Uranium(VI) reduction by nanoscale zero-valent iron in anoxic batch systems: the role of Fe(II) and Fe(III)

Sen Yan^{a,b,c,d*}, Yongheng Chen^b, Wu Xiang^a, Zhengyu Bao^a, Chongxuan Liu^d,

Baolin Deng^{c*}

^aState Key Laboratory of Bio-geology and Environmental Geology, School of Earth Sciences, China University of Geosciences, Wuhan, 430074, China

^bGuangdong Province & MOE Key Laboratory of Water Safety and Protection of Pearl River Delta, Guangzhou University, Guangzhou, 510006, China

^cDepartment of Civil & Environmental Engineering, University of Missouri, Columbia, Missouri 65211, USA

^dPacific Northwest National Laboratory, Richland, Washington 99352, USA

* Corresponding authors.

E-mail addresses: yansen2007@gmail.com (S. Yan), dengb@missouri.edu (B. Deng).

Tel: 1-509- 371-6880, Fax: 1-509- 371-6354, Pacific Northwest National Laboratory, PO Box 999, MSIN: K8-96, Richland, WA 99352, USA

Abstract

The role of Fe(II) and Fe(III) in U(VI) reduction by nanoscale zerovalent iron (nanoFe^0) was investigated using two iron chelators 1,10-phenanthroline and triethanolamine (TEA) under a CO_2 -free anoxic condition. The results showed that U(VI) reduction was strongly inhibited by 1,10-phenanthroline and TEA in a pH range from 6.9 to 9.0. For instance, at pH 6.9 the observed U(VI) reduction rates decreased by 81% and 82% in the presence of 1,10-phenanthroline and TEA, respectively. The inhibition was attributed to the formation of stable complexes between 1,10-phenanthroline and Fe(II) or TEA and Fe(III). In the absence of iron chelators, U(VI) reduction can be enhanced by surface-bound Fe(II) on nanoFe^0 . Our results suggested that Fe(III) and Fe(II) possibly acted as an electron shuttle to ferry the electrons from nanoFe^0 to U(VI), therefore a combined system with Fe(II), Fe(III) and nanoFe^0 could facilitate U(VI) reductive immobilization in the contaminated groundwater.

Keywords: Uranium(VI); nanoFe^0 ; Fe(II); Fe(III); electron shuttle

1. Introduction

Uranium contamination in groundwater has been detected at numerous sites throughout the world, including nuclear weapons manufacturing facilities (Riley and Zachara, 1992), mine tailings sites (Abdelouas, 2006; Wang et al., 2012), and agricultural evaporation ponds (Bradford et al., 1990). The solubility, and hence mobility, of uranium in the environment is controlled by its oxidation state (Abdelouas et al., 1999), which is influenced by numerous factors such as bacterial activity (Lovley et al., 1991; Suzuki et al., 2002), the mineralogy and organic content of the system (Langmuir, 1997; Wan et al., 2008; Shi et al., 2009; Latta et al., 2012; Fox et al.,

2013), and solution composition (Clark et al., 1995; Yan et al., 2010; Singh et al., 2012; Stylo et al., 2013). U(VI) is stable in oxic environments and commonly exists as soluble carbonate complexes in aerobic groundwater under neutral to alkaline conditions. The formation of anionic U(VI)-carbonate complexes (e.g., $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$) and ternary calcium-uranyl-carbonate species (e.g., $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$) has been known to increase the mobility of U(VI) (Clark et al., 1995; Hua et al., 2006; Yan et al., 2010; Stewart et al., 2011). In contrast, U(IV) is stable in the anoxic groundwater as sparingly soluble solids, even in the presence of common groundwater ligands such as carbonate, and thus tends to be relatively immobile. U(IV) is normally orders of magnitude less soluble than U(VI) under reducing conditions (Lovley et al., 1991; Suzuki et al., 2002). This difference in solubility has implications for the fate, transport, and remediation of uranium in the environment; for example, reductive immobilization of uranium could be implemented for remediating contaminated groundwater by reducing U(VI) to U(IV) (Lovley et al., 1991; Suzuki et al., 2002; Hua and Deng, 2008).

The Fe(II)–Fe(III) redox cycle is known to impact numerous geochemical redox transformations as highlighted by Stumm and Sulzberger (1992). Previous studies have confirmed the abiotic heterogeneous reduction of U(VI) by Fe(II) sorbed onto oxides and silicates surfaces (Liger et al., 1999; Jeon et al., 2005; Chakraborty et al., 2010; Fox et al., 2013), or by structural Fe(II) in pyrite (Wersin et al., 1994), mica (Ilton et al., 2006), green rust (O'Loughlin et al., 2003) and magnetite (Regenspurg et al., 2009; Latta et al., 2013) in the presence or absence of carbonate. These studies have revealed that the electron transfer reactions between U(VI) and Fe(II) are often facilitated by specific adsorption of Fe(II) and U(VI) to mineral surfaces, and generate Fe(III) oxides and U(IV). On the contrary, some other studies

found that Fe(III) in iron oxides could oxidize U(IV) and generate sorbed Fe(II) species (Sani et al., 2005; Senko et al., 2005; Ginder-Vogel et al., 2006; Ginder-Vogel et al., 2010). Previous studies have shown that U(VI) could be reduced in systems with iron filings or nanoscale zerovalent iron (nanoFe^0) (Cantrell et al., 1995; Charlet et al., 1998; Fiedor et al., 1998; Gu et al., 1998; Riba et al., 2008; Yan et al., 2010; Sheng et al., 2014), however, the role of Fe(II) and Fe(III) in the U(VI)- Fe^0 system has not been well understood. Understanding the role of Fe(II) and Fe(III) in the U(VI) reduction by nanoFe^0 is important for the use of nanoFe^0 in uranium remedial applications.

Theoretically, the role of Fe(II) and Fe(III) played in U(VI) reduction by nanoFe^0 can be probed by examining the impacts of iron-chelating agents, since iron–ligand complex formation could change the reduction potential of redox couples and thus their reactivity. Two major challenges need to be addressed for selecting chelating reagents in the system with iron in various oxidation states: 1) Fe(II) or Fe(III) should be able to form strong complex with the ligands; and 2) the selected ligands should not form strong complex with U(VI) and thus interfere with U(VI) analysis. Based on these two criteria, 1,10-phenanthroline and triethanolamine (TEA) were chosen for complexing Fe(II) and Fe(III), respectively (Brandt et al., 1954; Teixeira et al., 1999; Bobrowski et al., 2005; Luan and Burgos, 2012). Moreover, the interaction between U(VI) and surface-bound Fe(II) with nanoFe^0 was examined to obtain insights into the mechanism of U(VI) reduction by nanoFe^0 .

2. Experimental Section

All common chemicals used in this study (FeCl_2 , NaBH_4 , NaHCO_3 , 1,10-phenanthroline and TEA) were of ACS reagent grade. U(VI) standard solution (1000 mg L^{-1}) was purchased

from Sigma-Aldrich Company. Tris(hydroxymethyl)aminomethane (TRIS), which was used as a pH buffer, was obtained from BioRad Laboratory. NanoFe⁰ particles were synthesized following our previous procedure (Yan et al., 2010). The stock solutions of 1000 μ M U(VI), 500 mM NaHCO₃, 10 mM 1,10-phenanthroline, 10 mM TEA, 50 mM FeCl₂, 250 mM TRIS and nanoFe⁰ slurry were prepared in an anoxic system free of dissolved O₂ and CO₂, which was accomplished following an established procedure (Hua et al., 2006), and stored in the anoxic glovebox over 1 d prior to use. All the glassware and plastic tubes used in the experiments were cleaned by soaking in 1 M HCl for 24 h and rinsed with distilled water and then Mill-Q water.

The role of Fe(II) and Fe(III) were investigated by two sets of batch experiments. In the first set, batch systems contained nanoFe⁰, TRIS buffer, U(VI), and varying concentrations of 1,10-phenanthroline or TEA. U(VI) reduction by nanoFe⁰ was examined under various pH values (from 6.9 to 9.0) and concentrations of 1,10-phenanthroline (from 0 to 1.5 mM) and TEA (from 0 to 1.5 mM). Solution pH was controlled by 12.5 mM TRIS buffer. Experiments began by transferring desired amounts of nanoFe⁰ slurry, TRIS buffer, and 1,10-phenanthroline/TEA solution into a set of centrifuge tubes. U(VI) stock solution was then added to initiate the reaction. Each batch experiment initially contained 200 μ M U(VI), 27.6 mg L⁻¹ (i.e. 492.3 μ M) nanoFe⁰, and 0 or 1.5 mM 1,10-phenanthroline or TEA. The second set was to assess the interaction between surface-bound Fe(II) and U(VI) at pH 6.9. The examined batch system contained 200 μ M U(VI), 2.8 mg L⁻¹ (i.e. 50 μ M) nanoFe⁰, 1 mM FeCl₂, and 12.5 mM Tris buffer. There were two control experiments, one containing 200 μ M U(VI), 1 mM FeCl₂, and 12.5 mM Tris buffer, while the other containing 200 μ M U(VI), 2.8 mg L⁻¹ nanoFe⁰, and 12.5 mM Tris buffer.

All the experiments were conducted at the room temperature (25 ± 1 °C) in an anoxic glovebox (Coy Laboratory Products) with a 5% H₂ and 95% N₂ atmosphere. To minimize the ambient concentration of CO₂ in the glovebox, 2 L of 2 M NaOH solution was stored inside the glovebox for CO₂ gas absorption. All the kinetic experiments were duplicated and performed in 50 mL centrifuge tubes. The reaction tubes were agitated on a rotator (Bellco Glass) at ~60 rpm to maintain particles in suspension. At various time intervals, the reaction tubes were sacrificially sampled. A 40 mM bicarbonate extraction method was used to monitor the U(VI) reduction (Yan et al., 2010). The difference between the initial U(VI) and the extracted U(VI) concentrations was considered to be the reduced U(VI). After bicarbonate extraction, about 5 mL aqueous samples were withdrawn using 10 mL Becton-Dickinson syringes and filtered through 0.2 µm nylon membrane filters (Fisher Scientific) inside the glovebox, and then added into the pre-mixed spectrophotometric solutions. U(VI) concentrations were measured by the TAC colorimetric method (Yan et al., 2010). When 1,10-phenanthroline or TEA was introduced into the reaction system, the filtrate was divided into two portions, with one being used for the analysis of U(VI) and the other as a blank control.

3.Results

3.1. Effect of pH

The effect of pH on U(VI) reduction by nanoFe⁰ in the control system without iron-complexing reagents is illustrated in Fig. 1a. The results showed that U(VI) was reduced by 86% at pH 6.9 within 0.5 h; while the percentages of reduced U(VI) were only 63% and 48% after 0.7 h at pH values of 8.0 and 9.0, respectively. Our previous study indicated that the kinetics of U(VI) reduction by nanoFe⁰ was well fit by a pseudo-first-order kinetics model (Yan

et al., 2010). Other studies have also shown the satisfactory application of a pseudo-first-order model to describe the removal of U(VI) by Fe^0 (Cantrell et al., 1995; Gu et al., 1998). In this study, the U(VI) reduction rate was described by pseudo-first-order kinetics and all reported k_{obs} values were obtained with a regression coefficient (R^2) greater than 0.95. Figure 1b presents the k_{obs} values of U(VI) reduction by nanoFe^0 in the control systems at different pH values. The results indicated that the observed U(VI) reduction rates by nanoFe^0 in the control system decreased with increasing pH from 6.9 to 9.0.

3.2. Effect of 1,10-phenanthroline and TEA

3.2.1 Kinetics of U(VI) reduction

U(VI) reduction by nanoFe^0 in the presence of 1.5 mM 1,10-phenanthroline or TEA is shown in Fig. 2a. The U(VI) reduction rates for the systems containing iron chelating agents were comparable, but both were slower than those for the control system (Fig. 1a). The k_{obs} values normalized by the corresponding rate constants under control condition are plotted in Fig. 2b. It's interesting to note that U(VI) reduction was strongly suppressed by 1,10-phenanthroline and TEA. For example, at pH 8.0, in the presence of 1,10-phenanthroline or TEA, the reduction rates of U(VI) by nanoFe^0 decreased to 8% and 11% of that in the control system, respectively. Moreover, the observed U(VI) reduction rates in the systems with 1,10-phenanthroline or TEA also decreased with increasing pH values.

3.2.2 Speciation of Fe(II) and Fe(III)

The calculated Fe(II) species under the experimental conditions are shown in Fig. 3. The speciation calculations were performed with the chemical equilibrium modeling software MINEQL 4.61, using the thermodynamic data from the EPA's MINTEQA2 database and the

updated metal complex constants from the NIST Standard Reference Database 46 (NIST Critically Selected Stability Constants of Metal Complexes: Version 8.0). The log K value used for $\text{Fe}(\text{phen})_3^{2+}$ was 21.2, a value reported from the measurements of partition coefficients of 1,10-phenanthroline between three organic solvents and aqueous buffers containing known concentrations of ferrous iron at 25 °C (Irving and Mellor, 1962). As shown in Fig. 3, the Fe(II) speciation in the pH range from 6.9 to 9.0 is dominated by $\text{Fe}(\text{phen})_3^{2+}$ complex, which accounts for over 99% of the Fe(II) species under experimental conditions. Consequently, Fe(II) would be chelated by 1,10-phenanthroline when Fe(II) occurred in the system. To our knowledge, the exact formation constant for the Fe(III)-TEA complex is not reported; however, TEA is commonly used as a masking agent for Fe(III) (Downard et al., 1992), indicating the formation of strong complexes.

3.3 Interactions between aqueous/sorbed Fe(II) and U(VI)

The inhibition effect of 1,10-phenanthroline indicated Fe(II) played an important role in the reduction of U(VI). Under the experimental conditions, both aqueous Fe(II) and surface-bound Fe(II) can be present in the studied system. To distinguish the role of aqueous Fe(II) and surface-bound Fe(II), the interactions between aqueous/sorbed Fe(II) and U(VI) were also investigated at pH 6.9 by three batch tests under CO_2 -free anoxic condition. As shown in Fig. 4, no U(VI) reduction was observed within 4 h in the first batch system with only aqueous Fe(II), U(VI) was reduced to ~75% of original concentration after 1 h in the second batch system with 2.8 mg L⁻¹ nanoFe⁰, and U(VI) reduction was almost completed within 4 h in the batch system with both nanoFe⁰ and Fe(II). Furthermore, the molar ratio of U(VI) reduced to nanoFe⁰ consumed in the second system was about 1:1, which suggested that the reaction stoichiometry could be represented by

4. Discussion

As shown in Fig. 1, nanoFe⁰ was a good reductant for U(VI) in the pH range from 6.9 to 9.0 in the absence of iron chelators. However, the rate and extent of U(VI) reduction by nanoFe⁰ were significantly suppressed in the presence of 1,10-phenanthroline or TEA (Fig. 2). For instance, at pH 6.9, the observed U(VI) reduction rate constants in the systems with 1,10-phenanthroline or TEA decreased to 19% and 18% of that in the control system, respectively. It is not completely clear why 1,10-phenanthroline and TEA inhibit the reduction of U(VI) by nanoFe⁰. The inhibition by 1,10-phenanthroline could be attributed to complex formation between Fe(II) and 1,10-phenanthroline, which can prevent the formation and accumulation of ferrous iron corrosion products on nanoFe⁰ surface and thus prevent Fe(II) from reaction with U(VI). This stable complex also strongly hindered Cr(VI) reduction by Fe(0) in the presence of 1,10-phenanthroline (Zhou et al., 2008). Unlike the acceleration of Fe(III)-chelator for Cr(VI) reduction by Fe(0) (Zhou et al., 2008), however, U(VI) reduction by nanoFe⁰ is inhibited by Fe(III)-chelator (TEA). Theoretically, the complexation between Fe(III) and TEA can decrease the ratio of Fe(III)/Fe(II), thus decrease the redox potential based on Nernst equation, which should facilitate U(VI) reduction by Fe(II). However, the apparent U(VI) reduction rate and extent are suppressed in the presence of TEA, which could be due to the suppression of another reductant - Fe(0) - in our examined system. Although the Fe(III)-TEA complex may enhance the U(VI) reduction by Fe(II), this complex can probably prevent Fe(III) from serving as a mediator for electron transfer from nanoFe⁰ to U(VI).

The inhibitory effect of iron chelators indicates Fe(II) and Fe(III) played a critical role in U(VI) reduction by nanoFe⁰. Except for Fe(0), Fe(II) is the only potential reductant for U(VI) in the studied system. Although U(VI) reduction by aqueous Fe(II) is thermodynamically feasible, no U(VI) reduction was observed in the system containing 200 µM U(VI) and 1 mM FeCl₂ within 4 h at pH 6.9 (Fig. 4). This is consistent with the observation by Liger et al. (1999), who found no change in the dissolved U(VI) concentration over a three day period in the system with 0.5 µM U(VI) and 160.0 µM Fe(II) at pH 7.5. On the contrary, under the same condition, but in the presence of nanoFe⁰, the concentration of U(VI) extracted by NaHCO₃ decreased (Fig. 4). Furthermore, the rate and extent of U(VI) reduction in the system with both nanoFe⁰ and Fe(II) were much greater than those in the system with only nanoFe⁰. This result agrees well with the previous studies of U(VI) reduction by surface-bound Fe(II) (Charlet et al., 1998; Liger et al., 1999; Jeon et al., 2005; Jang et al., 2008; Fox et al., 2013; Sheng et al., 2014), indicating that U(VI) reduction by direct electron transfer between surface-bound Fe(II) and U(VI) on the nanoFe⁰ surface is a favorable reaction under the CO₂-free anoxic condition.

In fact, Fe(II) sorbed on mineral surfaces is considered to be a more powerful reductant than aqueous Fe(II) (Wehrli et al., 1989; Stumm et al., 1992). Numerous studies have demonstrated that surface-bound Fe(II) species are highly reactive to a variety of redox-sensitive contaminants. For instance, Buerge and Hug (1999) found Cr(VI) reduction by Fe(II) could be accelerated in the presence of various minerals. Cui and Eriksen (1996) reported the reduction of pertechnetate by Fe(II) sorbed onto magnetite. Sørensen and Thorling (1991) demonstrated nitrite ion could be rapidly reduced to N₂O by Fe(II) sorbed on lepidocrocite. Jang et al. (2008) observed about 80% of U(VI) was reduced by Fe(II) within 3 d with either hematite or hydrous ferric oxide. More recently, Sheng et al. (2014) demonstrated Fe(II) sorbed on bentonite can enhance U(VI)

reduction in the batch system with nanoFe⁰. As indicated by Liger et al. (1999), the reactivity of surface-bound Fe(II) is amplified by the donation of electron density resulting from the deprotonation of a water molecule from its hydration sheath.

In the examined nanoFe⁰-U(VI) system, nanoFe⁰ is the primary reducing agent. The oxidation of nanoFe⁰ can generate Fe²⁺ that potentially reduces U(VI). It has been postulated that U(VI) could be reduced by surface-bound Fe(II) species at the mineral-water interface (Charlet et al., 1998; Liger et al., 1999; Jeon et al., 2005; Jang et al., 2008; Sheng et al., 2014). The result herein also demonstrates that surface-bound Fe(II) on nanoFe⁰ is highly reactive for U(VI) reduction. Furthermore, the inhibition of TEA on U(VI) reduction indicates that Fe(III) has likely participated in the electron transfer chain from nanoFe⁰ to U(VI). Based on the aforementioned understanding, the following three reactions might be involved in the reduction of U(VI) by nanoFe⁰.

Initially, nanoFe⁰ transfers electrons to U(VI) sorbed on nanoFe⁰ surface to produce Fe(II) as described by the reaction (1). Then surface-bound Fe(II) can rapidly reduce U(VI), which can be described by the reaction (2) with Fe(III) as the oxidation product of Fe(II). It's important to note that the standard reduction potential of Fe(III)/Fe(II) (0.771 V) is much higher than that of U(VI)/U(IV) (0.327 V) (Haynes, 2013), suggesting Fe(III) is a stronger oxidant than U(VI). Consequently, the produced Fe(III) can further oxidize Fe(0) as shown by the reaction (3), and the Fe(II) produced in the reaction (3) rapidly reduces U(VI) again. This is similar to the electron

shuttling mechanisms found in other chemical and biotic reduction of metals and organics, for example, the redox cycle between oxidized and reduced humics that ferries electrons from an electron donor to an terminal electron acceptor such as Fe(III) oxides and nitrobenzenes (Lovley et al., 1996; Sposito, 2011). Herein, Fe(III) and Fe(II) possibly act as a similar electron shuttle to mediate the transfer of electrons from nanoFe⁰ to U(VI), and U(VI) is finally reduced to U(IV) as identified by X-ray Photoelectron Spectroscopy (Yan et al., 2010).

5. Conclusions

The inhibition by iron chelators and the enhancement of surface-bound Fe(II) on U(VI) reduction reveals the important role played by Fe(II) and Fe(III) for U(VI) reduction in the system with nanoFe⁰. NanoFe⁰ firstly transfers electrons to sorbed U(VI) to produce Fe(II), then the Fe(II) reacts with U(VI) and produces Fe(III), which further oxidizes Fe(0) to produce Fe(II) capable of additional U(VI) reduction. The net result is that Fe(II) and Fe(III) possibly act as an electron shuttle to ferry electrons from nanoFe⁰ to U(VI). This study highlights that a combined system with Fe(II), Fe(III) and nanoFe⁰ would facilitate the U(VI) reductive immobilization in the contaminated groundwater.

Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (41303084 and 40930743), the opening research fund of Guangdong Province & MOE Key Laboratory of Water Safety and Protection of Pearl River Delta (GZ201101), the U.S. Department of Energy's Joint EPA, NSF, and DOE program on Nanotechnology in the Office of Biological and Environmental Research (BER), and the U.S. National Science Foundation (CBET-0828411). We thank associate editor, Prof. Oliver J. Hao, and anonymous reviewer for their constructive comments and suggestions on this manuscript.

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Figure captions:

Fig. 1. Temporal Changes of $[U(VI)]_{\text{extracted}}$ (a) and observed rate constants (b) under control condition ($[U(VI)]_0 = 200 \mu\text{M}$, $[Fe^0] = 27.6 \text{ mg L}^{-1}$, error bars indicate standard deviation of duplicate samples).

Fig. 2. U(VI) reduction kinetics (a) and normalized observed rate constants (b) in the presence of 1.5 mM phenanthroline or triethanolamine ($[U(VI)]_0 = 200 \mu\text{M}$, $[Fe^0] = 27.6 \text{ mg L}^{-1}$, error bars indicate standard deviation of duplicate samples).

Fig. 3. Fe(II) speciation in the presence of 1,10-phenanthroline under experimental conditions.

Fig. 4. Temporal changes of $[U(VI)]_{\text{extracted}}$ under different conditions at pH 6.9 ($[U(VI)]_0 = 200 \mu\text{M}$, error bars indicate standard deviation of duplicate samples.).

430 **Figures:**

Fig. 1

Fig. 2

Fig. 3

Fig. 4