Remediation of arsenic-contaminated soils and washing effluents

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Introduction

Arsenic and other heavy-metal contaminations into water and soil systems are creating potentially serious environmental problems for humans and other living organisms. Mining wastes and acid mine drainages have released several heavy metals (arsenic, cadmium, copper, lead, mercury, chromium, etc.) to ground- and surfacewater systems as well as geological environments due to their solubility and mobility (Mulligan et al., 2001). Heavy-metal or toxic metalloid releases from about 894 among 900 of abandoned metal mines are raising significant environmental problems in Korea. Although the released arsenic can be immobilized in tailings or soil, it can be easily spread into other regions through the transport of arsenic-contaminated solids and arsenic dissolution occurred by changes in the geo-chemical environment to a reductive condition. Therefore, before arsenic reaches a waterbody or groundwater, arseniccontaminated soils must be treated. There are several technologies of reducing arsenic contamination or mobility. Mulligan et al. (2001) evaluated remediation technologies of heavy-metal contaminated soils and groundwater such as isolation and containment, mechanical and pyrometallurgical separation, chemical treatment, permeable treatment walls, electrokinetics, biochemical processes, phytoremediation, in situ soil flushing, and soil washing. Among remediation technologies, soil washing can physico-chemically extracts heavy-metals or metalloids adsorbed onto soils and reduce the volume of arsenic-contaminated soils. In addition, soil washing can be applied to large contaminated areas due to its rapid kinetics, operational easiness, and economical efficiency (USEPA, 2001). Several types of extractants can be used to extract heavy-metals from tailings or soil for soil washing technology. The application of inorganic salts (potassium phosphate, potassium chloride, potassium nitrate, potassium sulfate, or sodium perchlorate) (Alam et al., 2001), inorganic acids (sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, or mixed acid) (Tokunaga and Hakuta, 2002), organic acids (citric or acetic acids) (USEPA, 2002), and alkaline agents (e.g., sodium hydroxide) (Legiec et al., 1997; Jackson and Miller, 2000) have so far been studied. Alam et al. (2001) tried to apply several salts for arsenic extraction from a model soil and found that potassium phosphate was most effective in extracting arsenic with more than 40% extraction in the pH range of 6–8. Tokunaga and Hakuta (2002) studied acid washing by artificially contaminating Kuroboku soil with arsenic and washing with different concentrations of several acids or mixed acids. Phosphoric acid was found to be most effective in a wide range of concentrations. However, it was not possible to extract and remove selectively a target heavy metal since inorganic acids under $pH < 2$ extract heavy metals simultaneously from soil due to ionization effects at low pH conditions. Unlike inorganic acids, alkaline agents can selectively extract arsenic from solids into the liquid phase through ion exchange since hydroxyl ions have an affinity higher than other anionic species such as arsenic, phosphorus, or selenium (Johnston and Heijnen, 2001). Legiec et al. (1997) applied alkaline leaching to remove arsenic from contaminated soils in their soil washing technique. Although Legiec et al. found that sodium hydroxide could specifically extract arsenic with higher efficiencies than other reagents such as monoammonium phosphate, hydrochloric acid, and Na_2CO_3, the results were not properly explained. Furthermore, there were no studies on the optimization of the extraction process and treatment of alkaline washing effluents.

Thus, in this study, the following objectives were established to investigate the applicability of alkaline washing for arsenic contaminated tailings or soil remediation. The specific objectives are as follows: (1) determine the physico-chemical properties and arsenic partitioning into different compartments of tailings or soil through sequential extraction, (2) evaluate the kinetics of arsenic extraction with different types of extractants for arsenic-contaminated tailings or soil, (3) find the relationship between arsenic partitioning characteristics and arsenic extraction efficiencies, and (4) determine the removal efficiency of arsenic in washing solutions by pH adjustment or ferric chloride addition.

Materials and methods

Soil selection and characteristics

Samples were collected from arsenic-contaminated areas in which arsenic levels were over 15 mgkg$_{-1}$, corresponding to the concern level of the Soil Environment Conservation Act of Korea (MOE, 2003). As an original arsenic source and representative of high-level arsenic contamination, arsenic-contaminated tailings were collected from the Nakdong mine (Jungsun, Kangwondo, South Korea), which had been developed as an arsenic mine. As the secondary contaminated areas and representative of middle- and low-level arsenic contamination, two different soil samples were collected from a field and the other from river sediments located near the Suksan mine located in Gunwi (Kungsanbookdo, South Korea). Similar to the Nakdong mine, arsenic concentrations of tailings in the Suksan mine have also been known to have high and variable arsenic concentrations of 81–558 mgkg$_{-1}$ measured by the Korean Standard Test (KST) method (MOE, 2002). These soil samples were sieved through a 0.83-mm opening sieve (#20) to remove large particles and provide a homogeneous soil size. Characteristics of each sample such as pH, particle density, effective size (D_{10}), uniformity coefficient (D_{60}/D_{10}), and organic content were measured by Methods of Soil Analysis (Page et al., 1986). Measurement of cation exchange capacity (CEC) was conducted by EPA Method 9080 (USEPA, 1986b). The total arsenic concentration of soil samples was measured by EPA 3050B (USEPA, 1986a) that is a hot nitric acid digestion method for soil. After pulverizing dried soil samples homogeneously, about 1 g was inserted into a glass beaker and 10 ml of nitric solution (50%) was added. The beaker was covered with a watch glass and heated to about 95 ± 5 _C and refluxed for 15 min. After cooling the sample, the concentrated nitric acid was repeatedly added and evaporated to 5 ml, then, cooled again. Then, hydrogen peroxide (30%) was repeatedly added and 10 ml of concentrated hydrochloric acid was added, then, refluxed again for 15 min. The sample was filtered with Watman No. 41 and diluted to 100 ml at volumetric flask, and analyzed for arsenic concentration.

As a disposal or reuse criterion of arsenic-contaminated tailings or soil samples, the KST methods for soils were adopted from the Soil Environment Preservation Act (MOE, 2003) to extract arsenic, cadmium, and lead. The strictest regulation (6 mgkg_$_1$ of arsenic) for the KST methods was selected as a strategy of soil remediation, while toxicity characteristics leaching procedure (TCLP) tests were conducted to determine the suitability of landfilling treated soils in municipal landfills. The KST method is as follows: (1) add 50 ml of hydrochloric acid (1 M) to each 10 g of soil sample, (2) shake the suspension at a speed of 100 rpm and 30 _C for 30 min, (3) centrifuge 10 ml of suspension at 3200 rpm for 20 min, and (4) filter the supernatant with a 0.6-lm micropore filter, dilute the filtrate, and acidify the filtrate with HNO_3 until the concentration of HNO_3 reaches 1% before the arsenic analysis. The TCLP test was conducted by the method suggested by EPA (USEPA, 1992). Arsenic, lead, and cadmium concentrations of filtrates were measured using inductively coupled plasma spectrometry (ICP-1000VI, Shimadzu Company, Japan) under the concentration range of 0.02–20 mgl_$_1$. For the arsenic precipitation tests, concentrations of metal species such as iron, silicon, aluminum, and manganese were determined by ICP while arsenic were measured by atomic absorption spectroscopy (AA-6401F, Shimadzu _, Japan) connected with a continuous hydride generator (HVG-1, Shimadzu_, Japan) that has a detection limit of 0.5 lgl_$_1$. Duplicates, blank and EPA reference standards were analyzed with each set of samples as a quality control check on the analysis.

Arsenic sequential extraction procedure

In order to obtain the information of chemical speciation and bonding strength of arsenic species, the sequential extraction analysis procedure employed by Kim et al. (2003) was adopted. Although sequential extractions are operationally defined and not fully specific in extracting the element bound to a given fraction, it can provide comparative information to elucidate the relative contribution of target compound and aid in the predictions of elemental mobility (Keon et al., 2001; Pueyo et al., 2003). According to the target binding phases, apportions of arsenic in mgkg$_{\_1}$ can be quantified with high sensitivity (Keon et al., 2001). The detailed sequential extraction is as follows: (1) add 25 ml of 0.25 M KCl to 2.5 g of sample in a 250-ml volumetric flask to extract the soluble fraction of arsenic species and stir the slurry for 2 h; (2) extract the adsorbed fraction of arsenic species by adding 0.1 M Na_2HPO_4 (25 ml, pH 8.0) and stirring for 20 h; (3) extract the carbonate fraction by adding 1 M sodium acetate (25 ml) and stirring for 5 h, and add 0.1 M Na_2HPO_4 (25 ml) and stir for 20 h; (4) extract the soil organic matter fraction by adding 5% NaOCl (10 ml) at pH 9.5 and heating at 70 ± 0.5 _C for 30 min and repeat this step once; (5) extract the easily reducible oxide fraction by adding 0.1 MNH_2OH (25 ml) at pH 2 and stirring for 30 min, add 0.1 M KOH (25 ml), and stir for 20 h; (6) extract the amorphous oxide fraction by adding 0.25MNH_2OH/HCl (25 ml) and stirring for 30 min at 50 ± 0.5 _C, add 0.1 M KOH (25 ml), and stir for 20 h; and (7) extract the operationally defined crystalline mineral fraction of crystalline oxide and amorphous aluminosilicates by adding aqua regia (30 ml HCl and 10 ml HNO_3) and stirring for 1 h. The stirring condition of the above arsenic sequential extraction procedures was 120 rpm. An aliquot of 10 ml of supernatant was taken and centrifuged at 3200 rpm for 20 min, and then filtered with a 0.45-lm micropore filter.

Kinetics of soil washing

Hydrochloric acid and citric acid that have been reported to be effective for extracting heavy-metals in other studies (Benschoten et al., 1994; Cheong et al., 1997). These acids were selected to compare the effectiveness of arsenic extraction of contaminated tailings and soil with sodium hydroxide. Aliquots of 50 mM and 100 mM of each reagent were used for kinetic studies of arsenic extraction. Fifteen grams of each soil sample were carefully put in a 500 ml flask and then 300 ml of reagent solution was slowly added to achieve a ratio of reagent solutions (ml) to soil mass (g) of 20. The suspension was mixed at 20 ± 0.5 _C in a shaker at 300 rpm. At predetermined times (1, 2, 3, 6, 14, and 24 h), 10 ml of supernatant was centrifuged at 3200 rpm for 20 min and filtered with a 0.45-lm filter paper. In order to examine the arsenic extraction mechanism, kinetic data were fitted with four mathematical models: first-order, parabolic diffusion, Elovich, and power function. Through comparing the determination coefficients and standard errors of each model, the best fit model was found.

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