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Extraction of arsenic in a synthetic arsenic-contaminated soil using phosphate

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Abstract

An environment-friendly and cost-effective extraction method has been studied for the removal of arsenic from contaminated soil. A yellow-brown forest soil was contaminated with arsenic(V) and used as a model soil. Among various potassium and sodium salts, potassium phosphate was most effective in extracting arsenic, attaining more than 40% extraction in the pH range of 6–8 with minimum damage to the soil properties. Exchange mechanism is proposed for the extraction of arsenic from soil by phosphate. Sequential extraction shows that phosphate is effective in extracting arsenic of Al- and Fe-bound forms. Arsenic of residual form was not extracted. Arsenic was efficiently extracted by phosphate solution of pH 6.0 at 300 mM phosphate concentration and at 40°C. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Due to its highly toxic and carcinogenic properties to human beings, animals, and plants, arsenic has long been one of the elements of public concern. Soils have been contaminated with arsenic by human activities such as mining (Azcue et al., 1994), smelting, landfilling of industrial wastes, disposal of chemical warfare agents (Schneider and Johnson, 1999), and agriculture in many areas of the world. Soils contaminated by arsenic and heavy metals have been treated mainly by solidification/stabilization methods (Fujikura, 1998). However, there is always a risk of leaching of pollutants from treated soils over a long period of time. The most effective

method of remediation is to remove pollutants from soils.

Both arsenic(V) and arsenic(III) are little sorbed by soils in the alkaline pH range >11 (Tokunaga and Yokoyama, 1999). Accordingly, arsenic sorbed by soils can be extracted by washing with alkali solution (Legiec et al., 1997). Mixed acids such as aqua regia are also effective in extracting arsenic from soils. Treatment of soils with such strong alkali or oxidative acid results in serious damage to soil properties. With an aim of developing a more environment-friendly and cost-effective soil remediation process, the authors studied a new washing method for arsenic-contaminated soils using neutral salt. In the present paper, the following are studied: (1) comparison of the performance of neutral salts for extracting arsenic from a contaminated soil, and (2) evaluation of a phosphate salt for extracting arsenic at different pH, concentrations, reaction times and temperatures.

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2. Materials and methods

2.1. Soil sample

A yellow-brown forest soil sampled in Ibaraki, Japan was used in this study, which is one of the abundant soils in Japan. The soil was air dried at room temperature for a week and sieved through a 2 mm opening sieve. 1.5 kg of the fine fraction was subsequently contacted with 4.0 l of 25 mM sodium arsenate [As(V)] aqueous solution at pH 4. The mixture was intermittently shaken at room temperature for three months. The supernatant was withdrawn by decantation and the residue was washed three times with deionized water. The washed residue was recovered by filtration through a filter paper No. 2 (Advantec, Tokyo, Japan), dried at room temperature under vacuum, and stored in an air-tight plastic container. The characteristics of the arsenic-contaminated soil are shown in Table 1. The arsenic content of the soil sample was determined by hot digestion with $\text{HNO}_3 + \text{HClO}_4 + \text{H}_2\text{SO}_4$ (Standard Methods for Soil Analysis, 1994). The content of organic materials was determined by a TOC analyser furnished with a solid sample module (TOC-5000; Shimadzu, Kyoto, Japan). The contents of water-soluble Cl^- , NO_3^- and SO_4^{2-} ions were analysed by ion chromatography (LC-6A; Shimadzu, Kyoto, Japan). The particle size distribution was measured using standard sieves according to the meth-

ods specified by Craig (1987). The pH of the soil was measured by equilibrating it in deionized water at a soil-to-water ratio of 1:5. The electrical conductivity of the soil supernatant in deionized water was measured using an electrical conductivity meter (AOL-10; DKK, Tokyo, Japan). The cation exchange capacity (CEC) [$\text{cmol}(+) \text{kg}^{-1}$] was measured with an ammonium acetate solution.

2.2. Chemicals

As extractants for arsenic removal from a contaminated soil, potassium phosphate, potassium chloride, potassium nitrate, potassium sulphate and sodium perchlorate of reagent grade were used by dissolving in deionized water ($>16 \text{ M}\Omega \text{ cm}$ of conductivity). To adjust pH, either H_3PO_4 , HCl , HNO_3 , H_2SO_4 , HClO_4 or KOH was used for the respective salt solution. Due to the low solubility of potassium perchlorate, sodium perchlorate was used instead.

2.3. Extraction of arsenic from soil with various salts

A series of 25 ml of 900 mM potassium phosphate, potassium chloride, potassium nitrate, potassium sulphate or sodium perchlorate solutions of different pH values were prepared in 35 ml polycarbonate centrifuge tubes. The pH was adjusted in the range of 3–11 with the respective conjugate acid or KOH solution. Approximately 1.0 g of the contaminated soil was added to the solution and the suspensions were shaken for 24 h in a 20°C thermostat. The suspension was centrifuged at 9000 rpm with a refrigerated high-speed centrifuge (RB-181V, Tomy Seiko, Tokyo, Japan). The resulting supernatant was filtered through a $0.45 \mu\text{m}$ nitrocellulose membrane filter and the filtrate was analysed for pH, arsenic, aluminium, iron, magnesium and calcium.

Arsenic was determined by atomic absorption spectrometry (AA-6200; Shimadzu, Kyoto, Japan) with a continuous hydride generator (HVG-1; Shimadzu) and an electrically heated quartz cell (Watanabe, 1994). Aluminium, iron, magnesium, calcium, and phosphate were determined by inductively coupled plasma spectrometry (ICPS-7500; Shimadzu).

To study the concentration effect, the contaminated soil was treated with a 3, 10, 30, 100, 300, 900 or 1500 mM potassium phosphate solution in the same way as above. The initial pH was adjusted at 6.0 with HCl or KOH . As a control, the contaminated soil was treated with deionized water of pH 6.

2.4. Sorption selectivity

Approximately 1.0 or 0.5 g of unpolluted original soil was added to a 25 ml of mixture solution containing 5.0 mM potassium phosphate and 5.0 mM sodium

Table 1
Characteristics of contaminated soil

Characteristics	
Soil type	Yellow-brown forest soil
Soil class	Fersiallitic soil
Sampling location	Tsukuba, Ibaraki, Japan
Arsenic content (mmol kg^{-1})	49.0
CEC [$\text{cmol}(+) \text{kg}^{-1}$]	52.7
Soluble anions (mmol kg^{-1})	
SO_4^{2-}	0.79
Cl^-	14.8
NO_3^-	7.4
Particle size (%)	
Sand	93.9
Silt	5.96
Clay	0.10
Electric conductivity (mS cm^{-1})	0.54
pH-water	5.53
Water (%)	6.30
Organic matter (TOC, %)	0.93
Chemical composition (mmol kg^{-1})	
Al	5060
Fe	1810
Mg	258
Ca	92.7

arsenate (pH 6.0). The suspension was shaken for 24 h in a 20°C thermostat and centrifuged. The resulting supernatant was filtered through a 0.45 µm membrane filter and the arsenic and phosphate concentrations were analysed.

2.5. Fractionation of arsenic in soils before and after phosphate treatment

Arsenic in the contaminated soil before and after phosphate treatment was fractionated by the sequential extraction method (Sekiya, 1970). Calcium-, aluminium-, iron-bound arsenic, and residual arsenic were extracted with a 2.5% CH₃COOH, 1 N NH₄F, 0.1 N NaOH, and hot mixture of HNO₃ + HClO₄ + H₂SO₄, respectively.

2.6. Kinetic study

300 ml of 900 mM potassium phosphate solution (pH 6.0) was prepared in a 500 ml beaker. 12 g of the contaminated soil was added (soil-to-liquid ratio of 1:25) and the suspension was continuously stirred at 500 rpm with a magnetic stirrer in a 20°C thermostat. At prescribed intervals of time approximately 10 ml of aliquot was taken and filtered through a 0.45 µm membrane filter. The filtrate was subjected to analysis of pH, arsenic, and phosphate.

2.7. Repeated washing at different temperatures

The contaminated soil was treated with a 25 ml of 900 mM potassium phosphate solution (pH 6.0) at 10°C, 20°C, 30°C, 40°C, 50°C, or 80°C. After 1 h shaking the suspension was centrifuged and the resulting supernatant was entirely withdrawn with a plastic syringe and filtered for subsequent analysis. The residue was treated with another 25 ml of 900 mM potassium phosphate solution. The above procedure was repeated three times.

3. Results and discussion

3.1. Characteristics of arsenic-contaminated soil

Inorganic arsenic exists in soils in the forms of arsenate [As(V)] and arsenite [As(III)]. Organic arsenic compounds can also be detected in soils which are produced by biological methylation. In the present paper, only arsenate was studied because it is more strongly retained by soils than arsenite and organic arsenic compounds. A typical yellow-brown forest soil in Japan was artificially contaminated with sodium arsenate as a model contaminated soil. The physical and chemical characteristics of the artificially arsenic contaminated soil are presented in Table 1. The soil is a

weak acidic sandy soil with very small amount of organic matter. At the end of artificial contamination of the soil with 25 mM arsenic, the residual arsenic concentration in the supernatant was 0.002 mM, indicating that arsenic ions were entirely sorbed by the soil.

3.2. Extraction of arsenic from soil with various salts

Results of extraction of arsenic from the contaminated soil by 900 mM potassium chloride, potassium nitrate, potassium sulphate, and sodium perchlorate

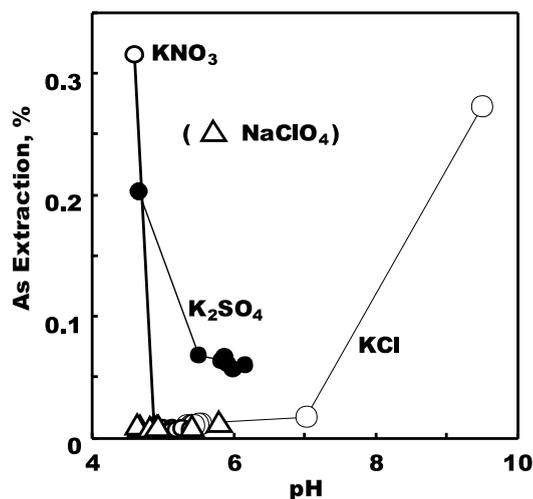


Fig. 1. Extraction of As from contaminated soil using salt solution as a function of pH (salt concentration: 900 mM; temperature: 20°C, shaking time: 24 h).

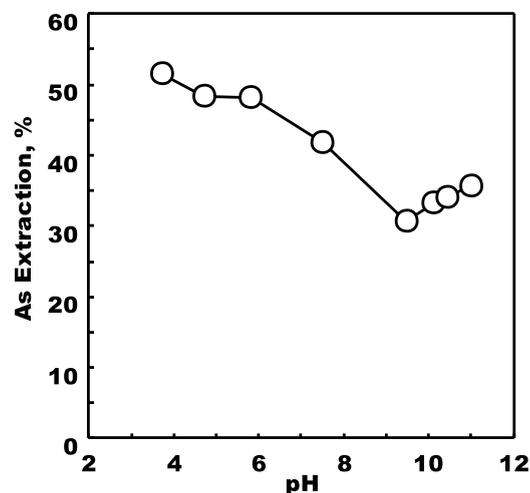


Fig. 2. Extraction of As from contaminated soil using potassium phosphate as a function of pH (potassium phosphate: 900 mM; temperature: 20°C, shaking time: 24 h).

solutions are shown in Fig. 1. Arsenic extractions are exhibited in percentage of amounts of arsenic in solution to those in the original soil. In every case, the arsenic extractions were lower than 0.3%, indicating that these salts are ineffective in removing arsenic from the soil. In other words, arsenic in the soil is stable against leaching with these aqueous salt solutions. Oxidative treatment seems also ineffective in extracting arsenic from the soil, since sodium perchlorate gave less than 0.03% of arsenic extractions. Due to the strong buffer action of the soil, the pH values converged to a narrow range from 5–6 from the initial pH range of 3–11.

Among the salts examined in this study, potassium phosphate was found to be most effective in extracting

arsenic. The results are given in Fig. 2. The arsenic extraction was slightly pH dependent. Unlike the above-mentioned salts, the equilibrium pH did not change significantly from the initial pH due to much stronger buffer function of phosphate ions than that of the soil. The percentage extraction was 50% or higher at pH around 3, giving 40% or higher in the neutral pH range of 6–8. A control experiment in the absence of phosphate in the pH range of 3–11 resulted in only less than 3% extraction, indicating that the much higher arsenic extractions are mainly due to the function of phosphate. Waste phosphate solution may be treated by conventional method such as precipitation with lime to reduce the volume of waste.

Table 2
Selectivity coefficient of forest soil^a

Soil (g)	Equilibrium		pH		Selectivity coefficient (K_s)
	Phosphate concentration (mM)	Arsenic concentration (mM)	Initial	Final	
1.0	1.75	3.04	6.0	6.3	3.4
1.0	1.79	3.05	6.0	6.3	3.8
0.5	3.05	4.11	6.0	6.2	3.6
0.5	3.04	4.07	6.0	6.2	3.3

^a Initial concentrations of phosphate and arsenic were 5.0 mM.

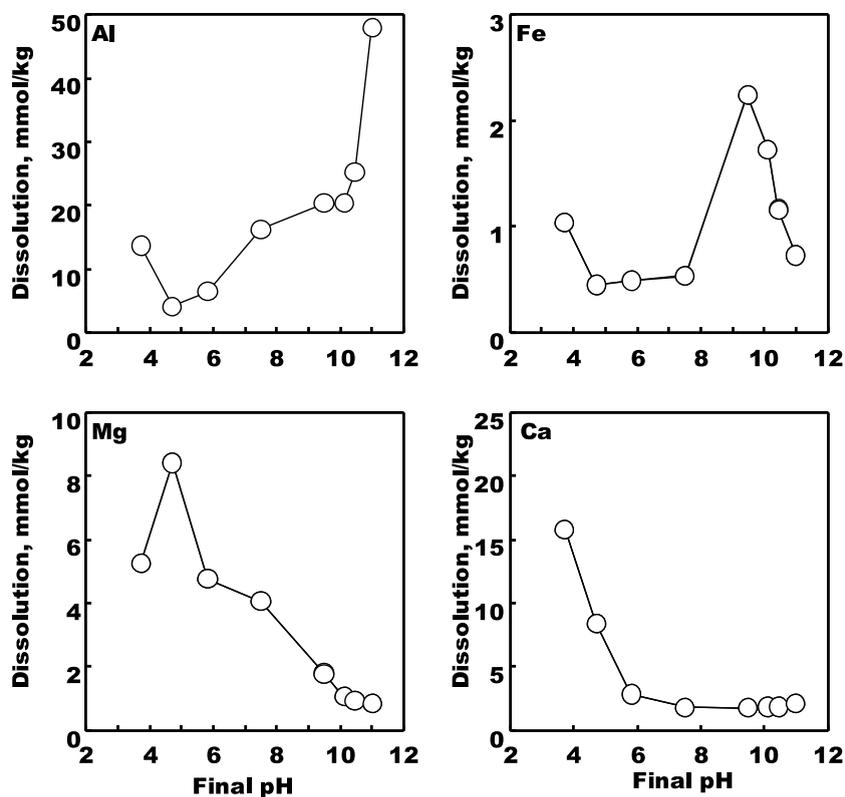


Fig. 3. Dissolution of Al, Fe, Mg and Ca by phosphate treatment as a function of pH from contaminated soil (salt concentration: 900 mM; temperature: 20°C, shaking time: 24 h).

To elucidate the mechanism of extraction of arsenic by phosphate, sorption selectivity of the original unpolluted soil for arsenic and phosphate was studied at a neutral pH. The results with different amounts of the soil are shown in Table 2. Sorption selectivity coefficient of a soil for phosphate against arsenic, K_s , is expressed as

$$K_s = \frac{[P \text{ in soil}] \times [As \text{ in solution}]}{[P \text{ in solution}] \times [As \text{ in soil}]}$$

The calculated K_s values are in the range of 3.3–3.8, indicating that the original unpolluted soil has significantly higher selectivity for phosphate than for arsenic. Hence, by adding excess amounts of phosphate to an arsenic-contaminated soil, arsenic is expelled from the soil and phosphate sorbed in turn.

Fig. 3 shows dissolution of major soil components such as aluminium, iron, magnesium, and calcium by phosphate treatment. The dissolution of these elements, except magnesium, increased with decreasing pH and reached a minimal value in the neutral pH range. By choosing a neutral pH value as an optimal condition, relatively high arsenic extraction can be attained, at the same time, damage to soil properties can be minimized. Thus, phosphate solution of pH 6 was chosen as an extractant and studied in detail in the following sections.

3.3. Fractionation of arsenic in soil

Of soil components, aluminium, iron, and calcium contribute sorption of arsenic by soils (Wasay et al., 2000) while silica and organic matter contribute little (Tokunaga and Yokoyama, 1999). Arsenic in the soil before and after phosphate treatment was fractionated by the sequential extraction procedure which was established for fractionation of phosphate in soils (Sekiya, 1970). The results are shown in Fig. 4. As expected from

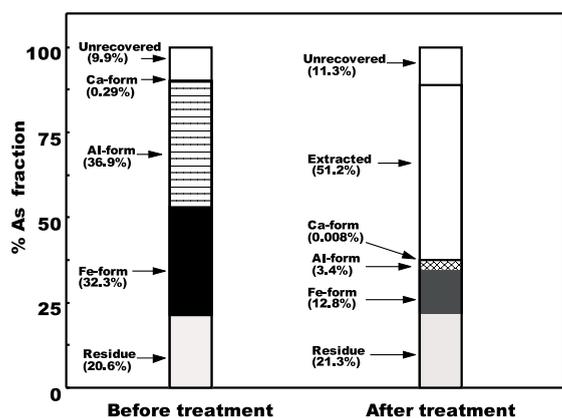


Fig. 4. Fractionation of As in contaminated soil before and after phosphate treatment.

the chemical composition in Table 1, arsenic was retained by the original soil mainly in Al- and Fe-bound form, while contribution of calcium was negligible. Significant amount of arsenic was retained by the soil in the residual form which stands for unextractable arsenic. By phosphate treatment, 51.2% of arsenic was extracted. The remaining arsenic in the soil was fractionated into 0.008% Ca-form, 3.4% Al-form, and 12.8% Fe-form, indicating that phosphate treatment is more effective in extracting arsenic of Al-form than that of Fe-form. After phosphate treatment, 21.3% of arsenic was measured as residual form, which shows that phosphate treatment was ineffective in extracting arsenic of residual form.

3.4. Concentration effect

Contaminated soil was treated with different concentrations of phosphate solutions (initial pH 6.0). The concentration was stepwise changed from 3–1500 mM which is near saturation. The results are shown in Fig. 5. The arsenic extraction with deionized water of neutral pH (control) was only 0.01%. The arsenic extractions abruptly increased by increasing phosphate concentration to 300 mM where approximately 35% extraction was attained. The concentration effect was not significant in the range of 900–1500 mM. Thus, the optimum phosphate concentration seems to be approximately 300 mM for soil treatment to avoid introduction of excess phosphate into soils. But 900 mM phosphate was used in the following experiments to make clear the effects of other parameters such as time and temperature.

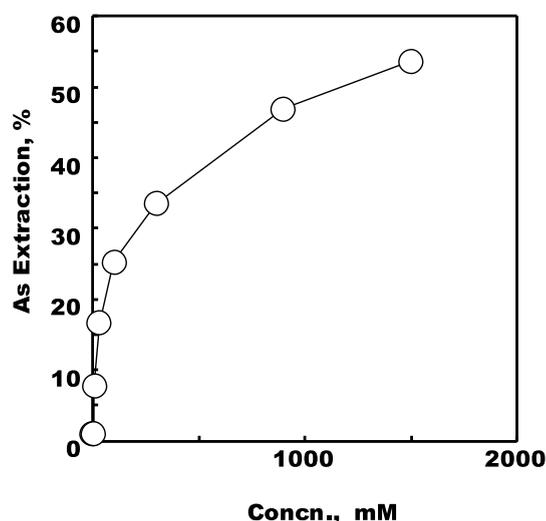


Fig. 5. Effect of potassium phosphate concentration on As extraction from contaminated soil (initial pH: 6.0; temperature: 20°C, shaking time: 24 h).

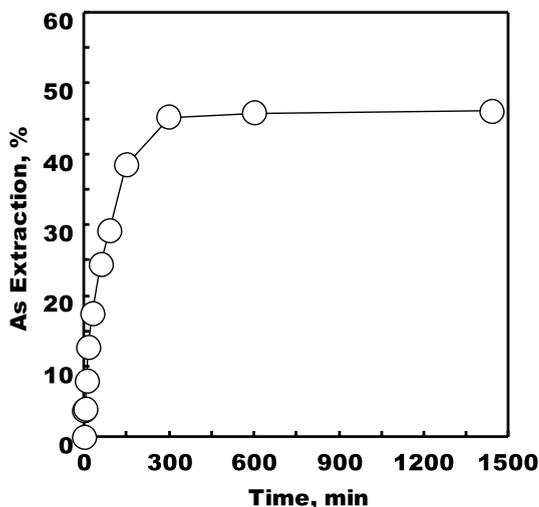


Fig. 6. Kinetics of As extraction using phosphate solution (phosphate concentration: 900 mM; initial pH: 6.0, temperature: 20°C).

3.5. Kinetic study

Rate of arsenic extraction by phosphate (initial pH 6.0) was measured on the contaminated soil. In Fig. 6 the arsenic concentrations in the aqueous solution are plotted against reaction time. Arsenic was extracted efficiently in the initial stage of the treatment, attaining 38% extraction in 150 min. The equilibrium was reached within 300 min. The arsenic extraction was found to follow a first-order reaction, which can be expressed as

$$\log(C_t/C_0) = -(k/2.303)t,$$

where C_t is the residual arsenic in soil (mmol kg^{-1}) at time t ; C_0 is the initial arsenic in soil (mmol kg^{-1}); k is the rate constant (min^{-1}); t is the time (min). The rate constant k was calculated to be 0.0037 min^{-1} at 20°C.

3.6. Repeated washing at different temperatures

As the kinetic study shows, extraction of arsenic proceeds rapidly in the beginning of the treatment, suggesting effectiveness of short-time treatment. One-hour washing was repeated three times by renewing phosphate solution at 10°C, 20°C, 30°C, 40°C, 50°C, and 80°C, and the results are shown in Fig. 7 where washing effects are expressed by cumulative percentage arsenic extractions of each step. Scrutiny of the results at 20°C indicates that the repeated washing does not significantly increase arsenic extraction. Only 40% or higher arsenic extraction was attained by repeating washing three times.

Temperature is also an important parameter that can influence the extraction process. Temperature affects

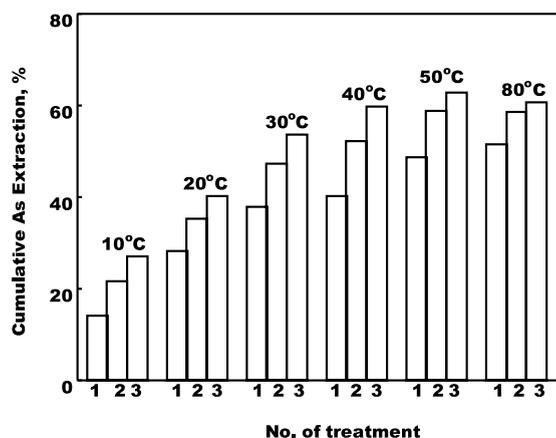


Fig. 7. Repeated washing of contaminated soil using phosphate solution (phosphate concentration: 900 mM; initial pH: 6.0, shaking time: 1 h).

conductivities, ionic mobilities, electroosmosis and sorption reactions. The cumulative arsenic extraction of the third stage significantly increased by raising temperature from 10–40°C. But raising temperature to 40°C or higher did not enhance arsenic extraction, attaining approximately 60% extraction at the third stage. As consumption of energy should be minimized, 40°C should be taken as an optimum temperature.

4. Conclusions

Laboratory batch experiments were conducted to develop an environment-friendly and cost-effective extraction method for the removal of arsenic from contaminated soil. Among various potassium and sodium salts, potassium phosphate was most effective in extracting arsenic, attaining more than 40% extraction in the pH range of 6–8 with minimum dissolution of aluminium, iron, and calcium from the soil. The selectivity coefficients of the original soil for phosphate against arsenic was 3.3–3.8, suggesting an exchange mechanism between arsenic and phosphate. Sequential extraction shows that arsenic was retained by the soil mainly in Al- and Fe-bound form. Phosphate treatment was effective in extracting arsenic of Al- and Fe-form. Arsenic of residual form was not extracted. The arsenic extractions abruptly increased by increasing phosphate concentration to 300 mM, attaining 35% extraction. The arsenic extraction follows the first-order reaction and the rate constant was calculated to be 0.0037 min^{-1} . One-hour repeated washing did not enhance arsenic extraction. But cumulative extraction significantly increased by raising the temperature to 40°C, attaining 60% extraction.

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