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Remediation of arsenic-contaminated soils via waste-reclaimed treatment agents: Batch and field studies

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ABSTRACT

The potential of three different waste-reclaimed treatment agents (WRTAs) for removing arsenic was evaluated via laboratory-scale batches, column experiments, and field tests. WRTA1 was synthesized using acid mine drainage sludge (AMDS), cement, and sand. WRTA2 and WRTA3 were synthesized by adding fly ash or $Ca(OH)_2$, respectively, to WRTA1. The maximum adsorption capacities of WRTA1, WRTA2, and WRTA3 for As(III) using the Langmuir model were 16.6 mg g^{-1}, 14.5 mg g^{-1}, and 20.6 mg g^{-1}, respectively, and for As(V) were 29.6 mg g^{-1}, 27.3 mg g^{-1}, and 31.3 mg g^{-1}, respectively. The pseudo-second-order equation for the adsorption of As(III) and As(V) fit the kinetics data well. The column study showed that the WRTAs are very effective adsorbents and exhibit $>$ 80% removal of As from the contaminated soil. The inhibition of As accumulation in plants (i.e., rice, chili, and sesame) by the WRTAs was evaluated and showed a 96% inhibition in As accumulation in chili roots for WRTA2. The suggested WRTAs are promising agents for the removal of As and heavy metals from heavily contaminated agricultural soil.

1. Introduction

Arsenic is one of the most toxic chemicals in the environment and has raised concerns of potential risks for humans and for the environment (Elizalde-Gonzalez et al., 2001). Arsenic is a metallic compound that can form inorganic (arsenite and arsenate) and organic (monomethylarsonic acid and dimethylarsinic acid) species. Inorganic forms of arsenic are primarily present as As(V) and As(III) species and can be methylated by microorganisms to form organic arsenic species such as monomethylarsonic acid and dimethylarsinic acid. The bioavailability, toxicity, and mobility of arsenic species in subsurface environments are greatly influenced by physiochemical parameters such as pH, redox potential, clay minerals, organic matter, Fe oxides, Mn oxides, and moisture content (Lee et al., 2015). As(III) is 25–60 times more toxic and mobile than As(V) in soil and groundwater (Hsu et al., 2008). Comparatively, organic arsenic compounds are generally less toxic than inorganic arsenic compounds (Bissen and Frimmel, 2003). Primary sources of arsenic in the environment are mineral weathering and dissolution, geothermal activity, and industrial activities such as the mining and smelting of metal ores. Arsenic pollution of groundwater and soils related to mining activities is extensive in many countries (Smedley and Kinniburgh, 2002; Williams, 2001).

Approximately 900 abandoned metal mines are located in South Korea (Lee et al., 2011). Tailings of abandoned mines may contain high levels of heavy metals and metalloid compounds, therefore causing serious problems for the food chain, subsurface environment, and eventually human health (Santos et al., 2017). X-ray diffraction (XRD) and scanning electron microscope (SEM) investigations (Jarosikova et al., 2017) have revealed that the primary arsenic-containing minerals in the tailings of abandoned mines in Korea are pyrite (FeS_2) and arsenopyrite (FeAsS). Arsenic from these mine tailings have been found to be transported as colloidal phases of As(V) adsorbed to Fe (hydro)-oxides or co-precipitated with hydroxysulfates such as jarosite (Gupta et al., 2005; Slowey et al., 2007). The primary species of As in soils in the vicinity of former As mines are those bound to Fe oxides (Krysiak and Karczewska, 2007).

Investigations of different advanced treatment technologies have been conducted in recent years. The adsorption of As onto Fe materials is an effective and cost-effective method to remediate As-rich water compared to ion exchange, membrane separation, coagulation, and electrolysis methods (Cui et al., 2010; Mohan and Pittman, 2007). The investigations of zero-valent iron and ferrous sulfate for the immobilization of As have been extensively conducted (Kim et al., 2003; Komarek et al., 2013; Kumpiene et al., 2012). However, higher dosages

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of zero-valent iron (> 5% by weight) are not advisable because they can deteriorate the soil structure, changing properties such as the porosity and aggregates, acidification of the soil, and water-solubility and re-release of immobilized As (Mench et al., 1999). Consequently, it is necessary to develop new eco-friendly and economic iron-containing immobilizers using industrial by-products or waste material (Bailey et al., 1999; Yang et al., 2009). In addition, adsorption methods need to consider the risk of recontamination in the soil caused by rising groundwater levels (Rahman et al., 2013). To prevent recontamination, a blocking adsorbent as a filtering barrier is needed that can block the migration of contaminants from contaminated soil layers to clean soil layers due to groundwater flow. Adsorbents have been synthesized from various materials such as chitin/chitosan, oyster shells, lignin, dead biomass, clay, fly ash, and iron-oxide-coated sand (Bailey et al., 1999; Gupta et al., 2005; Ko et al., 2013). In particular, various iron-oxide-coated sands have been applied as effective adsorbents for As removal (Gupta et al., 2005; Hsu et al., 2008; Rahman et al., 2013; Yang et al., 2015).

An estimated 1500 tons per year of neutralized acid mine drainage sludge (AMDS) are being produced in active treatment systems from abandoned mines in South Korea (Yang et al., 2015). AMDS from coal mine drainage sites is preferred due to their low concentration of impurities (such as Cd, Cu, As, and Zn) and high iron oxide mineral content compared to metal mines (Cui et al., 2010; Ko et al., 2013). Many previous studies have reported that iron oxide minerals have a high ability for As(III) and As(V) adsorption and have found that the AMDS was effective in the removal of arsenic from aqueous and solid phases.

The aim of the present study was to investigate the adsorption efficiency of potential waste-reclaimed treatment agents (WRTAs) for arsenic removal. In addition, this study assessed the potential effectiveness of WRTAs in the remediation of heavy metals that usually coexist in contaminated soil near abandoned mine areas. The most efficient of the WRTAs was chosen and used to test its applicability in field sites. The performances of the WRTAs for arsenic removal were tested by examining the adsorption kinetics, adsorption isotherm, and effect of pH. Moreover, the feasibility of the WRTAs was evaluated via column and test-bed (plant transition) experiments for the inhibition of arsenic release in soils.

2. Materials and methods

2.1. Chemicals, materials, and their characterization

The chemicals used in the present study were of analytical reagent grade and of the highest purity. Sodium (meta) arsenite ($NaAsO_2$), sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$), and calcium hydroxide ($Ca(OH)_2$) were purchased from Sigma Aldrich, USA. Portland cement and sand were purchased from Lafarge Halla Cement Co. Ltd. (Seoul, South Korea) and Joomoonjin Silica Sand Co. (Gangneung, South Korea), respectively. Fly ash was collected from the Yeongdong thermal power plant (Gangneung, South Korea). The acid mine drainage sludge (AMDS) was collected from a coal mining site in Tae-Beck, South Korea, and was generated from an active treatment system using $Ca(OH)_2$. The AMDS sample was dried at room temperature and was kept in a desiccator until further use. The size distribution of the AMDS particles was determined via the ASTM D 422-63 method (ASTM, 2007). The chemical constituents of the cement, sand, fly ash, and AMDS were determined via X-ray fluorescence spectrometry (XRF) (ZSX 100e, Rigaku, USA) (Table 1).

2.2. Synthesis and characterization of WRTAs

The waste-reclaimed treatment agents (WRTAs) were synthesized by mixing AMDS with cement, sand, fly ash, and/or $Ca(OH)_2$ as a support material for improving its strength and As adsorbing capacity (Supplementary Table 1). Three types of WRTAs were synthesized based on different types of additives. WRTA1 was mixed with AMDS, cement, and sand. Meanwhile, WRTA2 and WRTA3 were synthesized by adding fly ash or $Ca(OH)_2$, respectively, to WRTA1, followed by dry mixing for 5 min and forming a paste with water at a weight-to-volume ratio of 3:1. The mixing ratios of WRTA1, WRTA2, and WRTA3 are shown in Supplementary Table 1. The mixed paste was put into an injection-molding cylinder (∅ 2 mm) to prepare bar-shaped WRTAs using a piston. The WRTAs were cured via hydration for 7 days under 100% relative humidity. The manufacturing process for the bulk production of WRTAs for the test-bed study is shown in Supplementary Fig. 1. The toxicity characteristic leaching procedure (TCLP) test was performed to identify the leached heavy metals from WRTA1, WRTA2, and WRTA3 (USEPA, 1992). The leached solution was evaluated using inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 730-ES, USA). The point of zero charge (PZC) of the WRTAs was determined using the solid filtrated with an addition method (Mohan and Gandhimathi, 2009).

Table 1
Chemical analyses of AMDS, cement, sand, and fly ash via X-ray fluorescence.

Constituent (wt%)	AMDS[b]	Cement	Sand	Fly ash
SiO_2	4.7	21.2	79.6	50.0
Al_2O_3	2.5	5.5	10.8	26.0
Fe_2O_3	77.6	3.1	0.7	17.4
CaO	11.5	63.5	0.6	1.4
MgO	0.5	2.5	0.2	1.2
SO_3	N.D.[c]	2.6	0.1	1.4
K_2O	0.08	0.68	6.6	N.D.[c]
LOI[a]	3.12	0.92	1.4	2.6

[a] Loss on ignition.
[b] Acid mine drainage sludge.
[c] Not detected.

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2.3. Adsorption isotherm, kinetics, and effect of pH

A batch experiment was conducted for As(III) and As(V) adsorption using the three types of WRTAs. Stock solutions ($1000\ mg\ L^{-1}$) of As (III) and As(V) were arranged using distilled water. A total of 27 mL of varying initial concentrations ($1–300\ mg\ L^{-1}$) in 50 mL capped Nalgene tubes were shaken with 0.1 g of each WTRA for a specified period of contact time at 100 rpm and 25 °C (Jeio Tech Co., SWB-20 shaking water bath). All experiments were initiated at pH 7.0 ± 0.1. The experiments for the pH-edges of the As(III) and As(V) adsorptions were performed by varying the pH from 3 to 11 at $100\ mg\ L^{-1}$. The solutions were pH adjusted using 0.1 M HNO_3 or 1 M NaOH. The kinetics experiments were conducted using a $100\ mg\ L^{-1}$ initial concentration of the As(III) and As(V) solutions, and the contact time was varied from 5 min to 7 days. All experiments were conducted in duplicate.

2.4. Feasibility study of WRTAs as a blocking adsorbent via column and test-bed experiments

A column test was used to evaluate the adsorption capacity of the WRTAs as treatment agents for As removal. Arsenic-contaminated soils were collected from the Daesan mine in Yesan, South Korea, and the total As concentration of the soil was analyzed using US EPA 3050B (USEPA, 1966). The collected soil has $120\ mg\ kg^{-1}$ of As and a pH of 5.5. The soil was dried at room temperature and was passed through a 10-mesh sieve. The column used for this experiment was made of polyvinyl chloride (PVC) material with a length of 20 cm and a diameter of 8 cm. The soil column experiment was performed under four conditions, soil + clean sand (control), soil + WRTA1, soil + WRTA2,