



Simultaneous application of oxalic acid and dithionite for enhanced extraction of arsenic bound to amorphous and crystalline iron oxides

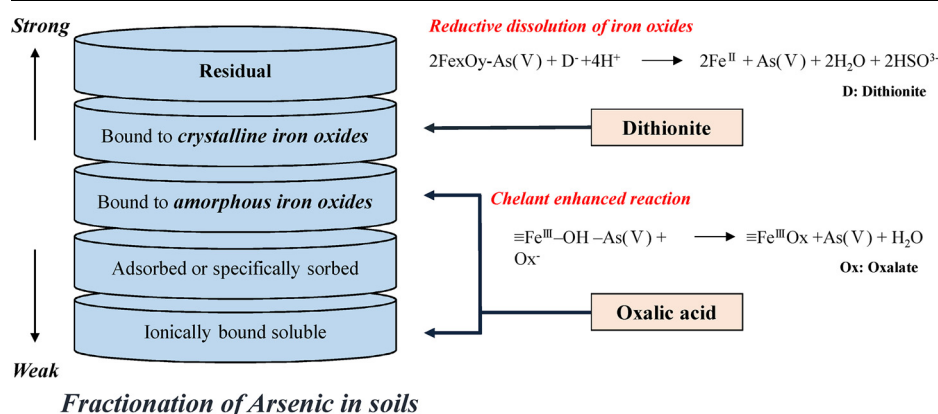
Myeong Eun Lee^a, Eun-Ki Jeon^a, Daniel C.W. Tsang^b, Kitae Baek^{a,*}

^a Department of Environmental Engineering and Soil Environment Research Center, Chonbuk National University, 567 Baekje-daero, Deokjin, Jeonju, Jeollabukdo, 561-756, Republic of Korea

^b Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Kowloon, Hong Kong, China



GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Reductive dissolution
Chelant-enhanced dissolution
Secondary minerals
Bioaccessibility
Chemical washing

ABSTRACT

To extract As bound to amorphous and crystalline iron oxides, this study proposed simultaneous application of oxalic acid and dithionite, which was observed to induce synergistic effect and accomplish effective extraction of As bound to both iron oxides. However, the formation of arsenic sulfide decreased overall removal of As because the insoluble precipitate form of As remained as a residual fraction of As in soil. Therefore, stepwise addition of dithionite in the simultaneous application was applied to minimize the formation of secondary minerals and maximize the As extraction. As a result, 74% of As bound to amorphous iron oxides and 65% of As bound to crystalline iron oxides were removed. More importantly, the stepwise application of oxalic acid and dithionite was effective to reduce the bioaccessible concentration of As in the treated soil. Therefore, the proposed application could reduce the potential risk of contaminated soil to human health by extraction-based remedial action.

1. Introduction

Land contamination by arsenic(As) has been recognized as a serious environmental problem in the world because As could affect the human

health via translocation from soils to plants [1–3]. To control the translocation of As to plants, As should be extracted from soils or stabilized/immobilized to reduce the phytoavailability [4–6]. In Korea and many other countries, the soil quality is regulated based on the

* Corresponding author.

E-mail address: kbaek@jbnu.ac.kr (K. Baek).

<https://doi.org/10.1016/j.jhazmat.2018.04.083>

Received 16 December 2017; Received in revised form 18 April 2018; Accepted 30 April 2018

Available online 01 May 2018

0304-3894/ © 2018 Elsevier B.V. All rights reserved.

Table 1
Chemical properties of soil.

Sample	CEC (meq/100 g)	OM ^a (%)	pH	Concentrations (mg/kg)			Fractionation of As (%)				
				As	Fe	Al	F1	F2	F3	F4	F5
S1	40.3	11.3	4.6	139.5	33794	18234	1	14	37	34	14
S2	34.1	11.5	4.8	77.7	38230	20819	N.D. ^b	10	67	5	18

^a Organic matter.

^b Not detected.

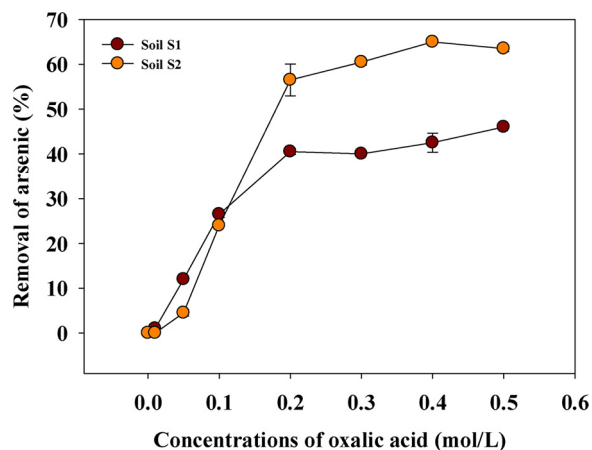


Fig. 1. Influence of oxalic acid concentration on removal of Arsenic. Two different types of soil were used at a ratio of 1:3 (soil: solution) for 3 h at room temperature.

total concentration through *aqua regia* extraction, therefore, As in the contaminated site should be removed or extracted from the soil to meet the legal regulation. Soil washing and electrokinetic remediation are common choices to achieve the extraction-based remediation purpose [4,7,8]. Soil washing has been applied to various As-contaminated sites from pilot to field scale because soil washing is a rapid remediation technique and removes the target pollutants permanently from the contaminated soil to minimize potential liability in the future [4]. However, the overall performance is highly dependent on the fractionation of As in soil and types of washing agents [4,9], and in some cases, the residual leachability and bioaccessibility of As is even adversely increased after chemical extraction [10–12].

Arsenic has a great affinity with iron oxides, which primarily determine the fate and transport of As [13–15], therefore, it is well known that As usually exists as bound to iron oxides in soils [1]. Iron oxides could be divided into two categories: amorphous and crystalline iron oxides, and As bound to iron oxides could be extracted via acid-enhanced dissolution, reductive dissolution, and chelant-enhanced dissolution [16,17]. Amorphous iron oxides could be dissolved by all the three mechanisms, while crystalline iron oxides are hardly dissolved by acid-enhanced and chelant-enhanced mechanisms [16,18]. In previous studies, oxalic acid extracted As bound to amorphous iron oxides by the complexation between oxalate and ferric iron [9,19–21]. Therefore, the maximum amounts of As extracted from the soil were limited to the As bound to amorphous iron oxides even though excessive oxalic acid was applied because the agent did not remove As bound to crystalline iron oxides [9]. Additionally, the stable fractionation of As could be changed to labile fractions by surrounding environment, therefore, the stable forms of As should be extracted further to meet the regulation level as well as potential risk.

To enhance the extraction of As bound to crystalline iron oxides, simultaneous application of oxalic acid and strong reducing agent was proposed [22]. Dithionite is one of that strong reductants to induce the reductive dissolution of crystalline iron oxides and it is more

economically feasible compared to other reducing agents [16,18]. However, dithionite is prone to self-decomposition and produces a reduced form of sulfur, especially hydrogen sulfide in acidic condition [23,24], which reacts with As and forms the precipitate of arsenic sulfide [25]. As a result, the As extracted into solution is re-adsorbed onto or retained with the soil due to the formation of arsenic sulfide, which converts the extracted As into residual fraction in the soil and presents a major challenge in the chemical extraction.

In view of the above concerns, this study proposed to enhance the extraction of As from soil by simultaneous application of oxalic acid for As bound to amorphous iron oxides and dithionite for As bound to crystalline iron oxides. We hypothesized that the oxalic acid prevents the formation of secondary minerals of dissolved iron by complexation of oxalate with ferric ions, which enhances the As extraction from soil. In addition, the amounts of dithionite were controlled to minimize the formation of arsenic sulfide, and bioaccessibility of As in the treated soils was analyzed to evaluate the remedial effectiveness of simultaneous application.

2. Materials & methods

2.1. Soil characterization

The As-contaminated soils were sampled from a former smelter site (S1 and S2) located at Janghang, Korea. The soil samples were air-dried and ground, and the soil of < 0.075 mm was used in this study for homogeneity. *Aqua regia* extraction was used to extract major elements from the soil as follow: 1 g of soil was added to a bottle containing extractants in a ratio of soil: hydrochloric acid: nitric acid of 3:21:7, the mixture was heated at 90 °C for 1 h, filtered using a filter paper, and the filtrate was analyzed inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent technologies, USA) [26–28]. The concentrations of As in S1 and soil S2 were 140 and 77.7 mg/kg respectively. The pH of soils was measured by using a pH meter (Istek, Korea) with a 1:5 suspension of soil and distilled water. The organic matter and cation exchange capacity (CEC) were measured by loss on ignition and determining the exchangeable ammonium using 1 N ammonium acetate solution based on standard test method for soil of Korea. The fractionation of As in soils (Table 1) was analyzed by sequential extraction of As suggested by Wenzel et al (Table S1) [29]. S1 consisted of 52% of labile fraction (F1 + F2 + F3) and 48% of stable fractions (F4 + F5), while S2 had 77% of labile fractions (F1 + F2 + F3) and 23% of stable fractions (F4 + F5). The major fractionation of As in S1 was bound to amorphous iron oxide (F3), while S2 contained similar amounts of amorphous (F3) and crystalline (F4) iron oxides even though the total concentration of As in S1 was almost two times higher than that in S2 (Table 1). The quality of analysis using ICP-OES was controlled by checking the concentration of a standard solution for every 20 samples. All the experiments and measurements were carried out in triplicate and the average values were used.

2.2. As extraction via simultaneous application of oxalic acid and dithionite

All experiments were carried out using an overhead shaker (FinePCR, Korea) at 20 °C and 40 rpm. Na₂S₂O₄ (sodium dithionite,

Download English Version:

<https://daneshyari.com/en/article/6968347>

Download Persian Version:

<https://daneshyari.com/article/6968347>

[Daneshyari.com](https://daneshyari.com)