



Arsenic removal from contaminated soil using phosphoric acid and phosphate

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Abstract

Laboratory batch experiments were conducted to study arsenic (As) removal from a naturally contaminated soil using phosphoric acid (H_3PO_4) and potassium dihydrogen phosphate (KH_2PO_4). Both H_3PO_4 and KH_2PO_4 proved to reduce toxicity of the soil in terms of soil As content, attaining more than 20% As removal at a concentration of 200 mmol/L. At the same time, acidification of soil and dissolution of soil components (Ca, Mg, and Si) resulted from using these two extractants, especially H_3PO_4 . The effectiveness of these two extractants could be attributed to the replacement of As by phosphate ions (PO_4^{3-}). The function of H_3PO_4 as an acid to dissolve soil components had little effects on As removal. KH_2PO_4 almost removed as much As as H_3PO_4 , but it did not result in serious damage to soils, indicating that it was a more promising extractant. The results of a kinetic study showed that As removal reached equilibrium after incubation for 360 min, but dissolution of soil components, especially Mg and Ca, was very rapid. Therefore dissolution of soil components would be inevitable if As was further removed. Elovich model best described the kinetic data of As removal among the four models used in the kinetic study.

Key words: arsenic (As); removal; phosphoric acid (H_3PO_4); potassium dihydrogen phosphate (KH_2PO_4); chemical extraction

Introduction

Arsenic (As) is known to be a very toxic element and carcinogen to humans (Moon *et al.*, 2004). In nature, As is released in the environment through weathering and volcanism (Juillot *et al.*, 1999). Arsenic is also released by anthropogenic activities, such as mining (Krysiak and Karczewska, 2007), smelting (Chen *et al.*, 2002), agriculture (Leist *et al.*, 2000), accident (Liu *et al.*, 2005), preservation of wood (Bhattacharya *et al.*, 2002), and illegal waste dumping (Tokunaga and Hakuta, 2002).

Arsenic can cause damage to human health through the food chain and water supply, and As contaminated soil is a major source of contamination in the food chain and water supply (Warren *et al.*, 2003; Guo *et al.*, 2007). Therefore, people have paid more attention to soil As contamination and remediation of As contaminated soils in recent years. Some countermeasures for remediation of As contaminated soil have been investigated and applied, including containment, capping, soil replacement, and solidification/stabilization (Tokunaga and Hakuta, 2002). However, As still remains in the environment after using such conventional countermeasures. There is always a risk of leaching, which can be caused by changes in the environmental conditions. To solve this soil contamination problem permanently, As must be removed from soils.

Phytoremediation and chemical extraction are the two most promising methods to remove soil As. However, one important limitation of phytoremediation is the time required to clean up a contaminated site. Salido *et al.* (2003) reported that if it was assumed that all soil As was targeted, and phytoextraction using Chinese brake ferns (*Pteris vittata*) was constant and independent of the soil As content, eight years with two harvests per year would be required to reduce the soil As contents from 82 mg/kg to a safe level (40 mg/kg). Compared to phytoremediation, chemical extraction can physicochemically extract heavy metals or metalloids absorbed in the soils and reduce the volume of As contaminated soils. In addition, chemical extraction can be applied to large contaminated areas because of its rapid kinetics, operational easiness, and economical efficiency (USEPA, 2001). For heavy metal contaminated soils, chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), have been successfully applied as extractants (Papassiopi *et al.*, 1999; Khodadoust *et al.*, 2005). However, these chelating agents are not effective in removing As, which is in an anionic form (Tokunaga and Hakuta, 2002). Therefore chemical extraction of As is more difficult than that of heavy metals and has received little attention. Very limited published data about As removal from contaminated soils are available. Lei *et al.* (2003) reported that phosphorus could reduce As adsorption by soil. Alam *et al.* (2001)

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applied several salts for As extraction from a model soil and found that phosphate was the most effective in extracting As, attaining more than 40% extraction. Tokunaga and Hakuta (2002) studied acid washing of an artificial As contaminated soil, and phosphoric acid proved to be the most promising in the extraction, attaining 99.9% As extraction at 9.4% acid concentration. Although phosphate and phosphoric acid proved to be effective in removing As from artificial contaminated soils, it was not known whether these two extractants were equally effective for naturally contaminated soils. Furthermore, there were no comparative studies on phosphate and phosphoric acid for remediation of As contaminated soils.

The purposes of this study were to compare the performances of phosphoric acid (H_3PO_4) and potassium dihydrogen phosphate (KH_2PO_4) in removing As from a naturally contaminated soil, and to compare the damages to soil properties resulting from using these two extractants, including changes in soil pH and dissolution of soil components.

1 Materials and methods

1.1 Soil sample

A calcareous paddy soil was collected from a farm in the suburb of Chenzhou in Hunan Province, southern China, which had been contaminated by an As smelting factory in 2000. The soil sample was air dried and passed through a 2-mm sieve to provide a homogeneous size. The main physico-chemical properties of this soil are given in Table 1. According to Chinese standard methods for soil analysis (Lu, 2000), soil pH value was measured with a pH electrode (Delta320, Mettler-Toledo, Switzerland) by mixing 5.0 g of soil sample and 25 ml of deionized water with shaking for 0.5 h. The cation exchange capacity (CEC) was measured with ammonium acetate solution, and the content of soil organic matter was determined by a volumetric method of potassium permanganate heating. Arsenic content in the soil was determined with atomic fluorescence spectrometry (AFS-2002E, Haiguang Instrumental Corp., China) after acid digestion with nitric acid/sulfuric acid (Lu, 2000), and exchangeable As content of soil was determined after extraction with ammonium chloride (Wu *et al.*, 2006).

1.2 As removal from soil using H_3PO_4 and KH_2PO_4

Arsenic extraction batch tests were conducted at different concentrations (0, 5, 10, 25, 50, 100, and 200 mmol/L) of H_3PO_4 solution or KH_2PO_4 solution. Fifteen grams of soil were carefully put in a 250-ml conical flask, 150 ml of H_3PO_4 solution or KH_2PO_4 solution was slowly added to achieve a solution-to-soil ratio of 10, and then the suspension was shaken in a $20 \pm 0.5^\circ\text{C}$ thermostat for 6 h. The suspension was centrifuged at 3000 r/min with a

centrifuge. The resulting supernatant was filtered through a $0.45\text{-}\mu\text{m}$ membrane and the filtrate was analyzed for As, Ca, Mg, Fe, Al, and Si. Arsenic was determined with atomic fluorescence spectrometry, and Ca, Mg, Fe, Al, and Si were determined with inductively couple plasma optical emission spectrometry (Optima 2000, Perkin-Elmer, USA).

1.3 Kinetics of As removal

H_3PO_4 solution or KH_2PO_4 solution of 100 mmol/L was used for kinetic studies of As removal. Ten conical flasks with 15 g of soil each were prepared, and then 150 ml of H_3PO_4 solution or KH_2PO_4 solution was slowly added to each flask. The suspension was shaken in a $20 \pm 0.5^\circ\text{C}$ thermostat. At the predetermined time (5, 10, 20, 40, 60, 120, 240, 360, 720, 1440 min), the flask was taken out from the thermostat, the supernatant was centrifuged at 3000 r/min and filtered through a $0.45\text{-}\mu\text{m}$ membrane, and the filtrate was analyzed for As, Ca, Mg, Fe, Al, and Si.

2 Results and discussion

2.1 As removal from contaminated soil using H_3PO_4 and KH_2PO_4

2.1.1 As removal from soil

Arsenic removal obtained from H_3PO_4 and KH_2PO_4 solutions is presented in Fig.1. Arsenic removal was only 0.89 mg/kg when 0 mmol/L H_3PO_4 solution was used and gradually increased by increasing H_3PO_4 concentration to 200 mmol/L, where As removal of 18.21 mg/kg was attained. Removal efficiency of soil As varied from 1.1%–22.8% on using H_3PO_4 . With increase in concentrations of KH_2PO_4 solutions, As removal also gradually increased from 0.81 mg/kg at 0 mmol/L to 16.10 mg/kg at 200 mmol/L, with removal efficiencies of 1.0%–20.2%.

According to the environmental quality standard for soil (EQSS) constituted by the State Environmental Protection Administration of China, As tolerance limit in soil is 30

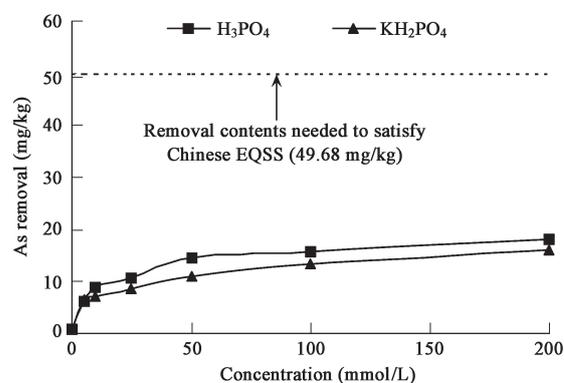


Fig. 1 Arsenic removal from soil at different concentrations of H_3PO_4 or KH_2PO_4 .

Table 1 Physico-chemical properties of the tested soil sample

Soil type	pH	CEC (cmol(+)/kg)	Organic matter (g/kg)	Total As (mg/kg)	Exchangeable As (mg/kg)
Paddy soil	7.91	17.5	21.9	79.68	1.12

mg/kg, which is very strict. The guideline limit of 50 mg/kg is given by the UK's Code of Good Agricultural Practice for the Protection of Soil (Warren *et al.*, 2003), and in Netherlands C standard, maximum permitted concentration in soil is also 50 mg/kg (Papassiopi *et al.*, 1999). To satisfy the EQSS, As removal of 49.68 mg/kg must be obtained, and obviously the aim was not achieved by using H_3PO_4 or KH_2PO_4 in this experiment. Even for chemical extraction of heavy metals from soils that was widely believed to be promising, tolerant limits of heavy metals according to this standard often cannot be satisfied after one extraction as per many previously published experimental results (Papassiopi *et al.*, 1999; Peters, 1999). Although EQSS was not satisfactory in the experiment, the results presented in Fig.1 indicated that, in terms of soil As content, As toxicity of the soil was clearly reduced through using H_3PO_4 or KH_2PO_4 . Both the extractants were effective in remediation of As contaminated soil.

Alam *et al.* (2001) studied sorption selectivity of unpolluted soil for arsenate and phosphate. They found that the sorption selectivity coefficients of the soil for phosphate against arsenate, expressed as: $K_s = C_{\text{P(soil)}} \times C_{\text{As(solution)}} / (C_{\text{P(solution)}} \times C_{\text{As(soil)}})$, were in the range of 3.3–3.8, indicating that soil had significantly higher sorption selectivity for phosphate than for arsenate. Hence, As removal could be attributed to As being expelled by the phosphate ion (PO_4^{3-}) from the soil and PO_4^{3-} being absorbed by the soil in turn. Tokugnaga and Hakuta (2002) reported that soil As could be displaced by PO_4^{3-} through ligand exchange, and the effectiveness of H_3PO_4 could be partially attributed to the function of the acid, which dissolved the metallic components in the soil, with which As was associated. Fig.1 clearly shows that As removal using KH_2PO_4 was less than that using H_3PO_4 , but the difference was not marked, indicating that the function of H_3PO_4 as an acid to dissolve metallic components had little effect on As removal, and acid washing using HCl and HNO_3 might be ineffective in remediating As contaminated soil.

2.1.2 Damage to soil

Both pH of H_3PO_4 and KH_2PO_4 solutions at different concentrations and the changes of soil pH on using these two series of solutions are shown in Fig.2. The results showed that, with increase in concentrations, pH of KH_2PO_4 solutions decreased 0.62–1.47 units, and pH of H_3PO_4 solutions decreased 3.33–4.43 units. Obviously, the former was milder than the latter. In addition, it was found that the soil samples were slightly acidified by using KH_2PO_4 (soil pH decreased 0.20–0.72), but were acidified by using H_3PO_4 (soil pH decreased 0.61–1.98). All these results supported the fact that H_3PO_4 was a middle strong acid and KH_2PO_4 was a weak acid salt.

To understand better the damage to soil resulting from these two extractants, the dissolution of soil components was evaluated (Table 2). The results showed that, with increase in concentrations of H_3PO_4 , the dissolution of Ca, Mg, and Si sharply increased. Ca dissolution was the highest, and there existed a significant linear rela-

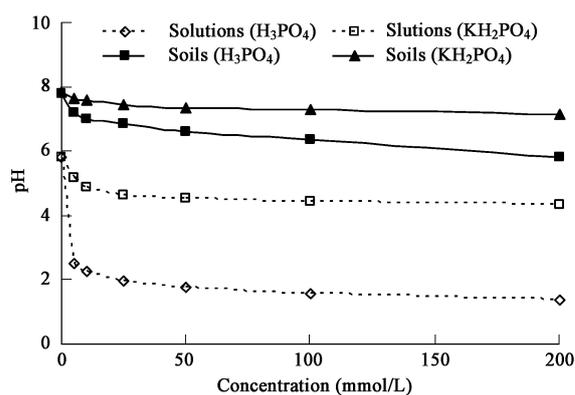


Fig. 2 Changes in soil pH on using H_3PO_4 and KH_2PO_4 .

tionship ($r = 0.999$; $n = 7$, $r_{0.01} = 0.798$), indicating that soil Ca dissolution was very sensitive to H_3PO_4 . However Fe and Al could hardly be detected, indicating that H_3PO_4 did not result in their marked dissolution. Si dissolution increased linearly with H_3PO_4 concentrations, simultaneously increasing with Ca and Mg dissolutions, indicating a chemical weathering of Ca or Mg minerals in the soil because of H_3PO_4 treatment. With increase in concentrations of KH_2PO_4 solutions, the dissolution of Mg and Si increased gradually. However, Ca dissolution initially increased and subsequently decreased. This might be because of aggradation of dissolved Ca^{2+} and PO_4^{3-} coalescence under the condition of high concentrations of Ca^{2+} and PO_4^{3-} with high pH. Just like H_3PO_4 , KH_2PO_4 hardly resulted in the dissolution of Fe and Al. KH_2PO_4 resulted in less dissolution of Ca, Mg, and Si when compared to H_3PO_4 . At a concentration of 200 mmol/L, H_3PO_4 resulted in 57.1, 2.8, and 1.6 times dissolution of Ca, Mg, and Si, as KH_2PO_4 . In a word, changes in soil pH, and dissolution of Ca, Mg, and Si showed that H_3PO_4 resulted in more serious damage to soil and, inversely, KH_2PO_4 was more environment-friendly.

The soil sample used in this study was a calcareous soil. Hence it was inevitable that a great deal of Ca was dissolved because of using these two extractants. In this experiment, however, concentrations of these two extractants were not high enough to dissolve Fe and Al. Of

Table 2 Dissolution of Ca, Mg, Fe, Al, and Si on using H_3PO_4 and KH_2PO_4 solutions

Extractant	Concentration (mmol/L)	Dissolution of the soil components (mg/kg)				
		Ca	Mg	Fe	Al	Si
H_3PO_4	0	395.96	4.08	1.08	nd	21.18
	5	1209.45	19.67	nd	nd	79.34
	10	2156.43	30.90	1.32	nd	100.13
	25	5426.17	51.64	nd	nd	140.70
	50	10758.38	68.39	nd	nd	179.33
	100	21867.30	89.64	nd	nd	233.00
KH_2PO_4	0	380.33	4.21	nd	nd	21.50
	5	663.02	13.09	nd	0.06	60.53
	10	905.73	19.16	0.46	nd	75.71
	25	1314.81	28.00	nd	nd	97.38
	50	1416.75	34.35	nd	nd	115.06
	100	1388.81	39.33	nd	nd	151.10
200	713.79	42.70	0.11	0.19	183.08	

nd: Not detected.

soil components, Ca, Fe, and Al contribute to sorption of As by soils, whereas, Si and other components contribute little (Alam *et al.*, 2001). H_3PO_4 resulted in more Ca dissolution than KH_2PO_4 , but hardly removed more As, indicating that Ca dissolution on using H_3PO_4 contributed little to As removal in the experiment.

2.2 Kinetics of As removal and soil components dissolution

Kinetic data of As removal and soil components dissolution are shown in Fig.3. In this kinetic study, 100 mmol/L H_3PO_4 solution or KH_2PO_4 solution was used. Although soil As was extracted efficiently in the initial stage of treatment, attaining 71.9% and 61.0% of equilibrium removal contents in 120 min for H_3PO_4 and KH_2PO_4 , respectively, the equilibrium was not reached until 360 min, implying that As in soil could not be rapidly removed. This result was not similar to the study of Tokunaga and Hakuta (2002) in an artificial As contaminated soil. Ca dissolution reached equilibrium almost instantly, and decreased slightly subsequently. Mg dissolution was also rapid, obtaining 85.9% and 94.5% of equilibrium dissolution contents in 20 min for H_3PO_4 and KH_2PO_4 , respectively. Si dissolution was rapid, before 120 min, and slowly increased subsequently, but did not reach equilibrium in the kinetic experiment. Just like the former tests, Fe and Al were hardly dissolved. Soil components, especially Ca and Mg, could be rapidly dissolved, hence, As could not be further removed if it was intended to control the dissolution of soil components. In addition, it was again found that the difference in efficiency of As removal between H_3PO_4 and

KH_2PO_4 was inappreciable, although, H_3PO_4 resulted in much more dissolution of soil components than KH_2PO_4 .

The kinetic data of As removal were analyzed using four different existing models, namely, first-order, parabolic diffusion, two-constant, and Elovich model. The linear forms, parameters, correlation coefficients, and standard errors of these models are given in Table 3. The correlation coefficients followed a similar sequence of Elovich > two-constant > parabolic diffusion > first-order for both H_3PO_4 and KH_2PO_4 treatments. Obviously, Elovich model was the best and first-order model was the worst, in terms of correlation coefficients, to describe the kinetic data of As removal in the study, respectively. The Elovich model was successfully applied to describe sorption and desorption of phosphorus in soils (Chien and Clayton, 1980), indicating that release of As from soil might be the same as release of phosphorus and could be a complicated process. In addition, for these two extractants, the same model was proved to best fit the kinetic data of As removal, which supported the conclusion that the mechanisms of As removal were similar for these two extractants.

3 Conclusions

Laboratory batch experiments were conducted to study As removal with H_3PO_4 and KH_2PO_4 from naturally contaminated soil. The results showed that both H_3PO_4 and KH_2PO_4 were effective in removing As from soil. Meanwhile, decrease in soil pH and dissolution of soil components (Ca, Mg, Si) resulted from using these two extractants, especially H_3PO_4 . Effectiveness of these two

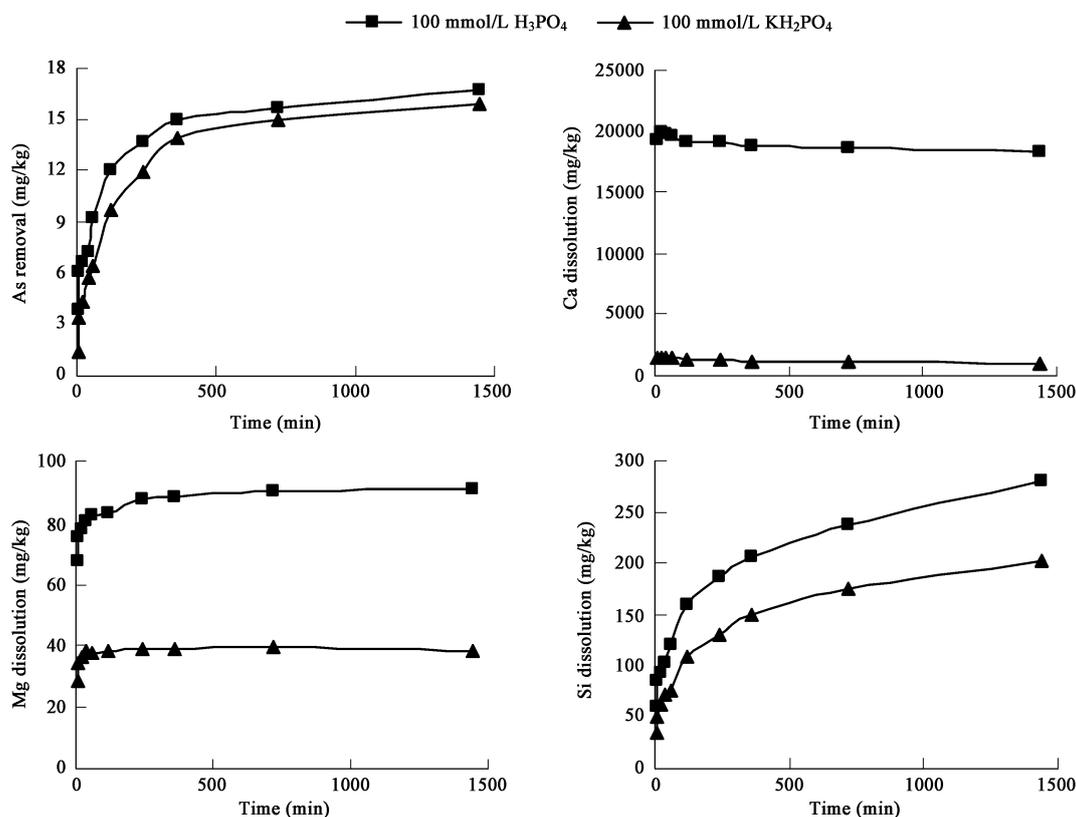


Fig. 3 Kinetics of As removal and dissolution of soil components on using H_3PO_4 and KH_2PO_4 .

Table 3 Kinetic models of As removal

Extractant	Model	Linear form	Parameter		<i>r</i>	SE
			A	B		
H ₃ PO ₄	First-order	$\ln(S_0 - S) = A + Bt$	4.267	-0.0001	0.780**	0.044
	Parabolic diffusion	$S = A + Bt^{1/2}$	5.832	0.3569	0.906**	2.056
	Two-constant	$\ln S = A + B \ln t$	1.1119	0.2576	0.972**	0.124
	Elovich	$S = A + B \ln t$	-0.2152	2.4241	0.986**	0.802
KH ₂ PO ₄	First-order	$\ln(S_0 - S) = A + Bt$	4.2982	-0.0001	0.804**	0.047
	Parabolic diffusion	$S = A + Bt^{1/2}$	3.2	0.4145	0.924**	2.120
	Two-constant	$\ln S = A + B \ln t$	0.1441	0.4034	0.960**	0.232
	Elovich	$S = A + B \ln t$	-3.61	2.7675	0.989**	0.834

** Significant correlation ($p < 0.01$). *t*: reaction time; S_0 : initial As content in soil; *S*: As removal content at time *t*; *r*: correlation coefficient; SE: standard error.

extractants could be attributed to replacement of As by PO₄³⁻. KH₂PO₄ removed almost the same soil As as H₃PO₄, but did not result in serious damage to soils, indicating that KH₂PO₄ was an effective and environment-friendly extractant. The results of kinetic study indicated that As removal reached equilibrium after incubation for 360 min, and dissolution of some soil components was inevitable if further As removal was attained. The Elovich model was the best to describe the kinetic data of As removal among the four existing models used in the kinetic study. Through lab-scale study, it could be expected that H₃PO₄ and KH₂PO₄ would be effective in remediating large-scale As contaminated areas, but some countermeasures, such as application of environment-friendly extractants and choice of proper concentrations of extractants, should be adopted to minimize damage of chemical extraction to soil.

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