



Oxalate-based remediation of arsenic bound to amorphous Fe and Al hydrous oxides in soil

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ABSTRACT

In this study, oxalate-based washing process was designed to remediate the arsenic (As)-contaminated soil, where As was mainly associated with amorphous iron–aluminum (Fe/Al) hydrous oxides. Oxalate is a naturally present organic acid and has been commonly used to extract Fe from amorphous oxides due to its reducing and chelating capacities. In the oxalate-based washing process, reductive and ligand-promoted dissolution of iron oxides occurred by oxalate and concurrently As bound to the iron oxides was released from the soil. In addition, desorption of As from the surface of soil could enhance the As removal when As(V) was reduced to As(III) by oxalate. As extraction by oxalate was effective for As bound to amorphous Fe/Al hydrous oxides, but was not effective for As combined with crystalline Fe/Al oxides and residual fraction. The germination test using the residual soil after soil washing showed that germination rate and growth of wheat (*Triticum aestivum* L.) and sunflower (*Helianthus annuus* L.) were improved on the soil after oxalate washing compared to those on the initial and HCl washed soils. Consequently, oxalate was effective to extract As bound to amorphous Fe/Al hydrous oxides and had positive influence on the soil quality for plant growth.

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1. Introduction

Recently, soil contamination by arsenic (As) has attracted great attention due to its wide spread of usages and high toxicities (Bissen and Frimmel, 2003). To remediate the As-contaminated sites, solidification/stabilization, soil washing, electrokinetic remediation and phytoremediation have been commonly applied (Dermont et al., 2008; Jang et al., 2005; Komárek et al., 2013; Kumpiene et al., 2008; Lombi et al., 2001; Virkutyte et al., 2002). Among these techniques, soil washing could be an effective way to remediate As-contaminated soil because the technique removes target metals permanently from the soil by extraction with washing agents and reduces the volume of contaminated soil significantly (Dermont et al., 2008; Jang et al., 2005). In soil washing technique, the selection of washing agents is a key factor for successful application because washing agents react directly to contaminants and remove them (Jang et al., 2007). Generally, inorganic acids (HCl, H₂SO₄ and H₃PO₄) (Giacomino et al., 2010; Ko et al., 2005) and chelating agents such as ethylenediaminetetraacetic acid (EDTA) (Leštan et al., 2008; Peters, 1999) have been used as washing agents for the remediation of metals-contaminated soil. EDTA can effectively extract various metals by forming stable aqueous complexes with metals and by increasing the

apparent solubility of metals. However, EDTA is not effective to remediate oxyanionic forms of metals including As, Se and Cr (Papassopi et al., 1999). Furthermore, EDTA is very hard to recover from EDTA–metals complexes due to its strong complexes with metals and high solubility in water (Leštan et al., 2008). Inorganic acids could extract metals by dissolution of soil minerals and direct ion-exchange between H⁺ and metals. However, strong acids could destroy the soil structure by the mineral dissolution (Bronick and Lal, 2005; Dermont et al., 2008). In addition, oxyanionic As released by the dissolution of soil minerals by acids could be re-adsorbed onto the positively charged soil surface in the acidic condition, which results in the low washing efficiency of As with the inorganic acids. Since EDTA and inorganic acids, the most commonly used agents for soil washing, are not effective for As removal, other washing agents should be applied to achieve high As removal and to minimize the destruction of soil structure. Thus, As extraction using alkaline solutions has been proposed, where As could be directly ion-exchanged with hydroxyl ions (OH[−]). Jang et al. (2007) reported that soil washing using sodium hydroxide could prevent re-adsorption of As, but As extraction was not effective by single-use extraction and additional steps were required. Organic acids such as oxalic, galic, citric and acetic acids have been also applied to soil washing process (Qin et al., 2004; Wasay et al., 1998). Among them, oxalic acid has shown to be able to dissolve various iron oxides by reductive dissolution and complexation (Cornell and Schwertmann, 2003; De Endredy, 1963; Lee et al., 2007; Panias et al., 1996).

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Table 1
4 Steps in the selective sequential extraction procedure [12].

Step	Fraction	Extractant	Soil solution ratio	Experimental conditions
1	Non-specifically adsorbed	0.05 M (NH ₄) ₂ SO ₄	1:25	4 h shaking (20 °C)
2	Specifically adsorbed	0.05 M NH ₄ H ₂ PO ₄	1:25	16 h shaking (20 °C)
3	Amorphous Fe/Al hydrous oxides	0.2 M NH ₄ -oxalate (pH 3.25)	1:25	4 h shaking in the dark (20 °C)
Washing		0.2 M NH ₄ -oxalate (pH 3.25)	1:12.5	10 min shaking in the dark (20 °C)
4	Crystalline Fe/Al hydrous oxides	0.2 M NH ₄ -oxalate + 0.1 M Ascorbic acid (pH 3.25)	1:25	30 min in a water bath at 96 ± 3 °C in the light
Washing		0.2 M NH ₄ -oxalate (pH 3.25)	1:12.5	10 min shaking in the dark (20 °C)
5	Residual	Aqua regia (HCl–HNO ₃)	1:50 (After digestion)	80 °C

As has great affinity with amorphous Fe/Al hydrous oxides. Generally, the adsorption of arsenate onto hydrous ferric oxides (HFO), goethite and magnetite is preferred to that of arsenite under acidic conditions (Dixit and Hering, 2003). Since the surfaces of the iron oxides under acidic conditions are positively charged due to the protons, iron oxides could adsorb negatively charged arsenate (H₂AsO₄[−]) more than uncharged arsenite (H₃AsO₃) under acidic conditions. The reduction of arsenate to arsenite could prevent the re-adsorption of arsenate in the acidic condition. Therefore, the basic hypothesis of this research is that As bound to iron oxides could be extracted by oxalic acid via reductive dissolution of iron oxides and/or reduction of arsenate to arsenite. In this study, we suggested a technique to remove As bound to amorphous hydrous oxides of Fe and Al. First, As extraction by oxalate was compared with those by widely used washing agents including inorganic acid, base and chelating agent and extraction mechanisms of each washing agents were verified. Second, the effects of process variables on As extraction including oxalate concentration, soil to liquid ratio, and solution pH were investigated. Third, the changes of As fractions in three different soil samples were investigated to clarify extraction of As associated with amorphous Fe/Al hydrous oxides. Finally, we evaluated soil qualities via germination test after soil washing with oxalate and hydrochloric acid.

2. Materials and methods

2.1. Characteristics of soils

Two different As-contaminated soils were taken from agricultural lands near former smelting plant (S1 and S2). The other soil was sampled from mine tailing in abandoned mine area (S3). The soil samples were air-dried and sieved by a #200 standard sieve for homogenization. The XRD analysis showed that quartz, kaolinite, and muscovite are the major clay minerals present in the soil samples. The soil pH was analyzed by mixing with deionized water at a ratio of 1:5 (soil:deionized water). EPA method 9081 was used to analyze the cation exchange capacities (CEC) of soil. The pseudo-total concentration of As, Fe, Al, and Mn was analyzed via inductively coupled plasma spectroscopy (ICP-OES, Agilent, USA) following *aqua regia* digestion according to the Korea Standard Test Method (Ministry of Environment, 2010). The fractionation of As was evaluated by sequentially extracting As from soils as suggested by Wenzel et al. (2001). Briefly, As in soils was sequentially extracted as non-specifically adsorbed As (exchangeable, F1), specifically adsorbed As (F2), As bound to amorphous Fe/Al hydrous oxides (F3), As bound to crystalline Fe/Al hydrous oxides

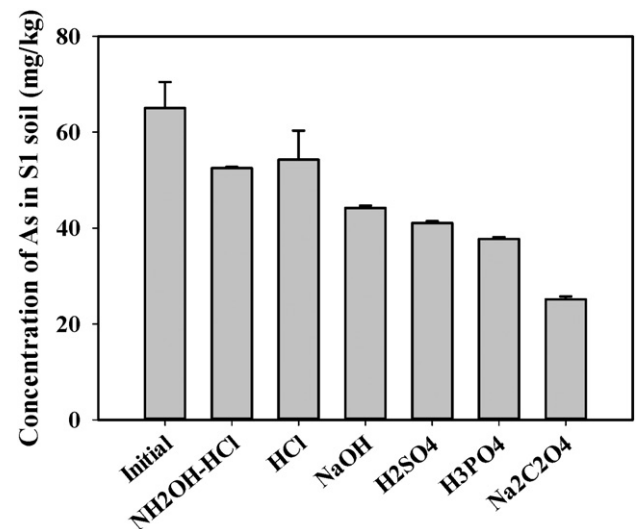
(F4), and residual As (F5). The detail procedure of sequential extraction is summarized in Table 1.

2.2. Experimental procedure

Simple washing tests were conducted to screen washing agents including phosphoric acid (H₃PO₄), sodium oxalate (pH 2, Na₂C₂O₄), hydrochloric acid (pH 2, HCl), hydroxylamine hydrochloride (NH₂OH–HCl), sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH). Hydrochloric acid, phosphoric acid and sulfuric acid were generally used in soil washing process, and hydroxylamine hydrochloride was used to extract reducible fraction (e.g. iron-manganese oxides form) of heavy metals in the Standards, Measurements and Testing Program (SM&T) sequential extraction method from the European Commission (continuation of the BCR and Measurements and Testing Programs) (Rauret et al., 1999). To evaluate the reduction of As(V) by oxalate, 5 mM of As(V) was mixed with 5 mM of oxalate solution (adjusting pH 2 using HCl) for 6 h, and then the amounts of As(III) were analyzed by ICP-OES following As(III) and As(V) fractionation using a Sepak C18 cartridge (Waters Associates, USA) (Gong et al., 2002; Jackson et al.,

Table 3
The concentration of As in each fraction.

Sample no.	Concentration of arsenic (mg/kg)					
	F1	F2	F3	F4	Residual	Sum
1	3.43	15.22	35.42	8.17	9.09	71.33
2	2.64	67.03	96.59	386.89	529.33	1082.48
3	648.159	3.517	67,054.750	18,791.150	6456.125	92,953.700

**Fig. 1.** The concentration of arsenic in S1 soil after applied various extractants. Error bars represent averages of each duplicated experiments.**Table 2**
Initial properties of each sample.

Sample no.	Concentration of metals (mg/kg)				Initial pH	CEC (meq/100 g soil)
	As	Fe	Al	Mn		
1	65.04	28,081.73	12,487.97	528.66	7.20	16.25
2	1127.96	67,210.5	11,721.22	328.14	5.76	21.06
3	94,627.45	140,724.5	2649.47	34.17	2.41	17.41

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