



## Research article

## Removal of divalent heavy metals (Cd, Cu, Pb, and Zn) and arsenic(III) from aqueous solutions using scoria: Kinetics and equilibria of sorption

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## ABSTRACT

Kinetic and equilibrium sorption experiments were conducted on removal of divalent heavy metals (Pb(II), Cu(II), Zn(II), Cd(II)) and trivalent arsenic (As(III)) from aqueous solutions by scoria (a vesicular pyroclastic rock with basaltic composition) from Jeju Island, Korea, in order to examine its potential use as an efficient sorbent. The removal efficiencies of Pb, Cu, Zn, Cd, and As by the scoria (size = 0.1–0.2 mm, dose = 60 g L<sup>-1</sup>) were 94, 70, 63, 59, and 14%, respectively, after a reaction time of 24 h under a sorbate concentration of 1 mM and the solution pH of 5.0. A careful examination on ionic concentrations in sorption batches suggested that sorption behaviors of heavy metals onto scoria are mainly controlled by cation exchange. On the other hand, arsenic appeared to be sensitive to specific sorption onto hematite (a minor constituent of scoria). Equilibrium sorption tests indicated that the removal efficiency for heavy metals increases with increasing pH of aqueous solutions, which is resulted from precipitation as hydroxides. Similarly, multi-component systems containing heavy metals and arsenic showed that the arsenic removal increases with increasing pH of aqueous solutions, which can be attributed to coprecipitation with metal hydroxides. The empirically determined sorption kinetics were well fitted to a pseudo-second order model, while equilibrium sorption data for heavy metals and arsenic onto scoria were consistent with the Langmuir and Freundlich isotherms, respectively. Natural scoria studied in this work is an efficient sorbent for concurrent removal of divalent heavy metals and arsenic.

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## 1. Introduction

Human activities introduce heavy metals and arsenic to the hydrosphere in many ways such as burning of fossil fuels, smelting of ores, municipal sewage, industrial effluent, mining activities, landfill, mineral weathering, underground toxic waste disposal, etc. [1,2]. These contaminants, regardless of their sources, are easily dispersed into the aquatic system, and tend to accumulate in living organisms, resulting in various disorders and diseases in the ecosystem.

Various treatment technologies have been employed for the clean-up of waters contaminated with trace toxic metals in aquatic environments. Conventional techniques usually involve the application of physico-chemical processes such as precipitation, oxidation, reduction, solvent extraction, electrolytic extraction, dilution, adsorption, (electro)dialysis, filtration, flocculation, sedimentation, evaporation, osmosis, ion-exchange, chelation, biosorption, etc. [3]. Among the techniques available,

it is known that sorption plays an important role in controlling the fate and transport of metal contaminants in ecosystem. Moreover, it is also important to select an appropriate sorbent for its successful application. Large-scale sorption processes for water treatment demand inexpensive, nontoxic, available sorbents of known kinetic parameters and sorption characteristics. To date, a number of researchers have focused on the development of cost-effective materials and have examined the effectiveness of various natural inorganic and organic materials on metal sorption, such as zeolite [4], palygorskite [5], bentonite [6], vermiculite [7], red mud [8], pyrite [9], fly ash [10,11], cocoa shells [12], and bio-bark [13]. Natural Jeju scoria, for example, has shown to adsorb larger amounts of zinc (about 1.5 times) compared to that of commercial activated carbon in batch-type sorption tests [14].

Scoria is bomb-sized, generally vesicular pyroclastic rock with basaltic composition, which is reddish brown to black in color and is of low density. It has been used in several industrial applications, such as the manufacturing of a lightweight concrete mixture, a heating-insulating material, low-cost fillers in paints, and sorbents [15,16]. Scoria is abundant in many places worldwide including Central America, Southeast Asia (Vietnam, etc.), East Africa (Ethiopia, Kenya, etc.), and Europe (Greece, Italy, Spain, Turkey, etc.)

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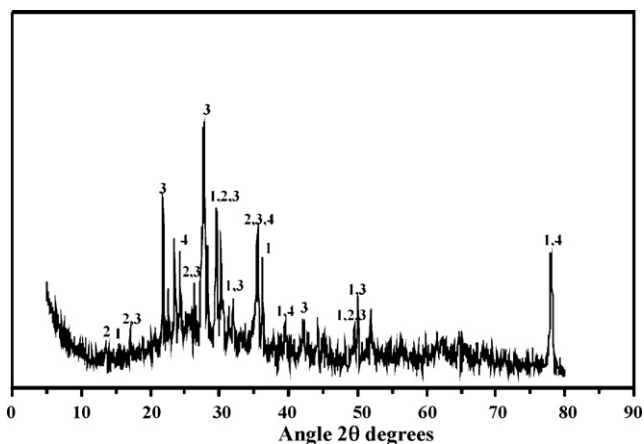
[14–16]. Despite its use in various industrial applications as well as the importance of the interactions between metal(loid)s and scoria, the sorption mode of metals onto scoria is still not clearly understood. Moreover, there is no systematic understanding of factors influencing metal uptake by scoria. Considering the potential use of scoria as a sorbent, knowledge of metal interactions with scoria is essential for predicting the long-term fate and transport of metal(loid)s in near-subsurface environments.

In the present study, we systematically evaluated the usefulness of scoria as a sorbent for the removal of inorganic contaminants, in particular divalent heavy metals (Pb, Cu, Zn, Cd) and trivalent arsenic. The major goals were (1) to estimate the affinity of the contaminants onto the sorbents, (2) to investigate the effects of diverse sorption variables such as pH, reaction time, metal concentration and competing ions, (3) to identify the sorption mechanism, (4) to examine the effect of competitive sorption in a multi-component system, and finally (5) to elucidate the theoretical significance of the empirical results using kinetic rate constants and sorption isotherms.

## 2. Materials and methods

### 2.1. Sorbents

The sorbent is a whole-rock sample of scoria, which consists of phenocrysts and glass and is typically vesicular, from volcanic cones of Jeju Island, Korea. The phenocrysts have different habits (rounded, subrounded, ovoid, lobate, and sometimes irregular) but with limited size variation (1  $\mu\text{m}$  to 3 mm). The groundmass delineating the vesicles is composed of dark blackish volcanic glass containing fine iron oxides. Small amounts of clay minerals are also present due to rock weathering. The mineral composition of the scoria powder was determined by X-ray diffraction analysis ( $2\theta$  range = 0–80°;  $2\theta$  steps = 0.04°; scanning speed = 4°/min; Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ )), and is composed of Mg-rich olivine, clinopyroxene, labradorite (An<sub>66</sub>), and hematite, as shown in Fig. 1. The bulk chemical composition of scoria, as determined by X-ray fluorescence (XRF), is given in Table 1. SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents make up about 63% of the scoria, and FeO and CaO compose about 21%. Compared to scoria used in other sorption studies [15,16], the Jeju scoria used in this study characteristically contains hematite and is slightly more enriched in Al<sub>2</sub>O<sub>3</sub>, total FeO, and MgO. Prior to sorption experiments, the scoria samples were washed repeatedly with deionized water to remove any dust and other water-soluble



**Fig. 1.** X-ray diffraction patterns of scoria used in the study. Numbers indicate identified phases: (1) Mg-rich olivine with the composition of Fo<sub>70.5</sub> ((Mg<sub>1.41</sub>Fe<sub>0.59</sub>)SiO<sub>4</sub>), (2) pyroxene [Fe-pigeonite (Fe<sub>1.6</sub>Ca<sub>0.4</sub>)Si<sub>2</sub>O<sub>6</sub>], (3) labradorite (An<sub>66</sub>; Ca<sub>0.66</sub>Na<sub>0.34</sub>Al<sub>1.66</sub>Si<sub>2.34</sub>O<sub>8</sub>), and (4) hematite (Fe<sub>2</sub>O<sub>3</sub>).

impurities and then dried at room temperature. Subsequently, the samples were crushed in tungsten carbide ball mills and separated as a 0.1–0.2 mm diameter fraction using nylon sieves because preliminary experiments showed no difference in sorption capacities between <0.1 and 0.1–0.2 mm sized fractions [14]. The surface area of the prepared fraction (0.1–0.2 mm) was determined by N<sub>2</sub> gas BET analysis using Micrometrics ASAP 2010, and the result was 4.77 m<sup>2</sup> g<sup>-1</sup>. The cation exchange capacity of scoria, also determined with 1 M ammonium acetate diffusion at pH 7 according to the ASTM D2974-00 standard method B, was 16.1 meq/100 g. Powdered commercial hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) was also prepared for discrete sorption experiments to examine the contribution of hematite which occurs as a minor constituent (~8%) of the Jeju scoria and is well known as a good sorbent of metals [17]. The commercial hematite (<0.03 mm in size) was washed with deionized water several times to remove any impurities and then dried in an oven at 105 °C. Finally, all the prepared sorbents were stored in desiccators until commencement of the sorption experiments.

### 2.2. Sorbates

All the chemicals used in our experiments were analytical reagent grade products from Aldrich, USA. Stock solutions of heavy metals (Pb(II), Cu(II), Zn(II), Cd(II)) and arsenic (As(III)) were prepared separately by dissolving appropriate quantities of Pb(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cd(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, and AsNaO<sub>2</sub> in deionized water. The varying concentrations of heavy metals and arsenic in solution for the sorption experiments were prepared by diluting each stock solution. In addition, variable amounts of 1.0 M HNO<sub>3</sub> were added to the prepared solutions in order to adjust the initial pH (pH<sub>ini</sub>) to 5.0 ± 0.1 to prevent any precipitation occurring before the sorption experiments. The pH of the solutions was measured using a multi-meter (Orion model 835) with a micro pH electrode calibrated with pH 4.01, 7.00, and 10.01 buffers.

### 2.3. Sorption experiments: procedures, chemical analysis, and data presentation

Two types of batch sorption experiments (kinetic and equilibrium) were carried out in acid-washed, 50 mL polypropylene centrifuge tubes which were soaked in a thermostat (25 °C) and were shaken at 150 rpm to homogenize and facilitate the reaction.

Throughout the kinetic experiments, reaction conditions were controlled as follows: contact (reaction) time from 2 min to 24 h; initial concentration of 1.0 mM; volume of sorbate was 50 mL; dose (absolute amount) of sorbent was 3.0 g. After completion of the experiments, the solution was separated from the solid by filtration using a 0.45  $\mu\text{m}$  cellulose nitrate membrane filter. An aliquot of the filtered solution was acidified with HNO<sub>3</sub> and was analyzed for the concentrations of ions (Ca, Mg, Na, K, Pb, Cu, Zn, Cd, and As) by inductively coupled plasma atomic emission spectrometry (ICP-AES; PerkinElmer ELAN 3000XL). The detection limits ( $\mu\text{g L}^{-1}$ ) of the analysis were: 1 for Cu, 2 for Cd, 5 for Pb, Ca and K, 7 for Mg and Na, and 30 for Zn and As. Duplicates, blanks, and reference standards were used to obtain accurate and precise analytical data. The relative standard deviations of the analytical data were measured to less than 5%.

To determine major parameters governing sorption kinetics, kinetic sorption data acquired empirically were fitted to the Lagergren pseudo-first order rate equation and the pseudo-second order rate equation, both of which have been widely used to describe metal and organic sorption on different sorbents [13,14,18–20]. The Lagergren pseudo-first order rate equation is expressed as:

$$\log(q_e - q) = \log q_e - \frac{k_{\text{ad}} t}{2.303} \quad (1)$$

**Table 1**  
Chemical composition (wt.%) of scoria, determined by XRF analysis.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	FeO <sup>a</sup>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	P <sub>2</sub> O <sub>5</sub>	L.O.I. <sup>b</sup>	Total
48.02	15.18	2.41	12.24	7.84	8.66	2.67	1.36	0.15	0.46	1.05	100.04

<sup>a</sup> FeO<sup>\*</sup> = FeO + Fe<sub>2</sub>O<sub>3</sub>.

<sup>b</sup> Loss of weight on ignition.

where  $q$  and  $q_e$  are the amounts ( $\mu\text{mol g}^{-1}$  sorbent) of heavy metals and arsenic removed at time  $t$  and equilibrium, respectively, and  $k_{\text{ad}}$  is the rate constant of sorption ( $\text{h}^{-1}$ ). On the other hand, the pseudo-second order kinetic rate equation is:

$$\frac{t}{q} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (2)$$

where  $q$  and  $q_e$  are the amounts ( $\mu\text{mol g}^{-1}$  sorbent) of metal sorbed at time  $t$  and equilibrium, respectively, and  $k$  is the rate constant of sorption ( $\text{g } \mu\text{mol}^{-1} \text{h}^{-1}$ ).

Equilibrium sorption experiments were also performed in a set of nine 50 mL centrifuge tubes, and the ratio of sorbate to sorbent was fixed to be identical to that of kinetic experiments. In contrast, initial pH and sorbate concentrations were varied in each solution. The  $\text{pH}_{\text{ini}}$  was adjusted by adding a variable amount of 1.0 M HNO<sub>3</sub> or 0.1 M NaOH solution. After pH adjustment, the solutions were permitted to attain equilibrium without further pH control. The sample tubes were agitated for at least 24 h at 150 rpm; the equilibration time was preliminarily determined by kinetic sorption experiments. Following equilibration, filtration using a 0.45  $\mu\text{m}$  membrane filter was performed for chemical analyses.

Sorption isotherms were obtained from equilibrium sorption experiments under a  $\text{pH}_{\text{ini}}$  value =  $5.0 \pm 0.1$  (25 °C) during 24 h. The empirical data were fitted to the Langmuir and Freundlich sorption isotherms in order to estimate sorption constants designating the sorption capacity and affinity of the sorbents [21].

The Langmuir sorption isotherm assumes a homogeneous surface of the sorbent and equivalent sorption energies for each sorption site, with no mutual interaction between the sorbed molecules. The Langmuir equation is expressed as the linear function [21]:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (3)$$

where  $C_e$  is the equilibrium concentration of sorbate in the bulk solution (mM),  $q_e$  is the amount of solute sorbed per unit weight of sorbent at equilibrium ( $\text{mmol g}^{-1}$  sorbent).  $Q$  ( $\text{mmol g}^{-1}$ ) and  $b$  ( $\text{L mmol}^{-1}$ ) are the Langmuir constants related to sorption capacity and energy, respectively.

The sorption data were also fitted to the Freundlich isotherm, which assumes the exponential distribution of sorption sites and energies and the interaction between sorbed molecules on the surface. The Freundlich equation is written as the logarithmic linear equation [21]:

$$\log q = \log K_f + \frac{1}{n} \log C \quad (4)$$

where  $q$  is the amount of solute sorbed per unit weight of sorbent ( $\text{mmol g}^{-1}$ ),  $K_f$  is the Freundlich constant indicative of the relative sorption capacity of the sorbent ( $\text{mmol g}^{-1}$ ),  $C$  is the aqueous concentration (mM), and  $1/n$  is the constant indicative of the intensity of the sorption.

### 3. Results and discussion

#### 3.1. Kinetics

The uptake ( $\mu\text{mol sorbate sorbed/g sorbent}$ ) and the removal efficiency (%) of divalent heavy metals and trivalent arsenic by the Jeju scoria were determined empirically.

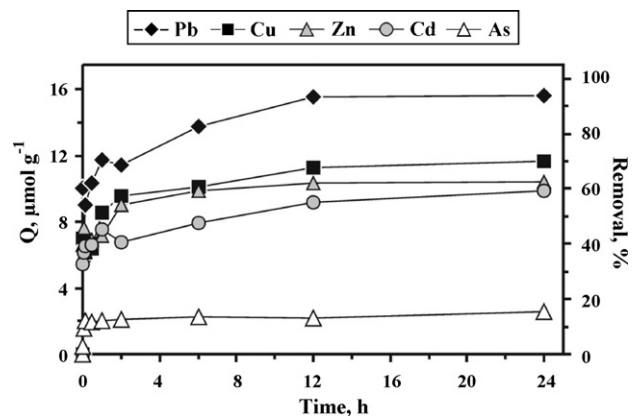
##### 3.1.1. Heavy metals and As sorption

To investigate the sorption capacity (and sorption kinetics) of the scoria for heavy metal ions (Pb(II), Cu(II), Zn(II), and Cd(II)) and arsenic (As(III)), the change of solution chemistry during the sorption reaction was monitored for 1 day (Fig. 2). The uptake and removal of heavy metals by scoria increased rapidly during the first 2 h and then became slower and finally approached an equilibrium state within the duration of the experimental period, and this confirmed that the sorption is quite rapid. The result indicates that the sorption mainly took place at the surface of the sorbent during the initial stage. The removal efficiencies of Pb, Cu, Zn, and Cd by the scoria were 94, 70, 63, and 59%, respectively, after a reaction time of 24 h (Fig. 2). The difference in the amount of heavy metal ions sorbed may be attributed to the different electronegativity of the metallic elements along with the hydrated ionic radii in the solutions [22–24]. For As(III), removal onto the scoria increased sharply in the initial stage (first 1 h) to 12%, and increased slightly up to 14% at the reaction time of 24 h.

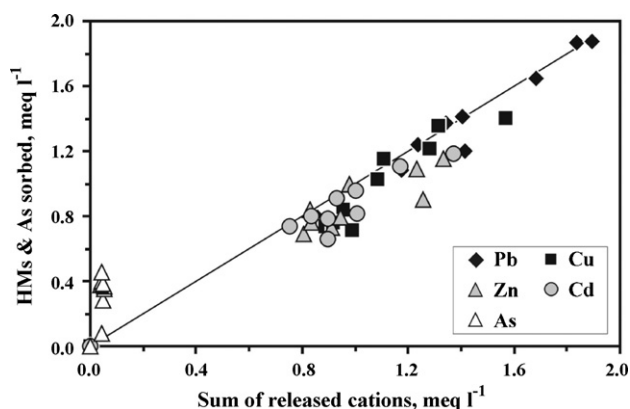
##### 3.1.2. Sorption mechanism

The term “sorption” usually defines the change in concentrations of chemical constituents in the solid phase as a result of mass transfer between solution and solid, and thus sorption includes various types of removal mechanisms such as adsorption, absorption, and exchange [25]. To understand the sorption mechanism(s) for the removal of divalent heavy metals and trivalent arsenic by scoria, we analyzed a number of cations in addition to target heavy metals and arsenic in the solutions using ICP-AES.

Through the leaching experiments of scoria using deionized water under condition equivalent to kinetic sorption tests, it was confirmed that the metal ions (Ca(II), Mg(II), Na(I), and K(I)) were



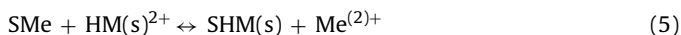
**Fig. 2.** Sorption kinetics of heavy metals and As(III) onto scoria. Initial sorbate concentration = 1.0 mM, particle size = 0.1–0.2 mm, sorbate/sorbent ratio = 50 mL/3 g, temperature = 25 °C.



**Fig. 3.** Correlations between the concentrations ( $\text{meq L}^{-1}$ ) of sorbed heavy metals (HMs) and arsenic and the sum of concentrations of ions released into solution with a 1:1 correlation line. All data used were obtained from kinetic sorption tests onto scoria.

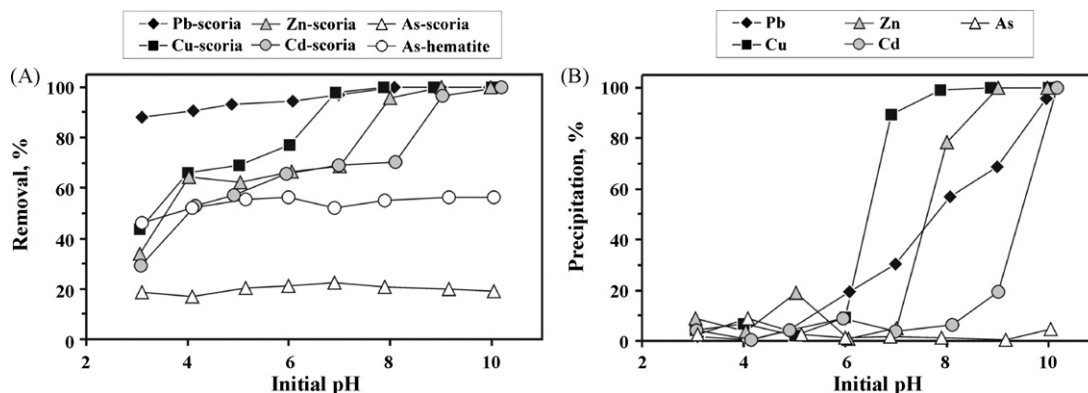
released at only very low levels of 0.3, 0.1, 1.0, and 0.5  $\text{mg L}^{-1}$ , respectively, after a reaction time of 24 h. The results indicate that the release of these cations from scoria is very slow under the experimental condition. However, in the sorption experiments for heavy metals, Ca, Mg, Na, and K concentrations gradually increased over the contact time. Concentrations increased up to 24, 6, 3, and 3  $\text{mg L}^{-1}$  for Ca(II), Mg(II), Na(I), and K(I), respectively, and the sequence of concentrations was  $\text{Ca(II)} > \text{Mg(II)} > \text{Na(I)} \approx \text{K(I)}$  at each sampling event.

The concentrations ( $\text{meq L}^{-1}$ ) of sorbed heavy metals and arsenic versus the sum of concentrations of released cations ( $\text{Ca(II)} + \text{Mg(II)} + \text{Na(I)} + \text{K(I)}$ ) within all the kinetic experiments is shown in Fig. 3. Except for arsenic, concentrations of heavy metals sorbed are strongly correlated with those of the cations released. This trend indicates that the heavy metals sorption onto scoria is likely dominated by cation exchange which can be expressed by the following balanced equations [14]:



$$\sum [\text{Me}^{(2)+}] = \sum \Delta[\text{HM(s)}^{2+}] \quad (6)$$

where Me and HM(s) represent weakly bound major cations (Ca(II), Mg(II), Na(I), K(I)) and sorbate metals (Pb(II), Cu(II), Zn(II), Cd(II)), respectively, and  $[\ ]$  denotes the concentration ( $\text{meq L}^{-1}$ ) in the solution. For the arsenic sorption experiments, the released cations are negligible, indicating the removal of arsenic(III) through specific sorption onto scoria.



**Fig. 4.** The removal percentages of heavy metals and arsenic (A) and the estimated percentages of the contribution of chemical precipitation to their removal (B) onto scoria and hematite as a function of initial pH. Temperature = 25 °C, particle size = 0.1–0.2 mm for scoria and <0.03 mm for hematite, sorbate/sorbent ratio = 50 mL/3 g, initial ion concentration = 1.0 mM, contact time = 24 h.

However, it is not certain which minerals in scoria play an important role in sorbing heavy metals and arsenic. The prediction of metal sorption at the whole-rock scale is still difficult because of the mineralogical complexity of natural rocks (i.e., nature of the phases in contact with water, density of sites, and surface area). Because the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of amorphous hematite, which is a minor constituent of the Jeju scoria, is generally higher (about 9.0) than the examined pH range (5.0–7.5), this characteristic of hematite can be related to the potential for scavenging As existing as an oxyanion in a solution. Arsenic(III) predominates in moderately reducing anaerobic environments, and redox potential (Eh) and pH control arsenic speciation. Under reducing conditions at  $\text{pH} < \sim 9.2$ , neutral  $\text{H}_3\text{AsO}_3$  is stable. Whereas As(V) species predominate and are stable in oxygen-rich aerobic environments, and the negatively charged  $\text{HAsO}_4^{2-}$  ( $\text{p}K_1 = 2.20$ ) and  $\text{H}_2\text{AsO}_4^-$  ( $\text{p}K_2 = 6.97$ ) are dominate at the low to intermediate pH range of about 3–9 in oxidizing conditions. The mineral surface may play a significant role in the catalysis of the oxidation of arsenite through an electron transfer mechanism [26], and Ko et al. [27] reported that hematite oxidized arsenite into arsenate to a level of about 20% of the total arsenic for 48 h at pH 6.9. Hence, As(III) removal by scoria can be summarized as follows: (1) the specific sorption of the neutral As(III) species on the mineral surface; and (2) the interaction between negatively charged As(V) species and positively charged surface of hematite after As(III) oxidation by hematite. On the other hand, it is unlikely that hematite is an efficient sorbent for heavy metals. Alternatively, it is speculated that the sorption of heavy metals is attributed to clay minerals such as smectite occurring as minor constituents in vesicles of the scoria. Clearly, a more detailed investigation into the mineralogical characteristics of the scoria used in this study is necessary to better interpret the sorption mechanisms.

### 3.2. Equilibrium

The equilibrium isotherm for the sorption of divalent heavy metals and trivalent arsenic onto sorbents (scoria and hematite for As sorption) were determined from equilibrium sorption experiments with varying concentrations of heavy metals and arsenic. The amounts of heavy metals and arsenic sorbed by the sorbents were calculated from the difference between total and equilibrium concentrations.

#### 3.2.1. Effect of initial pH

The pH condition has been considered as the most important variable in sorption investigations because it often dramatically affects the amounts of sorbed metals [28]. Fig. 4 shows the removal

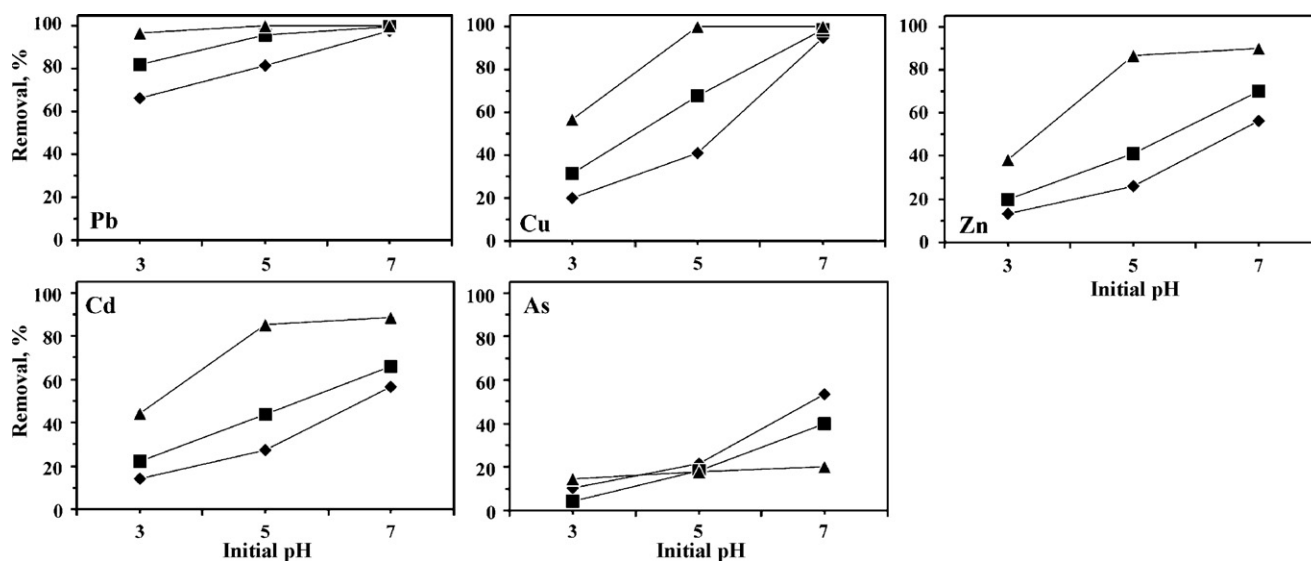


Fig. 5. Effect of the initial pH and sorbate concentration (0.1 mM (◆), 0.5 mM (■), 1.0 mM (▲)) on sorption of heavy metals and arsenic onto scoria in the multi-component system (Pb + Cu + Zn + Cd + As(III)). Particle size = 0.1–0.2 mm, temperature = 25 °C, contact time = 24 h, sorbate/sorbent ratio = 50 mL/3 g.

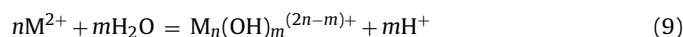
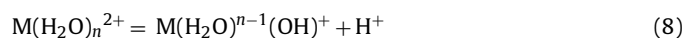
(%) of heavy metal ions and arsenic onto scoria and hematite (only for As) as a function of the initial pH ( $pH_{ini}$ ) under the initial sorbate concentration of 1.0 mM. A significant effect of the solution pH is observed: the removal of heavy metals onto scoria generally increases with increasing  $pH_{ini}$  (Fig. 4(A)). The greatest removal occurs at the highest pH as expected. Removal of Pb(II) increases gradually from about 88% to 99% as  $pH_{ini}$  increases from 3.1 to 10.0. The removal efficiencies for Cu(II), Zn(II), and Cd(II) can also be specified depending on the range of  $pH_{ini}$  values. At the lowest  $pH_{ini}$  (3.0–4.0), they are observed to be 43–67%, 34–63%, and 29–51%, and then gradually increase up to  $pH_{ini}$  6.0, 7.0, and 8.0, respectively. Finally, they appear to be over than 99% around  $pH_{ini}$  of 7.9, 9.0, and 10.2, respectively. An increase in removal of heavy metals in the higher pH ranges seems to be due to precipitation as hydroxides. In the case of As(III), its removal efficiencies by scoria and hematite are more or less constant throughout the  $pH_{ini}$  range investigated:  $20.0 \pm 1.7\%$  for scoria and  $53.7 \pm 3.5\%$  for hematite.

### 3.2.2. Contribution of precipitation on removal

In order to elucidate the attribution of precipitation to the sorption of heavy metals and arsenic, the change of their concentrations

in solution without sorbents were examined under various pH values ranging from 3 to 10. The percentages of divalent heavy metals and As(III) removed by precipitation are shown in Fig. 4(B), which can be compared with the total removal percentages (Fig. 4(A)). The role of As precipitation appears to be very small ( $2.8 \pm 2.7\%$ ) throughout the  $pH_{ini}$  range investigated. The precipitation percentages of Cu(II), Zn(II), and Cd(II) are also small ( $5.6 \pm 3.0\%$ ,  $7.5 \pm 7.0\%$ , and  $4.6 \pm 2.8\%$ , respectively) at  $pH_{ini}$  values below 6.0, 7.0, and 8.0, and then sharply increase up to almost 100% at  $pH_{ini}$  8.0, 9.0, and 10.0, respectively. Precipitation of Pb(II) increases gradually from about 1.8% at  $pH_{ini}$  3.1 to more than 96% at  $pH_{ini}$  10.0. In general, Pb(II) precipitation may be completed at low pH condition relative to that of the other heavy metals, while the trend observed in this study indicates that (1) the reaction time of 24 h is not sufficient to allow precipitation of Pb-bearing minerals or (2) the Pb-carbonate fraction, which is difficult to adsorb and precipitate, is more abundant than the Pb-hydroxide fraction in solution during the reaction [29]. Numerous investigators have found that the slope of a sorption capacity of metal ion versus pH decreases significantly somewhere between pH 6 and 8.5 in the presence of  $CO_2$ , with geomedia as diverse as quartz, layered silicates, and amorphous iron oxides (e.g., [30]) due to the formation of aqueous metal complexes with carbonate to a significant degree, whereas this decrease is not observed in  $CO_2$ -free systems [31,32].

Throughout the experiments of metal precipitation at varying pH conditions, it was confirmed that the role of precipitation should be taken into account under high pH conditions. Heavy metal ions in aqueous solution may suffer salivation, hydrolysis and polymerization [33], and can form several hydrolysis products, which exist under different conditions. The following reactions take place:



In dilute solutions, the formation of hydrolysis products of heavy metals occurs at  $pH > 6$  [33] and therefore the removal of heavy metals under alkaline conditions also takes place by precipitation caused when  $OH^-$  forms complexes with heavy metal ions. Nevertheless, the precipitation of metal hydroxides in pores or spaces around the particles is hardly possible because the sorption process

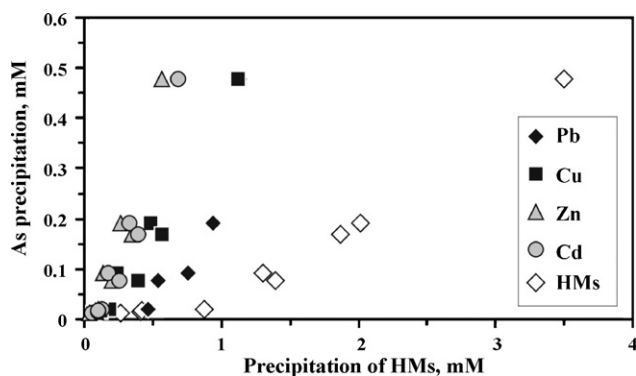


Fig. 6. Relationship between the concentration of precipitated heavy metals and that of removed arsenic in the multi-component system without any sorbent in the  $pH_{ini}$  range from 3 to 7. HMs indicates the total sum of the concentrations of precipitated heavy metals (Pb + Cu + Zn + Cd).

**Table 2**The rate constants and  $q_e$  calculated from the first- and second-order rate equations for sorption of heavy metals and arsenic onto scoria.

Sorbent	Sorbate	Pseudo-first order		Pseudo-second order			Experimental
		$k_{ad}$ ( $h^{-1}$ )	$R^2$	$k$ ( $g\ mol^{-1}\ h^{-1}$ )	$R^2$	$q_e$ ( $\mu mol\ g^{-1}$ )	$q_e$ ( $\mu mol\ g^{-1}$ )
Scoria	Pb	0.38	0.9388	0.20	0.9986	15.80	15.64
	Cu	0.22	0.9425	0.25	0.9987	11.74	11.69
	Zn	0.16	0.8950	0.27	0.9996	10.53	11.14
	Cd	0.12	0.9210	0.27	0.9958	9.92	10.02
	As	0.03	0.4539	1.18	0.9934	2.49	2.54

is kinetically faster than the rate of precipitation [34,35]. Consequently, removal of heavy metals by the Jeju scoria is dominantly controlled by sorption (specifically, cation exchange) under acidic conditions, but it can be slightly enhanced by metal hydroxide precipitation under alkaline conditions.

### 3.2.3. Competitive sorption in a multi-component system

In a natural setting, the presence of multiple competing ions is more frequent than the existence of only one kind of ion, and the sorption in multi-component systems becomes much more complicated due to the variety of solute–surface interactions involved. In order to determine the selectivity of heavy metals (Pb(II), Cu(II), Zn(II), Cd(II)) and arsenic (As(III)) by scoria in a multi-component system, a number of batch-type equilibrium experiments were carried out under the initial concentrations of 0.1, 0.5, and 1.0 mM for individual metals and at  $pH_{ini}$  values of 3.0, 5.0, and 7.0. The removal percentages of each sorbate ion after the reaction under varying conditions of solution are shown in Fig. 5. The overall removal of all sorbates increases with increasing  $pH_{ini}$ , and the sequence of their selectivity appears to be  $Pb > Cu > Zn \approx Cd > As$ , which is very similar to that of the single-sorbate system (Fig. 4(A)). Comparing the results for the concentration of 1.0 mM between the multi- and single-component system, except for As(III), the sorption of Pb(II) and Cu(II) does not appear to be affected by the interference of other ions. In the meantime, removal percentages of Zn(II) and Cd(II) are reduced to about 12% (from 68% for single- to 56% for multi-component system at  $pH_{ini}$  7.0), which are probably resulted from a deficiency of available sorption sites due to the preferential occupation of Pb(II) and Cu(II). However, As(III) removal by scoria in the multi-component system (53%) is significantly higher than that in the single-component system (22%). Furthermore, the removal efficiencies of heavy metals decrease with increasing sorbate concentration, while As(III) shows a somewhat different behavior in the multi-component system (Fig. 5). In order to account for the opposite tendency of As(III), a set of supplementary experiments on precipitation without scoria were undertaken. Fig. 6 shows the correlation between changes in concentrations of As(III) and divalent heavy metals due to precipitation. As(III) precipitation increases linearly with increasing heavy metal precipitation. The results suggest that As(III) can be removed from aqueous solutions through (co-)precipitation with precipitates of heavy metals.

**Table 3**

Calculated constants for Langmuir and Freundlich isotherms on sorption of heavy metals and arsenic onto scoria and hematite (25 °C, initial pH 5.0, particle size = 0.1–0.2 mm for scoria and &lt;0.03 mm for hematite).

Sorbents	Sorbate	Langmuir model			Freundlich model		
		$Q$ ( $\times 10^{-3}\ mmol\ g^{-1}$ )	$b$	$R^2$	$K_f$ ( $\times 10^{-3}\ mmol\ g^{-1}$ )	$1/n$	$R^2$
Scoria	Pb	33.46	4.38	0.9962	22.16	0.19	0.9795
	Cu	27.81	2.94	0.9920	15.83	0.30	0.9707
	Zn	22.66	4.40	0.9982	13.15	0.35	0.9551
	Cd	21.49	3.38	0.9946	12.33	0.33	0.9350
	As	21.20	0.14	0.1381	2.40	0.81	0.9496
Hematite	As	23.00	1.15	0.8565	9.01	0.41	0.9969

### 3.3. Theoretical model studies

For the calculation of rate constants, data obtained from the batch-type experiments using scoria were fitted to the pseudo-first order and pseudo-second order kinetic models. The  $k_{ad}$  values of the pseudo-first order rate equation were calculated from the slope of each regression line in the  $\log(q_e - q)$  versus time plots. In addition, the second order sorption rate constant ( $k$ ) and  $q_e$  values were evaluated from the slope and intercept of each regression line for  $t/q$  versus  $t$ . The results of regression are summarized in Table 2. Correlation coefficients for the linear plots using the pseudo-second order model are superior (in most cases >0.99), and theoretical and experimental  $q_e$  values show excellent agreement. Therefore, it is likely that the sorption of heavy metals and arsenic(III) by scoria is kinetically controlled as a second order reaction rather than a first order process. The pseudo-second order model assumes chemical sorptions as the rate-limiting process.

Equilibrium isotherms for the sorption of heavy metal ions (Pb(II), Cu(II), Zn(II), Cd(II)) and arsenic (As(III)) onto both sorbents (scoria and hematite for As) were determined from the batch experiments using varying concentrations of the sorbate for 24 h at 25 °C. Equilibrium isotherms determined at pH 5.0 were omitted for the sake of clarity. The isotherms are positive, regular and concave to the concentration axis of sorbates. Metal uptake by both sorbents is almost completed at low sorbate concentrations and decreases at higher concentrations. At low metal concentrations, metal sorption occurs at higher energy surface sites, and as the metal concentrations increase, sorption efficiency is decreased because higher energy surface sites are saturated and sorption begins on low energy surface sites. The equilibrium data are fitted using the Langmuir and Freundlich equations, and the corresponding Langmuir and Freundlich parameters and correlation coefficients are given in Table 3. Analysis of regression coefficients shows an excellent fit of the empirical data with both isotherms depending on the type of sorbate. The data for heavy metals are better fitted to the Langmuir model, while those for arsenic seem to be more consistent with the Freundlich isotherm. Langmuir and Freundlich constants,  $Q$ , and  $K_f$ , fundamentally differ, but their values lead to the consistent conclusion about the sequence of selectivity of  $Pb > Cu > Zn > Cd > As$ -hematite  $> As$ -scoria.

#### 4. Summary

In order to evaluate the potential use of scoria as an efficient sorbent, a variety of experimental studies on the sorption of heavy metals (Pb(II), Cu(II), Zn(II), Cd(II)) and As(III) using scoria from Jeju Island, Korea were carried out.

From the results of this study, the following conclusions are drawn:

- (1) Sorption of contaminants onto scoria mainly takes place at the outside surface at the initial stage. Changes of ionic composition during sorption experiments suggest that cation exchange is likely the dominant mechanism of heavy metals sorption onto scoria, while considerable As(III) removal by scoria is explained by specific sorption of the neutral As(III) species and electrical adsorption of negatively charged As(V) species via As oxidation onto hematite.
- (2) Under acidic conditions, the competition of heavy metal ions with hydrogen ions for the available sites results in a slight decrease of removal capacity. Conversely, precipitation of heavy metal hydroxides also acts to slightly increase heavy metal removal under alkaline conditions. The sorption process typically follows the trend of cation sorption, showing increasing heavy metal removal with increasing pH, and the selectivity sequence of sorption is  $Pb > Cu > Zn \approx Cd$ . Under alkaline conditions, As(III) removal increases by chemical species conversion and coprecipitation as well as specific sorption.
- (3) The kinetic sorption data of both sorbents best fit a pseudo-second order model that shows the rate-limiting sorption step between sorbates and sorbents. Heavy metal sorption onto scoria is explained by the Langmuir sorption model, while As(III) sorption better fits the Freundlich sorption model.

The experimental investigation conducted here demonstrates that the Jeju scoria is able to concurrently reduce concentrations of heavy metals and arsenic in aqueous solutions. We recommend scoria as an economic and efficient sorbent for heavy metals and arsenic in contaminated water.

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