



Enhanced reductive extraction of arsenic from contaminated soils by a combination of dithionite and oxalate



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HIGHLIGHTS

- As extraction from soils was studied by a combination of dithionite and oxalate.
- Reductive As extraction by dithionite was greatly enhanced by oxalate addition.
- Iron extraction from soil were dependent on oxalate to iron concentration ratio.
- Optimum dithionite concentrations were affected by As concentration and speciation.
- Effective As remediation can be obtained with limited impact on soil environment.

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ABSTRACT

Iron oxide minerals are the most important sinks of arsenic in arsenic contaminated soils. Therefore, the effective extraction of arsenic bound to the iron oxides is essential to increase the efficiency of arsenic removal from soils. In this study, the reductive extraction of arsenic from contaminated soils was studied with a combination of dithionite and oxalate in order to remediate arsenic-contaminated soils via the reductive dissolution of arsenic associated iron oxides. The addition of oxalate greatly enhanced the reductive arsenic extraction by forming strong complexes with iron, which could prevent the precipitation of a new iron oxide phase and also enhance the iron oxide dissolution via a non-reductive dissolution pathway. Iron in soils can either be extracted as a soluble $\text{Fe}(\text{C}_2\text{O}_4)_2^{2-}$ or remain in the soil as a solid $\text{Fe}(\text{C}_2\text{O}_4)$ precipitation depending on the oxalate to iron molar ratio. Arsenic extraction was hindered by an excess of dithionite, and the optimum dithionite concentration was affected by the arsenic concentrations and the speciations present in the soils. Relatively high arsenic extraction could be obtained by a combination of dithionite and oxalate at a wide range of pH conditions.

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1. Introduction

Arsenic is a naturally occurring trace element that has adverse effects on human health. In the natural environment, arsenic is present as a major constituent of many minerals including sulfides and oxides, such as arsenopyrite (FeAsS), realgar (As_4S_4), orpiment (As_2S_3), arsenolite (As_2O_3), and scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) [1]. The arsenic present in these minerals can be mobilized and introduced to the surrounding air, water, and soil environments by various

human activities, such as mining, smelting, and the burning of fossil fuels. Soils close to mine and smelter sites have been highly contaminated with arsenic in many parts of the world, which can pose a significant risk to groundwater quality, food safety, and human health [1]. Therefore, it is important to effectively remediate arsenic contaminated soils.

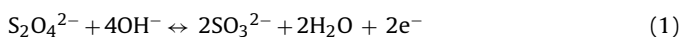
In arsenic-contaminated soils, soil minerals play important roles in regulating arsenic retention and its solid-state speciation, which strongly influences the mobility and bioavailability of arsenic in soil [2–5]. Among soil minerals, iron oxide minerals, such as hydrous ferric oxide, goethite, and hematite, are considered to be the most important sinks of arsenic due to their affinity to arsenic and their abundance in the environment [1,6]. Therefore, the effective extraction of arsenic bound to iron oxides is essential in order to increase the efficiency of arsenic removal from soils. Under reduced conditions, iron oxides could be reductively dissolved and concurrently

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release the arsenic associated with the iron oxides to the aqueous phase. Reductive dissolution of iron oxides has been considered to primarily contribute to arsenic contamination under anaerobic conditions such as in groundwater [1,7,8]. In addition, the reduction of arsenate (As(V)) to arsenite (As(III)) under reducing conditions can promote the desorption of arsenic from iron oxides and clay minerals. Therefore, in an aspect of soil remediation, the manipulation of the redox conditions could enhance the arsenic extraction from soils via the reductive dissolution of the iron oxides and arsenic desorption from the soil minerals.

In our previous study, the reductive arsenic extraction from soils was studied with various reducing agents in order to remediate arsenic contaminated soils [9]. Our study indicated that the addition of chelating agents to reducing agents improved the arsenic extraction by enhancing the dissolution of the iron oxides and the arsenic extraction was influenced by both the reducing and chelating agents. Thus, there the need remained for further studies in order to understand the arsenic extraction mechanism by each combination of reducing and chelating agents. Therefore, the objective of this study was to investigate the mechanism of enhanced reductive arsenic extraction from contaminated soils by dithionite combined with oxalate in order to develop an effective remediation technology for arsenic-contaminated soils. Dithionite ($S_2O_4^{2-}$) is a strong reducing agent, which has standard reduction potential (E°) of -1.12 V in alkaline conditions as in the following Reaction (1) [10–12]:



On the other hand, oxalate ($C_2O_4^{2-}$) is a mild reducing agent ($E^\circ = -0.18$) as well as a strong chelating agent, which can form strong complexes with both ferrous (Fe^{2+}) and ferric (Fe^{3+}) iron [13]. Its stability constants ($\log K_1$) for the complexation of Fe^{2+} and Fe^{3+} are >4.7 and 9.4 , respectively [14]. In addition, oxalic acid is a naturally occurring substance in many plants and vegetables, and it is biologically degradable in the environment [15]. Therefore, oxalic acid offers advantages for metal remediation, since it has a high chelating capacity with heavy metals, but it has low toxicity and a limited impact on the soil environment in comparison to the commonly applied chelating agents, such as EDTA [16].

2. Materials and methods

2.1. Soil sampling and characterization

Arsenic-contaminated soil samples were collected at a former non-ferrous metal refinery plant and an abandoned gold mine tailing site in Korea. Two smelter soil samples (smelter-1 and smelter-2) and a mine tailing soil sample (mine), which were primarily contaminated with arsenic, were studied for the reductive extraction of arsenic. The soil samples were taken from the 0–30 cm layer and air-dried. Then, they were sieved using a 2-mm screen, ground to $<75 \mu m$, and homogenized for the experiments. The pH of the soil was measured in a 1:5 soil:deionized water suspension with a pH meter (ISTEK Inc., Korea). The total major and trace elements were analyzed via inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent Tech, USA) following aqua regia digestion. The physical and chemical properties of soil samples are

Table 1
Physical and chemical properties of soil samples.

	pH (1:5)	As (ppm)	Pb (ppm)	Cu (ppm)	Fe (%)	S (%)	Organic C (%)	Sand (%)	Silt (%)	Clay (%)
Smelter-1	5.22	65.2	147	98.3	2.55	0.18	0.52	20.2	49.8	30
Smelter-2	6.21	1150	645	33.2	5.56	0.12	0.69	30	40.8	29.2
Mine	2.35	100330	27700	370	18.6	10.7	1.19	78.9	6.92	14.2

summarized in Table 1. The arsenic concentrations in the smelter-1, smelter-2, and mine soils were 65.2, 1150, and 100,330 mg/kg, respectively. When conducting sequential extraction as suggested by Wenzel et al. [17], the arsenic in the smelter-1 soil was primarily bound to amorphous iron oxides, while the arsenic in the smelter-2 soil was primarily associated with crystalline iron oxides and the sulfide phase (Fig. S1 in the Supplementary data). The arsenic in the mine soil was primarily present as scorodite ($FeAsO_4 \cdot 2H_2O$). The detailed chemical and mineralogical characteristics of the soil samples, including the arsenic solid phase speciation, can be found in our previous studies [5,9].

2.2. Reductive extraction of arsenic

All of the experiments were conducted in a completely mixed batch reactor system. One gram of the soil sample was reacted with 25 mL of a combination of various concentrations of sodium dithionite ($Na_2S_2O_4$) and sodium oxalate ($Na_2C_2O_4$) (Sigma-Aldrich) after adjusting the pH using 0.1 M HCl or 0.1 M NaOH in a polypropylene copolymer centrifuge tube (Nalgene™, 30 mL) at 20 °C and 150 rpm. The enhanced reductive extraction of arsenic from soils was investigated with a combination of dithionite and various concentrations of oxalate. The soils were reacted with 0.1 M of sodium dithionite combined with 0, 0.005, 0.01, 0.05, 0.1, and 0.2 M of sodium oxalate at pH 7 for 24 h. Reductive extraction kinetics were conducted with 0.1 M of sodium dithionite and 0.1 M of sodium oxalate at pH 7 for various reaction times up to 24 h at 20 °C and 150 rpm. The effects of the dithionite concentrations on the reductive arsenic extraction from soils were studied with various concentrations of dithionite (0, 0.01, 0.05, and 0.1 M) combined with 0.1 M of oxalate at pH levels of 4, 7, and 10 for 24 h. All of the reactions were carried out in duplicate. After the reaction, the samples were centrifuged at 7000 rpm for 10 min, filtered, and analyzed via ICP-OES.

2.3. Solid characterization

The minerals in the soils before and after extraction were qualitatively identified via X-ray diffraction (XRD) analysis. The XRD data were collected on a powder X-ray diffractometer (MAX-2500, Rigaku, Japan) using Cu K α ($\lambda = 1.54059 \text{ \AA}$) radiation obtained at 40 kV and 30 mA. Scans were taken between 5 and 70° 2 θ with 0.02° step sizes. The organic carbon and sulfur contents were analyzed using an elemental analyzer (Vario EL, Elementar, Germany). The transmittance spectra of the soils before and after extraction in the middle infrared (400–4000 cm^{-1}) were obtained using a Fourier transform infrared (FTIR; Spectrum GX, PerkinElmer, USA) spectrometer.

3. Results and discussion

3.1. Enhanced reductive extraction of arsenic

The enhancement of reductive arsenic extraction by dithionite from arsenic contaminated soils was studied with the addition of various concentrations of oxalate. The reductive extraction rates of arsenic and iron from the soils are summarized in Fig. 1. In

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