Journal of Hazardous Materials 235–236 (2012) 359–366

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Enhanced reductive dechlorination of tetrachloroethene during reduction of cobalamin (III) by nano-mackinawite

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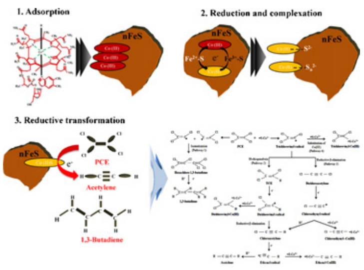
HIGHLIGHTS

- Adsorption and reduction of Co(III) occurred on nFeS surface.
- Co(III) was reduced to Co(II) by $\equiv Fe^{2+}$.
- Co(II) formed complexation with $\equiv S^{2-}$ and $\equiv S_n^{2-}$.
- $\equiv S^{2-}$—Co(II) and $\equiv S_n^{2-}$—Co(II) enhanced reductive dechlorination of PCE.
- PCE was transformed to acetylene and 1,3-butadine.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 April 2012
Received in revised form 3 August 2012
Accepted 6 August 2012
Available online 14 August 2012

Keywords:
Nano-mackinawite
Cobalamin(III)
Sulfidecobalamin(II)
Reductive dechlorination
Tetrachloroethene

ABSTRACT

We demonstrated adsorption and reduction of cobalamin(III) (Co(III)) on nano-mackinawite (nFeS) surface and their impact on reductive dechlorination of tetrachloroethene (PCE). The adsorption of Co(III) on the nFeS surface followed Langmuir isotherm and the reduction of Co(III) provided different reactive surface chemical species on nFeS surface. Content of Fe^{2+}—S on nFeS surface decreased (45.9–14.5%) as Fe^{2+}—S was oxidized to Fe^{3+}—S and Fe^{3+}—O coupled with the surface reduction of Co(III) to cobalamin(II) (Co(II)). S^{2-} and S_n^{2-} contents on the nFeS surface also decreased by 48.5% and 82.3%, respectively during the formation of sulfidecobalamin(II) ($\equiv S^{2-}$—Co(II)) by the reactive surface sulfur. PCE was fully degraded in nFeS—Co(III) suspension at pH 8.3 in 120 h. The dechlorination kinetic rate constant of PCE in the nFeS—Co(III) suspension ($k_{FeS-Co(III)} = 0.188 \pm 0.003\ h^{-1}$) was 145 times greater than that in nFeS suspension, showing a potential role of $\equiv S^{2-}$—Co(II) as an electron transfer mediator to shuttle electrons for the enhanced reductive dechlorination. PCE was transformed to acetylene and 1,3-butadiene as major products via reductive β-elimination and isomerization reactions, respectively. The experimental findings can provide basic knowledge to identify a reaction mechanism for the enhanced reductive dechlorination of chlorinated organic by biogeochemical reactions possibly observed in natural reducing environments.

1. Introduction

Toxic and persistent chlorinated organic contaminants are widespread in sub-surface soil and groundwater systems due to their intensive usage from industrial activities [1]. Tetrachloroethene (PCE), one of the chlorinated organics frequently found in the sub-surface environments, has been detected in at least 771 of the 1430 National Priorities List Sites of the United States and widely known as a carcinogen and mutagen to human beings and animals [2]. To solve these serious anthropogenic environmental problems, continuous efforts have been directed towards increasing the basic understanding of reductive dechlorination of chlorinated organics via abiotic and biotic reactions and interactions between them in natural and engineered environments.

Remediation technologies based on abiotic reductive dechlorination by iron-bearing soil minerals (IBSMs) have been developed

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http://dx.doi.org/10.1016/j.jhazmat.2012.08.017

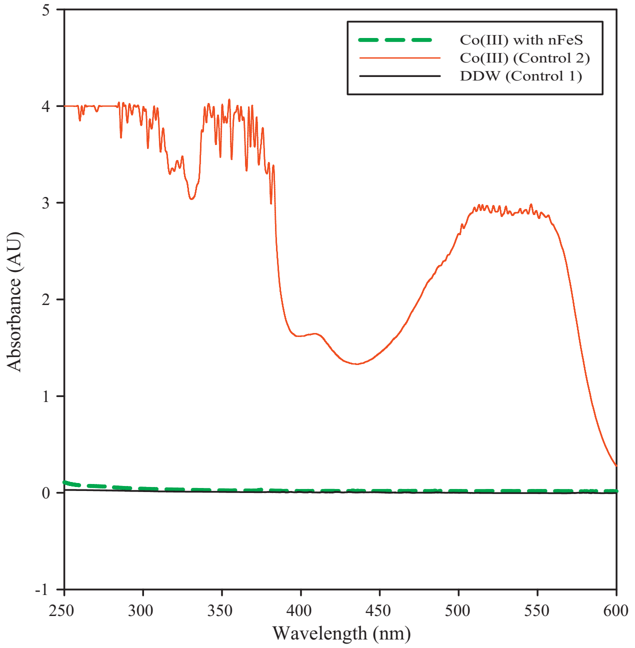

Fig. 1. Adsorption of Co(III) on nFeS surface at pH 8.3. [Co(III)] = 0.5 mM, [nFeS] = 4.17 g/L.

and used as practical and efficient ways to treat soil and groundwater contaminated with chlorinated organics [3–5]. FeS is one of the most abundant and widely studied IBSMs for the reductive dechlorination of PCE due to high density of reactive chemical species such as ≡FeOH and ≡FeSH on its surface [6,7]. Reductive dechlorination kinetics of chlorinated organics by FeS are much faster than those by siderite and iron oxides [6]. Laboratories studies have shown that the reductive dechlorination of PCE by FeS via β-elimination and/or hydrogenolysis pathways can form much more toxic products such as trichloroethene (TCE), cis-dichloroethene (cis-DCE), and 1,1-dichloroethene (1,1-DCE) [8,9]. In natural systems in which microbes are abundant, microbial activity and biogenic products via interactions with indigenous chemical species and soil minerals significantly influence reductive dechlorination of PCE [10,11], i.e., nano-sized FeS (nFeS; 100–300 nm) can form by microbial reduction of sulfate to sulfide by sulfate-reducing bacteria (SRB) and subsequent precipitation of sulfide with ferrous iron [12,13]. Reductive dechlorination of PCE by nFeS may be faster due to its higher surface area than that by micro-sized FeS (mFeS) which has been used in most laboratory studies. Excretion of active transition metal coenzymes from SRB, methanogens, and acetogens [12,13] may also affect dechlorination kinetics and byproducts distribution in the reductive transformation of PCE by FeS. However, there have not been significant investigations on the potential effect of these biogeochemical factors on the reductive dechlorination of PCE by nFeS in the natural and engineered environments.

Literatures show that active transition metal coenzymes such as cobalamin(III) (Co(III)), hematin, and cofactor F_{430} can play an important role as electron transfer mediator (ETM) in reductive dechlorination of chlorinated organics [11,14–18]. Among the coenzymes, Co(III) shows the fastest dechlorination kinetics of PCE and TCE with titanium(III) citrate [19]. Reduced cobalamin species (cobalamin(II) (Co(II)) and cobalamin(I) (Co(I))) have played the important role to shuttle electrons between diverse solid reductant surfaces and chlorinated organics [20–22]. Laboratory study demonstrated that redox couple (Co(II)/Co(I)) significantly transformed toxic products of PCE to non-toxic products, i.e. cis-DCE, 1-1-DCE, and vinyl chloride were transformed to acetylene, ethene, and ethane in titanium(III) citrate solution with Co(III) at neutral pH [23]. However, in practice, reduction of Co(III) to Co(I) by titanium(III) citrate did not appear to be effective in the reductive dechlorination of 1,1,1-trichloroethane (1,1,1-TCA) due to precipitation of titanium(III) citrate by indigenous bacteria in sub-surface soil [24]. Recently, a laboratory study demonstrated that an interaction between FeS and extracellular compounds such as Co(III) from methanogens enhanced dechlorination kinetics of 1,1,1-TCA to 1,1-DCE twice faster than abiotic reduction by FeS or microbial reduction by the methanogens. Oxidation reduction potential (ORP) of the methanogenic degradation system has significantly decreased (−90 to −135 mV) after the addition of FeS [25]. However, the role of FeS in the reduction of Co(III) and influence of reduced cobalamins on the enhanced reductive dechlorination of chlorinated organics are still unclear and poorly understood. In this study, we elucidated the role of nFeS in the reduction of Co(III) and characterized the reductive dechlorination of chlorinated organic by nFeS with Co(III). PCE was selected as a representative target chlorinated organic. To fulfill the goals of this research, (1) adsorption and reduction of Co(III) on nFeS surface was investigated, (2) transformation products for the reductive dechlorination of PCE by nFeS with Co(III) was monitored, and (3) reaction mechanisms for these complex reactions were identified.

2. Experimental

2.1. Chemicals and synthesis of nFeS and mFeS

Descriptions of chemicals and synthesis of nFeS and mFeS are included in Supporting Information.

2.2. Experimental procedures

For experiment in an anaerobic system, all the samples were prepared and experimental procedures were conducted in the anaerobic condition. To characterize reduction of cobalamin (III) by nFeS, vials (24 mL) were filled with 4.17 g/L of nFeS slurry and 0.5 mM Co(III) solution containing 50 mM tris buffer to keep the suspension pH constant at 8.3. Deaerated deionized water (DDW) was used as zero background (control 1), because it has no detectable absorbance at any wavelength using UV–Vis spectrometer. 0.5 mM Co(III) solution containing 50 mM tris buffer (control 2) was prepared to determine Co(III) peak at wavelength 550 nm. Samples were mixed on a tumbler for 1 h at 7 rpm, and at room temperature (25 ± 0.5 °C). Then, they were centrifuged at 3000 rpm for 5 min and aliquots of aqueous solution were transferred to quartz cuvettes (3 mL). Aqueous concentrations of reduced cobalamin species (e.g., Co(II) and Co(I)) were measured by UV–Vis spectrometer. All the samples were prepared in duplicates. Additional experimental procedures are included in Supporting Information.

2.3. Analytical procedures

Description for analytical procedures is included in Supporting Information.

3. Result and discussions

3.1. Reduction of Co(III) by nFeS

3.1.1. Adsorption of Co(III) on nFeS surface

Fig. 1 shows UV–Vis spectra of aqueous solutions from nFeS suspension with Co(III) (nFeS—Co(III)) and controls at pH 8.3. No peak was observed in deaerated deionized water (DDW: control 1) indicating that there was no cationic and anionic chemical species in the aqueous solution. In Co(III) solution (DDW + Co(III): control