 10 μg/L.1–3 On a worldwide scale, it has been estimated that over 137 million people in more than 70 countries are affected by arsenic poisoning of drinking water.4

The principal forms of arsenic in natural waters are arsenate [As(V)] and arsenite [As(III)]. Arsenate exists as oxyanions (H₂AsO₄⁻ or HAsO₄²⁻) in a pH range of 2–12, while arsenite remains as neutral undissociated species (H₃AsO₃) below a pH of 9.2.5,6 As(III) oxidation to As(V) by dissolved oxygen alone is kinetically slow.6,7 Traditional remediation technologies rely largely on adsorption for removing arsenic in water using materials such as iron oxides, activated alumina, granular activated carbon, and silica with various degrees of success.5,10 Recent studies suggest that nanoscale zerovalent iron (nZVI), a highly reactive engineered nanomaterial extensively evaluated for groundwater remediation and hazardous waste treatment, is effective for arsenic removal in water, but the reaction mechanisms of arsenic on nZVI are not well understood. Because of nZVI’s strong reducing capabilities toward chlorinated hydrocarbons and numerous inorganic contaminants, it is expected that both arsenic(V) and arsenic(III) are amenable to reduction by nZVI. Prior publications indicate, however, the transformation of As(V) to As(III) is kinetically slow, and no clear evidence for the formation of elemental arsenic [As(0)] has been published so far.5,11,12 On the other hand, several recent studies suggest that, instead of reduction, oxidation of arsenic(III) is the prevalent reaction under oxic conditions through peroxide or radicals generated by Fenton reactions.8,13 The majority of these studies rely on solution phase arsenic analysis, and there is a lack of studies investigating arsenic speciation on nZVI surfaces that can provide more direct evidence of the reactions between nZVI and arsenic.

The objective of this work was to examine surface reactions of arsenate and arsenite with nZVI by using high-resolution X-ray photoelectron spectroscopy (HR-XPS), which can provide valuable information about the valence states and abundance of various arsenic species on nanoparticle surfaces. The results are interpreted in light of the fundamental structure of nZVI, and the implications of these findings on arsenic treatment and remediation are discussed.

Materials and Experimental Methods

The iron nanoparticles (nZVI) used in this study were prepared from sodium borohydride reduction of ferric iron as reported previously.14,15 The nanoparticles have a mean diameter of 60 nm and a BET-measured surface area of 30 m²/g.14 Reagent grade sodium arsenate or arsenite was used to make As(III) or As(V) stock solutions. To eliminate dissolved O₂ as a potential oxidant in these solutions and to simulate prevalent anoxic conditions encountered in groundwater environments,
the arsenic solutions were purged with high-purity N₂ for 30 min prior to adding nZVI. HR-XPS analysis was performed on reacted nZVI residues using a Scienta ESCA 300 X-ray photoelectron spectrometer. Detailed experimental procedures and details concerning XPS analysis including spectral deconvolution are available in the Supporting Information.

**Results and Discussion**

Figure 1 displays XPS spectra of the As3d region of nZVI before (a) and after reactions with As(V) (b) and As(III) (c) species, respectively. The XPS peak positions were assigned by comparison to As3d5/2 binding energies reported in the literature.¹⁶ No arsenic was detected on pristine nZVI, but As peaks were clearly detected on reacted nZVI. The XPS spectra reveal the presence of multiple arsenic valence states, viz., As(V), As(III), and As(0) on the nZVI surfaces. Curve fitting of the As peaks involved six curves, since the As3d peak for each chemical state has two unresolved components due to spin–orbit splitting corresponding to the As3d5/2 (at higher BE) and As3d3/2 (at lower BE) peaks separated by 0.7 eV (held constant herein). The relative abundance of each chemical species can be quantified from the respective peak areas. In addition, information on the total As surface composition obtained from XPS is summarized in Table S1 of the Supporting Information, and these data are used below to infer the relative extents of different reactions that occurred on nZVI surfaces.

**Reactions with As(V).** When nZVI (5 g/L) was added to 100 mg/L arsenate [As(V)] solution, significant amounts of As(III) and As(0) were detected on the nZVI surface in 24 h (Figure 1b), establishing As(V) reduction to As(III) and As(0). The amounts indicated in Figure 1 are the proportions of the respective arsenic species as percentages of the total arsenic detected. It should be noted that each of these spectra was not affected by increasing the X-ray irradiation time by a factor of 6 under the instrument conditions used in this study; i.e., XPS analysis had no observable effect on the arsenic valence state detected. We have also analyzed nZVI reacted with arsenic for up to 15 days, and the results indicate no significant change in arsenic distributions compared to samples reacted for 24 h under the same conditions. While earlier studies reported the reduction of arsenate to arsenite species by iron fillings or nanoscale ZVI with considerably slower kinetics (e.g., >30 days before As(III) was detected),⁶,¹¹ the formation of As(0) has only been suggested but not substantiated, and the predominant mechanism for As(V) uptake is generally thought to be surface sorption and precipitation.¹¹,¹⁷ The results presented in Figure 1 clearly show that nZVI is capable of reducing As(V) with reasonably fast kinetics and reduction to elemental arsenic is also a feasible mechanistic step. As will be discussed later herein, the variances in environmental conditions, in particular arsenic concentration and solution pH, and the properties of iron materials play crucial roles in determining the final arsenic speciation.

**Reactions with As(III).** When nZVI was added to an arsenite [As(III)] solution (Figure 1c), 51% of the surface-bound arsenic remained as As(III). Meanwhile, 14 and 35% of the total arsenic emerged as As(V) and As(0), respectively, indicating that both As(III) oxidation and reduction had occurred to significant extents. While As(III) oxidation by ZVI was noticed in prior studies,⁵,²² the concomitant observation of oxidation and reduction of arsenic(III) has not been reported before. This behavior implies that the nanoparticles used here have a more complex character than being a monofunctional reductant as widely acknowledged.

To understand the properties of nZVI, advanced transmission electron microscopy (TEM) techniques were used to analyze the material constituents present in individual nZVI particles. Bright field TEM imaging showed a composite layered structure comprised of a dense metallic center enclosed by a thin layer of iron oxide material (Figure 2a). Phase-contrast TEM imaging did not reveal periodic lattice fringes in the oxide layer, which suggests a disordered oxide structure (Figure 2b). The oxide outer shell appears to vary from 10 to 20 nm in thickness and has a stoichiometric composition of FeOOH, as determined previously from Fe2p and O1s XPS spectra.¹⁸ The oxide layer is thought to form instantaneously upon nZVI synthesis to passivate the highly reactive Fe⁰ core, and it may be practically viewed as an inherent part of the nanoparticle.¹⁹ The extremely thin dimension and disordered nature of the oxide layer support earlier notions that the oxide phase is able to allow electron passage via tunneling effects or defect sites,¹⁵,¹⁹ thereby conserving the reducing characteristics of Fe⁰ and accounting for As(III) reduction. On the other hand, iron oxides have been extensively studied to possess strong adsorptive ability for both
As(III) and As(V), and certain iron oxides formed from Fe\(^0\) corrosion are able to cause As(III) oxidation to As(V).\(^5,20\) In our studies, the nanoparticles are comprised of an Fe\(^0\) core and iron oxide at the interface between Fe\(^0\) and aqueous solution. The two phases are present in a nanoscale core–shell configuration that allows each component to exert its distinctive reactivity without significant kinetic constraints. The composite particles therefore possess dual properties of the two components, and this leads to unconventional chemical behavior such as the concurrent oxidation, reduction, and sorption of As(III) illustrated in Figure 1c.

**Effect of As(III) Concentrations.** The effect of arsenite concentration on the product speciation has not been examined before. Figure 3 presents results following reaction of nZVI with arsenite at different initial As(III) concentrations. The initial As(III) concentration in the solution was in the range 50–1000 mg/L. Clearly, the relative amount of As(0) formed is the greatest at the lowest initial concentration of As(III) (50 mg/L), with approximately one-half of the total arsenic present as As(0). The proportion decreased to 35% when the initial As(III) concentration was increased to 100 mg/L, and no As(0) was detected when the As(III) concentration was increased to 500 and 1000 mg/L.

The solution \(E_h\) and pH conditions corresponding to different As(III) concentrations are presented in Table S2 of the Supporting Information. The equilibrium pH changed from circumneutral (pH 8.5) to alkaline (pH 11) as the As(III) concentration increased from 50 to 1000 mg/L. The equilibrium pH was largely influenced by the starting pH, which showed an increasing trend as the As(III) initial concentration increased due to arsenite hydrolysis and the release of hydroxyl ions (AsO\(_2^-\) + H\(_2\)O → H\(_3\)AsO\(_4^+\)/H\(_2\)AsO\(_4^-\) + OH\(^-\)). The alkaline condition associated with high Ar(III) concentrations promotes ferric ion precipitation. This point is corroborated by the O1s XPS spectra of the reacted samples (Figure S2, Supporting Information), which show a pronounced increase in the OH\(^-\) peak size with increased initial arsenic loading. Iron oxide precipitates are also evident in scanning electron microscopy (SEM) images (Figure S4, Supporting Information), where the sample after reaction with 1000 mg/L As(III) exhibited extensive platelet formation resembling typical solid precipitates from iron corrosion (Figure S4c, Supporting Information). In contrast, the oxide growth was less predominant in the 100 mg/L sample (Figure S4b, Supporting Information). A further piece of evidence in support of oxide buildup comes from solution \(E_h\). The \(E_h\) potentials registered a sharp increase with As(III) concentration at 500 and 1000 mg/L. (Table S2, Supporting Information), suggesting the prevalence of iron oxidation products observed in HR-XPS and SEM at those high concentrations forms a barrier layer on top of metallic iron and diminishes the reducing capability of Fe\(^0\). Taken together, As(III) concentration exerts a pronounced effect on As(III) reduction by controlling solution chemistry and influencing the nZVI surface conditions. Formation of As(0) was more evident at lower concentrations, and it was absent at above 100 mg/L due to substantial iron oxidation and precipitate formation. Although the concentration range evaluated here is higher than arsenic occurrence in natural waters (typical range 1–5000 µg/L),\(^4\) the trend revealed in Figure 3 strongly implies that reduction of arsenite at trace levels such as in natural waters is likely to occur in the presence of nZVI. As(0) not being observed in previous studies may be attributed to instrumental limitations and the specific reaction conditions used. In those studies, relatively high As(III) concentrations were used, since conventional XPS analysis requires a significant amount of arsenic deposited on the particle surfaces to be detected. Under those conditions, As(0) formation is not favored for the reasons just mentioned above, and surface saturation with adsorbed arsenic species may attenuate the already weak As(0) signal. In the present HR-XPS study, we used a Scienta ESCA 300 instrument, which has an intense rotating anode X-ray source and enhanced signal detection utilizing a 300 mm radius hemispherical analyzer and position-sensitive detector, thereby greatly lowering the arsenic detection limit and improving the energy resolution. This enables us to study nZVI reactions with arsenic at lower initial concentrations, which are conditions more relevant to the natural systems.

Compared to reduction of As(III) to As(0), oxidation of As(III) to As(V) is less sensitive to the initial As(III) concentration (Figure 3). In all cases, As(V) exists as a minor species on the nanoparticle compared to the other two valence states. As(III) oxidation by nZVI has been reported in previous studies, although the exact mechanism remains uncertain. It is purported that more than one oxidant exists, including peroxide or radical species generated from Fe\(^0\) corrosion, hydroxide species, and iron oxides.\(^5,20–22\) Peroxide- or oxygen-containing radical generation requires dissolved O\(_2\) in an acidic medium\(^21,22\) and is not likely to be involved considering our reaction conditions. As(III) oxidation in the aqueous phase by hydroxyl ions is plausible,\(^20\) but the resultant As(V) species in the solution phase is unlikely to reattach to the nZVI surface due to surface charge repulsion between As(V) and the oxide layer at neutral to alkaline pH.\(^22\) It is more likely that As(III) was oxidized by iron oxide, which proceeded via formation of iron oxide–As(III) surface complexes.\(^5\) The lack of a distinct trend for As(III) oxidation within the concentration range studied is probably a result of several interacting effects, since the affinity of As(III) for iron oxides, the amount of iron oxides available as adsorptive sites, and the oxidation potential of iron oxides are intricately affected by pH.

The evidence for the simultaneous occurrence of oxidation, reduction, and adsorption of As(III) on the nZVI surface...
suggests that the two components of nZVI are able to bring about different reactions in parallel, which is an interesting property that has not been noted before. A time-dependent study of arsenic speciation on the nZVI surface (Figure S3, Supporting Information) provides a clue to the relative kinetics of the respective reactions. As shown in Figure S3 in the Supporting Information, As(0) accumulation is relatively slow in comparison to As(III) adsorption and oxidation. It may also be implied from the figure that the products formed initially, e.g., As(V), may be reduced back to As(III) and then to As(0); hence, there is a dynamic change in arsenic speciation at the nZVI surface on top of continuous arsenic sequestration from the aqueous phase. Additional experiments are needed to elucidate the individual reaction rates and the interrelations among these processes.

Conclusion

Simultaneous oxidation and reduction of As(III) and the reduction of As(V) to As(III) and As(0) on nZVI surfaces have been observed. The elusive As(0) species suggested in previous studies was clearly detected. The reactions can be reasonably explained on the basis of the core–shell structure of nZVI, in which the oxide outer layer and metallic core bestow distinctive mechanisms for arsenic removal. The results shown here may help in the understanding of the reaction mechanisms and the stability of arsenic on ZVI surfaces and lead to better design of arsenic sequestration technologies. In particular, in view of the conventional adsorptive methods, which are critically affected by arsenic speciation, concentration, and pH, the multifaceted functionality of nZVI exhibited here may offer a more robust and effective method for arsenic removal.

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Supporting Information Available: The Supporting Information contains a detailed description of the experimental methods utilized in these studies of the reaction of As(III) and As(V) with nZVI in solution. It provides experimental parameters and procedures used in the acquisition and curve fitting of the XPS spectra. Table S1 gives the surface composition of samples analyzed by XPS, and Table S2 provides solution pH and $E_h$ values before and after reactions. Figure S1 reports solution pH values for various initial As(III) concentrations, indicating the equilibrium conditions at which $\text{H}_2\text{AsO}_3^{-}$ dissociates into $\text{H}_2\text{AsO}_4^{-}$. Figure S2 provides O1s HR-XPS spectra obtained for different concentrations of As(III) and indicates the different species of oxygen that form the oxide thin film encapsulating the metallic iron core in nZVI. Figure S3 shows As3d HR-XPS spectra from nZVI particles reacted with 100 mg/L As(III) for different reaction times. Figure S4 gives SEM images of fresh and reacted nZVI samples. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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