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Effects of Silicic Acid on Leaching Behavior of Arsenic from Spent Calcium-Based Adsorbents with Arsenite

Hajime Sugita *, Terumi Oguma, Junko Hara, Ming Zhang and Yoshishige Kawabe

Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba 305-8567, Japan; t.oguma@aist.go.jp (T.O.); j.hara@aist.go.jp (J.H.); m.zhang@aist.go.jp (M.Z.); y-kawabe@aist.go.jp (Y.K.)

* Correspondence: hajime.sugita@aist.go.jp

Abstract: The spent adsorbents that remain after being used to purify As-contaminated water constitute waste containing a large amount of As. These spent adsorbents, after being disposed, are likely to come into contact with silicic acid leached from the soil or cementitious solidification materials. Thus, it is crucial the evaluate the effects of silicic acid on spent adsorbents. In this study, the effects of silicic acid on spent Ca-based (CaO and $Ca(OH)_2$) adsorbents with arsenite were investigated. The As leaching ratio for the spent adsorbents decreased with an increase in the initial concentration of silicic acid in the liquid. Under the tested conditions, the As leaching ratio decreased from 8–9% to less than 0.7% in the presence of silicic acid at an initial Si-normalized concentration of 100 mg/L. The primary mechanism behind the inhibition of As leaching by silicic acid was determined to be re-immobilization via the incorporation of arsenite during the formation of calcium silicates. In the presence of silicic acid, spent Ca-based adsorbents with arsenite had a lower As leaching ratio than those with arsenate. Therefore, spent Ca-based adsorbents with arsenite were found to have a higher environmental stability than those with arsenate.

Keywords: arsenite; adsorbent; leaching; calcium oxide; calcium hydroxide; silicic acid

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1. Introduction

There are numerous reports on groundwater contamination with arsenic (As), which is a global problem. In recent years, it has become a major challenge in regions across Asia (such as Bangladesh [1–5], Pakistan [6,7], Iran [8], India [9–11], Sri Lanka [12], Vietnam [13,14], Cambodia [15], and China [16–18]), Latin America (such as Argentina [19,20], Uruguay [21], and Mexico [22,23]) and West and South Africa [24,25]. Podgorski and Berg [26] reported the arsenic pollution in groundwater around the world; the proportion of affected area in Asia was 64%, in South America 14%, North America 10%, Africa 9%, Oceania 2% and Europe 1%. The proportion of total affected population in Asia was 94%, in Africa 3.7%, South America 1.6%, North America 0.6%, Europe 0.2% and Oceania 0.01%. In addition, the population per country exposed to As-contaminated groundwater was reported by Shaji et al. [27]. In some areas, in particular, such as South Asia and Southeast Asia, there is a high risk of health damage because groundwater contaminated with As is often used directly as drinking water.

Moreover, numerous studies have investigated methods for purifying As-contaminated water, such as the coprecipitation method using flocculants, ion exchange method using ion exchange resins, adsorption methods using various adsorbents such as activated carbon, silica gel, iron-based adsorbents, and aluminum-based adsorbents, microfiltration methods using microfiltration membranes, nanofiltration membranes, ultrafiltration membranes, or reverse osmosis filtration membranes, chemical or biological oxidation methods, and electrocoagulation methods. These have been outlined by Jadhav et al. (2015), Sarkar and Paul (2016), Ghosh et al. (2019), and Kumar et al. (2019) [28–31]. In developing countries, As treatment methods utilizing inexpensive adsorbents are considered more likely to be

introduced with respect to economic and operational conditions. In addition, although the constituents of adsorbents often leach from the adsorbents, both Mg and Ca are essential and safe substances for human health. Furthermore, Mg-based [32–34] and Ca-based adsorbents [35–38] are expected to have high As removal performance.

In particular, certain calcium compounds are often used in combination with other adsorbents or as auxiliary agents to other treatment methods, in addition to being used alone as Ca-based adsorbents. Camacho et al. [35] looked to determine the effect of calcium addition as a stabilization agent on arsenic desorption from ferric water treatment residuals. They conducted laboratory and field tests using calcium agents such as lime (CaO or $Ca(OH)_2$) and reported that: (1) desorption from laboratory ferric water treatment residuals did not generate any arsenic when calcium was present in solution, especially when excess calcium that did not join the surface of the treatment residual was present; similarly (2) arsenic leaching decreased when the field treatment residuals were treated with lime as a stabilizing agent; finally (3) the immobilization of arsenic in the treatment residuals may be achieved through treatment with lime and cement. Similarly, Montes-Hernande et al. [36] investigated the removal of oxyanions from an aqueous solution using the carbonation of $Ca(OH)_2$ under moderate pressure (PCO_2 = 20 bar) and temperature (30 °C). The study involved calcium hydroxide carbonation with compressed carbon dioxide in order to stabilize the solid matter. The authors reported that the $Ca(OH)_2$ carbonation reaction allowed the successful removal of selenite (>90%), arsenate (>78%), and phosphate (almost 100%) from synthetic solutions. In another study, Olyaie et al. [37] evaluated the use of CaO_2 nanoparticles in removing As (III) from contaminated water. CaO_2 is an oxidant that decomposes in high humidity to produce $Ca(OH)_2$ and H_2O_2. CaO_2 nanoparticles effectively removed total As under natural pH conditions (6.5 and 8.5). The removal efficiency was enhanced by increasing the CaO_2 nanoparticle dosage and reaction time, but decreased with increasing arsenic concentration and pH. Electrocoagulation has also been investigated as a method to remove arsenate; Hu et al. [38] studied the effect of calcium on arsenate removal by electrocoagulation with an aluminum electrode. The calcium salt used was $CaCl_2$. The calcium ions could neutralize the negative surface charges of the precipitate and increase the binding energy of As–O; thus, the addition of calcium salt dramatically improved the removal efficiency of As(V). The addition of calcium also prevented the formation of a deposit layer on the anode surface, which caused an increase in the applied potential and decreased the concentration of dissolved aluminum.

On the other hand, spent adsorbents that have adsorbed As will become waste containing a large amount of As. Therefore, proper recovery treatments for spent adsorbents are essential. Without suitable treatment prior to disposal, As may leak from spent adsorbents, leading to secondary environmental pollution. Previous studies [39–42] have reported the leaching of As from spent Mg-based (MgO, $Mg(OH)_2$, and $MgCO_3$) and Ca-based (CaO and $Ca(OH)_2$) adsorbents. One particular area that should be explored is the influence of silicic acid on spent adsorbents, as after disposal the spent adsorbents are likely to come into contact with silicic acid leached from soils or cementitious solidification materials. Therefore, Sugita et al. (2017) and Sugita et al. (2018) evaluated the effects of silicic acid on the leaching behavior of As from spent adsorbents; spent Mg-based and Ca-based adsorbents with arsenate were examined using silicic acid solution via shaking tests (leaching tests) [40,41]. Spent adsorbents based on $Mg(OH)_2$ and $MgCO_3$ were strongly affected by silicic acid, which significantly reduced their environmental stability and leaching of As. However, MgO-based adsorbents had extremely high environmental stability against silicic acid and hardly leached As [40]. In addition, the As leaching ratio for the spent adsorbents based on CaO and $Ca(OH)_2$ decreased with increasing initial concentration of silicic acid in the test solution [41].

However, these studies focused on arsenate, As(V), and no similar tests have been conducted on arsenite, As(III). Arsenic is often reduced to arsenous acid underground. For example, a groundwater survey in Bangladesh reported more than 95% of soluble As is in the form of arsenous acid [1]. In general, arsenous acid is known to be more toxic

than arsenic acid, and understanding the leaching behavior of arsenous acid is essential for understanding the leaching behavior of arsenic acid. In addition, As(III) differs greatly from As(V) in terms of its chemical characteristics, such as pH dependence. Clarifying the differences among the leaching characteristics of various valences of As is beneficial from a scientific point of view and may help evaluate the potential of spent adsorbents with hazardous substances to cause secondary environmental pollution. Therefore, an evaluation of the effects of silicic acid on spent adsorbents with arsenite would be valuable.

In this study, spent Ca-based adsorbents containing arsenous acid were studied, and shaking tests with silicic acid solution were conducted. In these tests, the leaching behavior of both As and Ca from the spent adsorbents with arsenite as well as the decreasing level of silicic acid in the liquid phase were investigated. Subsequently, the effects of silicic acid on the environmental stability of spent Ca-based adsorbents with arsenite were evaluated. To evaluate the environmental stability of spent adsorbents, using protocols detailed in previous studies [39–41], the following were assessed: (1) the difficulty of As leaching from the spent adsorbents; and (2) the difficulty in elution of the base material components of the adsorbents.

2. Materials and Methods

The reagents listed in this article were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan, formerly Wako Pure Chemical Industries, Ltd.), unless specified otherwise.

2.1. Spent Ca-Based Adsorbents

The spent Ca-based adsorbents with arsenite used in the experiments in this study were the same as those reported in our previous study [42]. An overview of the preparation of the spent adsorbents is provided below.

2.1.1. Ca-Based Adsorbents (Unspent)

Two types of Ca compound reagents, CaO and $Ca(OH)_2$, were used in this study. These were commercially available and purchased from FUJI-FILM Wako Pure Chemical Co. The nominal values of the purity of CaO and $Ca(OH)_2$ were 99.9% and 96%, respectively. In addition, the measured values of Ca content in CaO and the $Ca(OH)_2$ were 71.2% and 53.5%, with a median particle size of 19.6 and 41.7 μm, and BET surface area of 2.7 and 14.3 m^2/g, respectively [39].

2.1.2. Synthetic As-Contaminated Water

The powdered reagents of Sodium arsenite ($NaAsO_2$, 90%) and sodium hydrogen arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$, 99%) were dissolved in deionized water, and stock solutions of arsenite and arsenate with a concentration of 2000 mg-As/L were prepared. A portion of the stock solution was diluted with deionized water to prepare a 20 mg-As/L solution. This solution was used as synthetic As-contaminated water after adjusting the pH to near neutral by adding hydrochloric acid.

2.1.3. Preparation of Spent Ca-Based Adsorbents

The unspent Ca-based-adsorbent (1 g) was weighed in a TPX beaker. Synthetic As-contaminated water (200 mL) was added to the beaker and stirred with a magnetic stirrer (approximately 500 rpm). After stirring for about a day, suction filtration was performed using a Teflon filter (pore size 0.45 μm) for solid liquid separation. As and Ca in the filtrate were quantified via ICP-MS (Agilent 7700X or Shimadzu ICPM-8500) and ICP-AES (SII SPS3500DD), respectively. The analytical results of the filtrate are outlined below [41,42].

The data on the production of spent adsorbents with As(III) or As(V) are shown in Tables 1 and 2, respectively. W_{AD} is the amount of unspent adsorbent added to the synthetic As-contaminated water in mg, V is the liquid volume of the synthetic As-contaminated water in L, and W_{AD}/V is the addition concentration of the unspent adsorbent in mg/L.

pH_0 is the pH of the solution immediately before adding the adsorbent, which is referred to as "the initial pH". C_{AS0} is the initial As concentration in mg/L in As-contaminated water, C_{AS} is the As concentration in the filtrate, and R_{AS} is the As removal ratio, which is defined by the following equation:

$$R_{AS} = (C_{AS0} - C_{AS})/C_{AS} \times 100. \quad (1)$$

W_{Ca}/V in Table 2 is the Ca addition concentration in mg/L, which is defined by the following equation:

$$W_{Ca}/V = W_{AD}/V \times \alpha_{Ca}/100 \quad (2)$$

where α_{Ca} is the Ca content of the Ca-based adsorbent.

Cca in Table 2 is the Ca concentration in the filtrate (= the concentration of Ca leached from the adsorbent). β_{Ca} is the Ca leaching ratio, which is defined by the following equation:

$$\beta_{Ca} = C_{Ca}/(W_{Ca}/V) \times 100. \quad (3)$$

For both CaO and $Ca(OH)_2$, the R_{AS} for As(III) was slightly lower than that for As(V). On the other hand, for both As(III) and As(V), β_{Ca} for CaO was clearly lower than that for $Ca(OH)_2$.

Table 1. Data on As for production of spent Ca-based adsorbents.

No.	Adsorbent	As(Valence)	W_{AD}/V [mg/L]	pH_0	C_{AS0} [mg/L]	C_{AS} [mg/L]	R_{AS} [%]
(1) [1]	CaO	As(III)	5009	7.09	22.347	1.437	93.6
(2) [1]	$Ca(OH)_2$	As(III)	5009	7.09	22.725	1.378	93.9
(3) [2]	CaO	As(V)	5013	7.58	20.085	0.093	99.5
(4) [2]	$Ca(OH)_2$	As(V)	5014	7.58	20.563	0.737	96.4

[1] The data of No. (1) and (2) were obtained by Sugita et al., 2020 [42]. [2] The data of No. (3) and (4) were obtained by Sugita et al., 2016 [39].

Table 2. Data on Ca for production of spent Ca-based adsorbents.

No.	Adsorbent	As(Valence)	α_{Ca} [%]	W_{Ca}/V [mg/L]	C_{Ca} [mg/L]	β_{Ca} [%]
(1) [1]	CaO	As(III)	71.19	3566	837	23.5
(2) [1]	$Ca(OH)_2$	As(III)	53.51	2680	858	32.0
(3) [2]	CaO	As(V)	71.19	3569	965	27.0
(4) [2]	$Ca(OH)_2$	As(V)	53.51	2683	903	33.7

[1] The data of No. (1) and (2) were obtained by Sugita et al., 2020 [42]. [2] The data of No. (3) and (4) were obtained by Sugita et al., 2016 [39].

The adsorbents with As recovered by the solid liquid separation operation were dried at a low temperature (approximately 40 °C) for about half a day in a constant temperature dryer and then stored in a closed polypropylene bottle. The adsorbents with As were used as "spent adsorbents" in the shaking test, as described later. The outline of the calculation method for As content of the spent adsorbent is shown below [41,42].

The residual ratio of adsorbent γ as a percentage is defined by the following equation:

$$\gamma = 100 - \beta_{Ca.} \quad (4)$$

The amount of As adsorbed per unit mass of the adsorbent remaining as solid δ (mg/mg) is defined by the following equation:

$$\delta = (C_{AS0} - C_{AS})/[(\gamma/100) \times W_{AD}/V]. \quad (5)$$

The weighed value of the spent adsorbent is the total value of the adsorbent and As adsorbed on its surface. Therefore, the As content per unit mass of the recovered spent adsorbent Q_{AS} in mg-As/g can be easily obtained by the following equation:

$$Q_{AS} = \delta/(1 + \delta/1000). \quad (6)$$

Table 3 shows Q_{AS} obtained by previous studies [39,42].

Table 3. As content per nit mass of spent adsorbent.

No.	Adsorbent	As(valence)	Q_{AS} [mg-As/L]
(1) [1]	CaO	As(III)	5.42
(2) [1]	$Ca(OH)_2$	As(III)	6.23
(3) [2]	CaO	As(V)	5.44
(4) [2]	$Ca(OH)_2$	As(V)	5.93

[1] The values of No. (1) and (2) were obtained by Sugita et al., 2020 [42]. [2] The values of No. (3) and (4) were obtained by Sugita et al., 2016 [39].

2.2. Silicic Acid Solution

The silicic acid solutions used in this study were the same as those reported in a previous study [40,41]. An overview of the preparation of the silicic acid solution is provided below.

The stock solution of silicic acid was prepared by dissolving approximately 1 g of the sodium silicate solution (21.2–23.8%, SiO_2/Na_2O = 3.0–3.6 mol ratio at nominal value) in 1 L of deionized water. The Si concentration in the stock solution was measured using an ICP-AES. A portion of the stock solution was diluted with deionized water to obtain the desired concentration. The silicic acid solution obtained after the pH was neutralized with hydrochloric acid and sodium hydroxide solution immediately before adding the spent adsorbent in the shaking test was used as the test solvent. No pH buffering agent was used in our studies because the use of pH buffering agents may affect the reaction between the adsorbent, silicic acid, and As. In this study, the pH of the solution immediately before adding the adsorbent (the pH of the test solvent) is referred to as "the initial pH" (denoted as pH_0), and the pH of the eluate recovered by filtration after shaking is referred to as "the final pH" (denoted as pH_f). The pH meter and electrode used in this study were a LAQUA F-72 and a Micro ToupH Electrode 9618S-10D, respectively, manufactured by HORIBA, Ltd. (Kyoto, Japan).

The Si concentration of the test solvent was divided into five levels: 0, 5, 25, 50, and 100 mg/L. The total Si concentration was measured using ICP-AES, and the concentration of monosilicic acid (silica monomer) was measured using the molybdenum yellow method. Silicic acid refers to H_4SiO_4 (or $Si(OH)_4$), and silica refers to SiO_2; however, in this study all concentrations of silicic acid species are described as values converted to Si concentration. Here, the Si concentration is referred as "Si-normalized concentration." The Si-normalized concentrations quantified using ICP-AES and the molybdenum yellow method are referred to as "total Si-normalized concentration" and "Si-normalized monomer concentration," respectively, and denoted as $C_{Si\text{-}T}$ and $C_{Si\text{-}M}$. In addition, the difference between $C_{Si\text{-}T}$ and $C_{Si\text{-}M}$ was assumed to correspond to the concentration of polysilicic acid (silica polymer including colloidal silica), which is referred to as "Si-normalized polymer concentration" and is denoted as $C_{Si\text{-}P}$. In addition, the Si polymer concentrations in the test solution before adding the spent adsorbent are denoted as $C_{Si\text{-}T0}$, $C_{Si\text{-}M0}$, and $C_{Si\text{-}P0}$. Table 4 shows the data on the Si-normalized concentrations and pH_0 for the test solvents used in the shaking tests. In the test solvent with a Si-normalized concentration of 100 mg/L, approximately 13 mg/L of polysilicic acid was present in the Si conversion. However, most of the silicic acid present in the solution was in the form of monosilicic acid, as shown in Table 4.

Table 4. $C_{Si\text{-}T0}$, $C_{Si\text{-}M0}$, $C_{Si\text{-}P0}$, and pH_0 for test solvent used in this study.

Si-Normalized Concentration	$C_{Si\text{-}T0}$ [mg/L]	$C_{Si\text{-}M0}$ [mg/L]	$C_{Si\text{-}P0}$ [mg/L]	pH_0
0 mg/L	0	0	0	7.05
5 mg/L	4.93	4.90	0.03	7.18
25 mg/L	24.7	23.0	1.71	6.95
50 mg/L	50.4	50.0	0.38	7.15
100 mg/L	98.0	84.7	13.3	7.41

2.3. Shaking Test with Spent Ca-Based Adsorbents and Silicic Acid Solution

The shaking tests were performed using a procedure described in previous studies [40,41], an overview of which is provided below.

About 0.1 g of the spent adsorbent and 50 mL of the test solvent (the aforementioned silicic acid solution or deionized water) were added to a reaction tube (50 mL polypropylene centrifuge tube). The tube was sealed with a cap and shaken in a thermostatic shaker (150–180 rpm at room temperature). After shaking for 24 h, the tube was placed in a centrifuge (4500 rpm for 20 min). After centrifugation, the supernatant was filtered through a syringe filter (0.45 μm pore size), and the filtrate (eluate) was collected in a polypropylene bottle. The concentration of As in the eluate was measured using ICP-MS, and those of Ca and Si were determined via ICP-AES. Si quantification using the molybdenum yellow method was also performed. In addition, in order to confirm the reproducibility of the shaking test, shaking tests using the spent adsorbents of CaO and $Ca(OH)_2$ were conducted three times under the same conditions ($C_{Si\text{-}T0}$ = 50 mg/L).

3. Results

3.1. pH of Eluate

Table 5 lists the values of pH_f measured during the shaking tests. The $C_{Si\text{-}T0}$ values displayed in Table 5 are not the actual measured values and thus, for convenience, are shown by substituting the corresponding values of the Si-normalized concentration. Figure 1 shows a plot of pH_f against $C_{Si\text{-}T0}$.

For comparison with As(III), the results for the spent Ca-based adsorbents with As(V) (reported in a previous study [41]) are also shown in Table 5 and Figure 1. The pH_0 values were near neutral (pH 6.95 to 7.41); however, the pH increased significantly after adding the spent adsorbents, consistent with the results of previous studies [41]. For both As(III) and As(V), no significant difference was observed between the pH_f values of CaO and $Ca(OH)_2$, as shown in Figure 1. In addition, for both CaO and $Ca(OH)_2$, the values of pH_f for As(III) were higher than those for As(V).

Table 5. Values of pH of eluate (pH_f).

			$C_{Si\text{-}T0}$ [mg/L]				
No.	**Adsorbent**	**As(Valence)**	**0**	**5**	**25**	**50**	**100**
(1)	CaO	As(III)	12.65	12.64	12.50	12.63	12.49
(2)	$Ca(OH)_2$	As(III)	12.66	12.64	12.51	12.61	12.45
(3) [1]	CaO	As(V)	12.53	12.47	12.44	12.48	12.42
(4) [1]	$Ca(OH)_2$	As(V)	12.51	12.47	12.44	12.46	12.38

[1] The values of No. (3) and (4) were obtained by Sugita et al., 2018 [41].

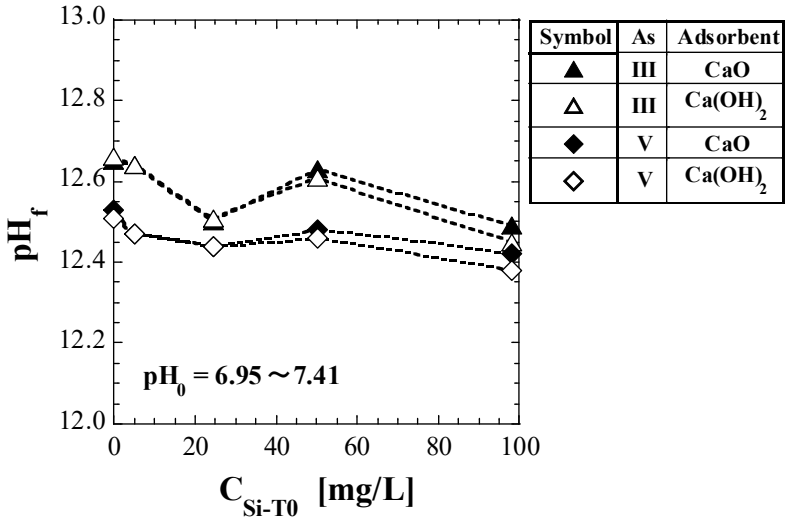


Figure 1. Change in pH of eluate with initial total Si-normalized concentration.

3.2. As Concentration in Eluate

Table 6 shows the values of As concentration and C_{AS}, as per the shaking tests. Figure 2 shows a plot of C_{AS} against $C_{Si\text{-}T0}$. The test results for As(V) reported in a previous study [41] are also shown in Table 6 and Figure 2. For both CaO and $Ca(OH)_2$, the C_{AS} tended to decrease with increasing $C_{Si\text{-}T0}$. For As(III), no significant difference was noted between the C_{AS} values of CaO and $Ca(OH)_2$; however, the C_{AS} value of $Ca(OH)_2$ was clearly higher than that of CaO at $C_{Si\text{-}T0}$ = 0 mg/L. C_{AS}, which was around 1 when $C_{Si\text{-}T0}$ = 0 mg/L, decreased to less than 0.1 mg/L when $C_{Si\text{-}T0}$ = 100 mg/L. For As(V), regardless of $C_{Si\text{-}T0}$, the C_{AS} values for CaO were higher than those for $Ca(OH)_2$. With respect to CaO, regardless of $C_{Si\text{-}T0}$, the C_{AS} values for As(V) were higher than those for As(III). With respect to $Ca(OH)_2$, the C_{AS} values for As(V) were higher than those for As(III), except that the C_{AS} value for As(III) was clearly higher than that for As(V) at $C_{Si\text{-}T0}$ = 0 mg/L.

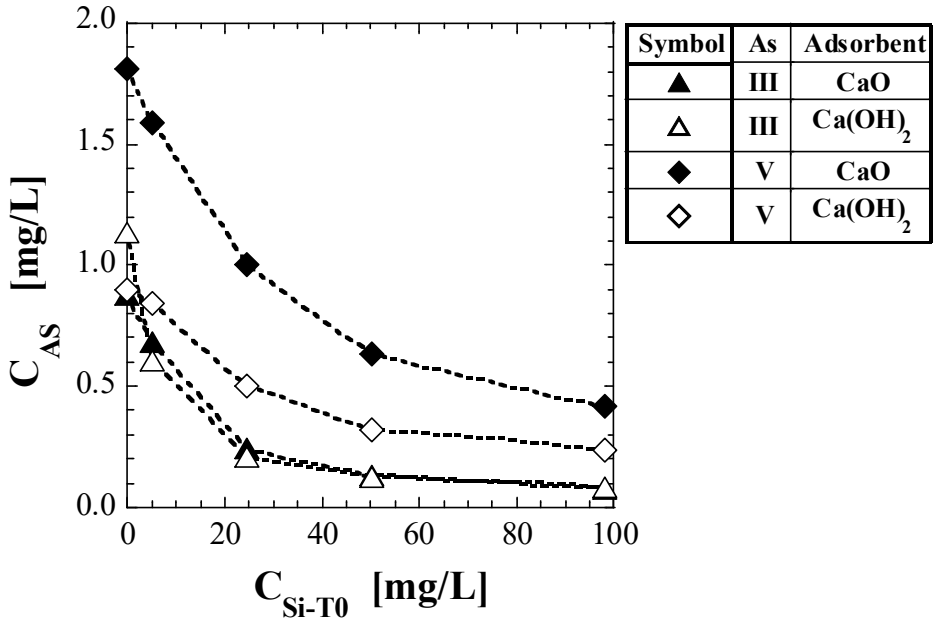


Figure 2. Change in As concentration in eluate with initial total Si-normalized concentration.

Table 6. Values of As concentration in eluate (C_{AS}).

			$C_{Si\text{-}T0}$ [mg/L]				
No.	**Adsorbent**	**As(valence)**	**0**	**5**	**25**	**50**	**100**
(1)	CaO	As(III)	0.874	0.680	0.246	0.130	0.076
(2)	$Ca(OH)_2$	As(III)	1.135	0.606	0.205	0.127	0.086
(3) [1]	CaO	As(V)	1.807	1.592	1.005	0.626	0.416
(4) [1]	$Ca(OH)_2$	As(V)	0.895	0.836	0.498	0.323	0.233

[1] The values of No. (3) and (4) were obtained by Sugita et al., 2018 [41].

3.3. Ca Concentration in Eluate

Table 7 shows the Ca concentration, C_{Ca}, as quantified via shaking tests. Figure 3 presents a plot of C_{Ca} against $C_{Si\text{-}T0}$. The test results for As(V) reported in a previous study [41] are also shown in Table 7 and Figure 3. For the set of $Ca(OH)_2$ and As(III), C_{Ca} gradually decreased with increasing $C_{Si\text{-}T0}$. For the set of CaO and As(III), C_{Ca} did not appear to change significantly in the $C_{Si\text{-}T0}$ range of 0–100 mg/L. For As(V), both the C_{Ca} for CaO and $Ca(OH)_2$ decreased significantly in the $C_{Si\text{-}T0}$ range of 0–5 mg/L and did not seem to change significantly in the $C_{Si\text{-}T0}$ range of 5–100 mg/L. Thus, even if the base material of the spent adsorbent was the same, the value of C_{Ca} differed depending on whether As(III) or As(V) was adsorbed.

Table 7. Values of Ca concentration in eluate (C_{Ca}).

			$C_{Si\text{-}T0}$ [mg/L]				
No.	**Adsorbent**	**As(valence)**	**0**	**5**	**25**	**50**	**100**
(1)	CaO	As(III)	817	786	754	789	768
(2)	$Ca(OH)_2$	As(III)	818	794	771	743	693
(3) [1]	CaO	As(V)	745	595	661	671	628
(4) [1]	$Ca(OH)_2$	As(V)	712	633	646	650	576

[1] The values of No. (3) and (4) were obtained by Sugita et al., 2018 [41].

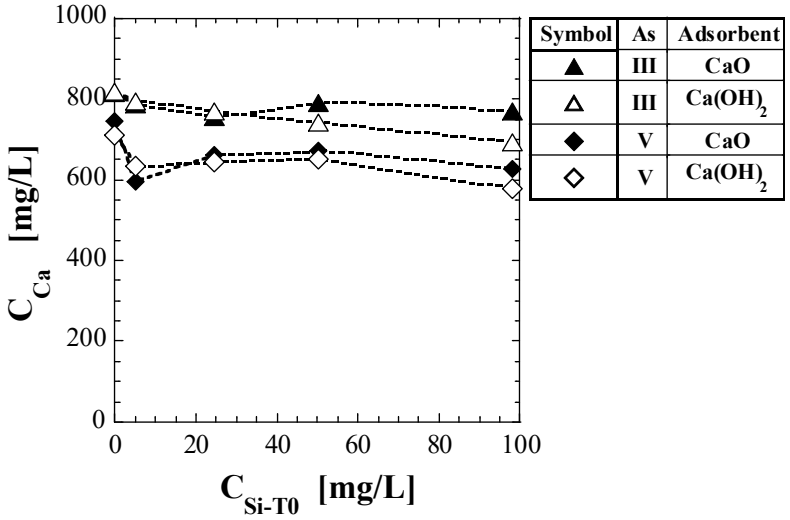


Figure 3. Change in Ca concentration in eluate with initial total Si-normalized concentration.

3.4. Total Si-Normalized Concentration in Eluate

Table 8 shows the values of total Si-normalized concentration, $C_{Si\text{-}T}$, quantified via shaking tests. Figure 4 shows a plot of $C_{Si\text{-}T}$ against $C_{Si\text{-}T0}$. The test results for As(V) reported in a previous study [41] are also shown in Table 8 and Figure 4. The straight line of $C_{Si\text{-}T}/C_{Si\text{-}T0} = 1$ is also shown in Figure 4. If $C_{Si\text{-}T}$ does not change from the initial value

($C_{Si\text{-}T0}$), the plots should be on this straight line; however, all the plots are located well below the straight line.

The $C_{Si\text{-}M}$ measurements were approximately equal to those of $C_{Si\text{-}T}$. Therefore, in the following, only $C_{Si\text{-}T}$ was handled as the Si-normalized concentration.

Table 8. Values of total Si-normalized concentration in eluate ($C_{Si\text{-}T}$).

			$C_{Si\text{-}T0}$ [mg/L]				
No.	**Adsorbent**	**As(valence)**	**0**	**5**	**25**	**50**	**100**
(1)	CaO	As(III)	0.00	0.16	0.23	0.06	0.23
(2)	$Ca(OH)_2$	As(III)	0.00	0.17	0.23	0.14	0.26
(3) [1]	CaO	As(V)	0.00	0.28	0.28	0.49	0.40
(4) [1]	$Ca(OH)_2$	As(V)	0.00	0.29	0.23	0.53	0.39

[1] The values of No. (3) and (4) were obtained by Sugita et al., 2018 [41].

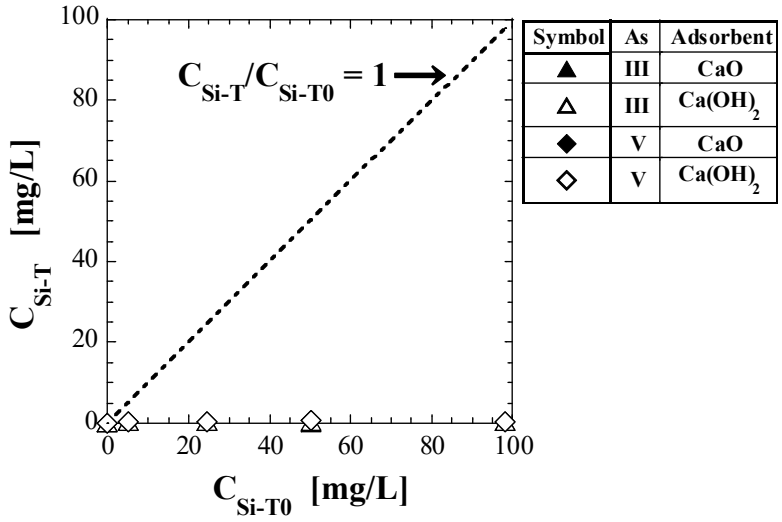


Figure 4. Change in Si concentration in eluate with initial total Si-normalized concentration.

3.5. Reproducibility of Experimental Data

The shaking tests with the silicic acid solution ($C_{Si\text{-}T0}$ = 50 mg/L) and spent adsorbents (CaO and $Ca(OH)_2$) with As(III) were conducted three times. The relative standard errors for the pH_f, C_{AS}, C_{Ca}, and $C_{Si\text{-}T}$ values estimated via these tests were 0.1%, 3%, 4%, and 1% for CaO and 0.2%, 2%, 5%, and 1% for $Ca(OH)_2$, respectively. Based on these results, it was confirmed that the reproducibility of the experimental data was good.

4. Discussion

4.1. Relative Evaluation Using As Leaching Ratio

The As content of the spent adsorbent varied depending on the type of spent adsorbent (see Table 3). The As leaching ratio, E_{AS} [%], defined by the following equation, was used for the evaluation:

$$E_{AS} = C_{AS}/(Q_{AS} \times W_{SP}/V) \times 100 \quad (7)$$

where W_{SP} is the amount of spent adsorbent added to the test solvent [g], V is the liquid volume of the test solvent [L], and W_{SP}/V is the addition concentration of the spent adsorbent [g/L]. Table 9 lists the values of the E_{AS} obtained using Equation (7). Figure 5 shows a plot of E_{AS} against $C_{Si\text{-}T0}$. For comparison with As(III), the E_{AS} for spent Ca-based adsorbents with As(V), reported in a previous study [41], is also shown in Table 9 and Figure 5. For all spent Ca-based adsorbents, the E_{AS} values decreased significantly with increasing $C_{Si\text{-}T0}$. For As(V), the E_{AS} values of $Ca(OH)_2$ were significantly lower than those of CaO, regardless of $C_{Si\text{-}T0}$. For As(III), there was no significant difference between the

E_{AS} values of CaO and $Ca(OH)_2$. E_{AS}, which was 8–9% when $C_{Si\text{-}T0}$ = 0 mg/L, decreased to less than 0.7% when $C_{Si\text{-}T0}$ = 100 mg/L. On the other hand, the values of E_{AS} for CaO and $Ca(OH)_2$ when $C_{Si\text{-}T0}$ = 100 mg/L were 3.78 and 1.94% for As(V), respectively, and both were less than 0.7% for As(III). Therefore, it appeared to be difficult for As leaching to occur in spent Ca-based adsorbents with As(III), compared to those with As(V) (Figure 5).

Table 9. Values of As leaching ratio (E_{AS}).

			E_{AS} [%]				
No.	**Adsorbent**	**As(valence)**	**0**	**5**	**25**	**50**	**100**
(1)	CaO	As(III)	8.00	6.17	2.23	1.19	0.695
(2)	$Ca(OH)_2$	As(III)	8.89	4.81	1.62	1.01	0.670
(3) [1]	CaO	As(V)	16.5	14.6	9.13	5.70	3.78
(4) [1]	$Ca(OH)_2$	As(V)	7.43	7.00	4.13	2.71	1.94

[1] The values of No. (3) and (4) were obtained by Sugita et al., 2018 [41].

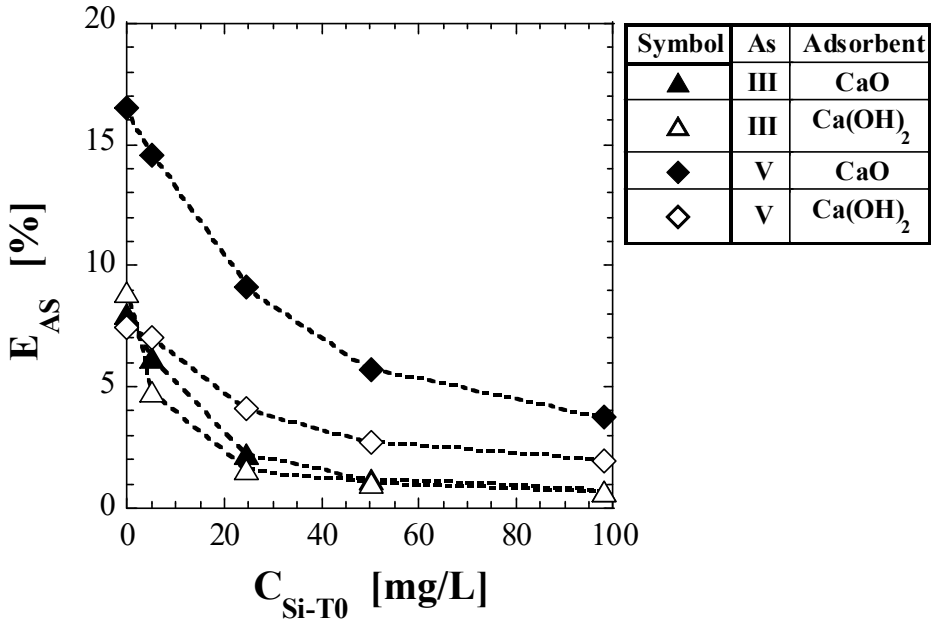


Figure 5. Change in As leaching ratio with initial total Si-normalized concentration.

If the leaching of As from the spent adsorbents is simply due to the dissolution of the spent adsorbent, there should be a quantitative correlation between the leaching amount of As and that of Ca. To test this hypothesis, C_{AS} was plotted against C_{Ca} (Figure 6). In the set of As(III) and $Ca(OH)_2$, C_{AS} increased with increasing C_{Ca}. However, in the other sets, there was no clear correlation between the C_{AS} and C_{Ca}. A previous study [41] concluded that the mechanism of As leaching from spent Ca-based adsorbents with As(V) is the desorption reaction of arsenate on its surface. Considering the results in Figure 6, the mechanism of As leaching from the spent Ca-based adsorbents with As(III) is presumed to be the desorption reaction of arsenite.

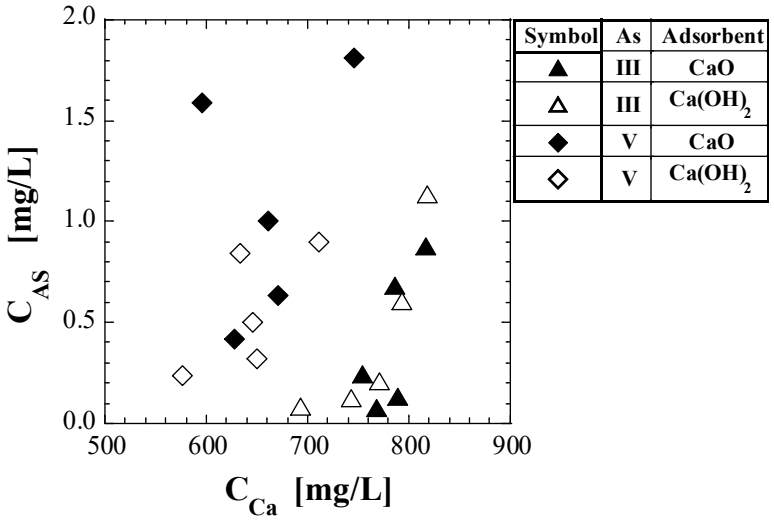


Figure 6. Plot of As concentration against Ca concentration in eluate.

4.2. Dissolved Forms of Siliacic Acid in Liquid

Similar to previous studies [40,41], the dissolved form of silicic acid in liquid was considered based on the dissociation formulas of silicic acid.

$$H_4SiO_4 \longleftrightarrow H_3SiO_4^- + H^+ \quad (8)$$

$$H_3SiO_4^- \longleftrightarrow H_2SiO_4^{2-} + H^+ \quad (9)$$

When the equilibrium constants of the dissociation Equations (8) and (9) are denoted as Ka_1 and Ka_2, respectively, the following equations are applicable:

$$[H_3SiO_4^-]/[H_4SiO_4] = 10 \exp (pH - pKa_1) \quad (10)$$

$$[H_2SiO_4^{2-}]/[H_3SiO_4^-] = 10 \exp (pH - pKa_2) \quad (11)$$

where the units of the applicable molecular formula are mol/L, $pKa_1 = 9.86$, and $pKa_2 = 13.1$ (25 °C) [43].

The values of pH_f quantified via the shaking tests on As(III) are in the range 12.45–12.66 (see Table 5). Substituting these values into Equation (10) yields values in the range of 389–631. When converted to the ionization ratio, these values corresponded to a range of 99.7–99.8%. This means that most of the silicic acid in the solution was ionized. Substituting the values of pH_f into Equation (11) yields values of 0.22–0.36. When converted to a percentage, this corresponds to 73–82%. This means that the main dissolved form is $H_3SiO_4^-$, which is a monovalent ion, with the remaining 18–27% being $H_2SiO_4^{2-}$, a divalent ion. A previous study on As(V) reported that 78–84% of the dissolved form was $H_3SiO_4^-$ and 16–22% was $H_2SiO_4^{2-}$ [40,41]. The difference in the analytical values for As(III) and As(V) is due to the difference in pH_f. In addition, in the test solvent before adding the spent adsorbent, the ionization ratio of silicic acid was estimated to be 0.1–0.4%. Therefore, most of the silicic acid in the test solvent is considered to exist as an uncharged monosilicic acid [40,41].

4.3. Dissolved Forms of Arsenous Acid in Liquid

As(III) in the spent Ca-based adsorbents is presumed to be adsorbed (immobilized) on the solid surface as follows: Solid-O-Ca-O-$As(OH)_2$ followed by a reaction wherein As(III) on the surface of the adsorbent is desorbed in a neutral or alkaline solution, as represented by Equations (12) and (13), respectively.

$$\text{Solid-O-Ca-O-As(OH)}_2 + H_2O \rightarrow \text{Solid-O-Ca-OH} + As(OH)_3 \quad (12)$$

$$\text{Solid-O-Ca-O-As(OH)}_2 + \text{OH}^- \rightarrow \text{Solid-O-Ca-O-As(OH)}_2 + \text{As(OH)}_2\text{O}^- \quad (13)$$

In addition, the dissolved form of As(III) leached from the spent adsorbent is represented by the following dissociation reaction formulas for arsenous acid:

$$\text{H}_3\text{AsO}_3 \longleftrightarrow \text{H}_2\text{AsO}_3^- + \text{H}^+ \quad (14)$$

$$\text{H}_2\text{AsO}_3^- \longleftrightarrow \text{HAsO}_3^{2-} + \text{H}^+ \quad (15)$$

$$\text{HAsO}_3^{2-} \longleftrightarrow \text{AsO}_3^{3-} + \text{H}^+ \quad (16)$$

where $pKa_1 = 9.1$, $pKa_2 = 12.1$, and $pKa_3 = 13.4$ (25 °C) [43]. In this study, as $pKa_1 << pH_f$, the abundance of H_3AsO_3 was considered to be extremely small and negligible. The values of pKa_2 and pKa_3 were applied to Equations (15) and (16), respectively. Then, substituting the pH_f values (12.45–12.66), the values of $(HAsO_3^{2-})/(H_2AsO_3^-)$ and $(AsO_3^{3-})/(HAsO_3^{2-})$ were calculated to be 2.24–3.63 and 0.11–0.18, respectively. Based on the results, the main dissolved form of As leached from the spent Ca-based adsorbents was presumed to be $HAsO_3^{2-}$, a hydrogen arsenite ion.

It is possible that the valence of As may change during the shaking test, however, in this study neither oxidizing nor reducing agents were used, and the shaking time was only one day. Therefore, we assumed that the valence of As did not change between them.

4.4. Stoichiometric Considerations on Spent Ca-Based Adsorbents

Similar to previous studies [40,41], stoichiometric considerations were made using the values obtained by converting the mass-based concentration C_X (mg/L) to the molar-based concentration M_X [mmol/L].

4.4.1. Formation Reactions of Calcium Silicate Species

The dissolution reactions of the base materials of the spent Ca-based adsorbents in water are expressed by Equations (17) and (18), respectively:

$$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad (17)$$

$$\text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \quad (18)$$

In this study, CaO was assumed to dissolve after being converted to $Ca(OH)_2$ by the hydration reaction represented by Equation (17). The Ca^{2+} leached from the Ca-based adsorbents may then react with the silicic acid species in the solution to form calcium silicate species. The silicic acid species present in the pH range of the test solution in this study were mainly H_4SiO_4 and $H_3SiO_4^-$ (see Section 4.2); therefore, the silicic acid species that react with Ca^{2+} to produce calcium silicate species were assumed to be the two aforementioned silicic acid species. Assuming H_4SiO_4 as the reactive silicic acid species, the reaction formulas for the formation of the calcium silicate species are as follows:

$$\text{Ca}^{2+} + 2\text{H}_4\text{SiO}_4 + 2\text{OH}^- \rightarrow \text{CaSi}_2\text{O}_2(\text{OH})_6 + 2\text{H}_2\text{O} \rightarrow \text{CaSi}_2\text{O}_5 + 5\text{H}_2\text{O} \quad (19)$$

$$\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 2\text{OH}^- \rightarrow \text{CaSiO(OH)}_4 + \text{H}_2\text{O} \rightarrow \text{CaSiO}_3 + 3\text{H}_2\text{O} \quad (20)$$

$$2\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 4\text{OH}^- \rightarrow \text{Ca}_2\text{SiO}_2(\text{OH})_4 + 2\text{H}_2\text{O} \rightarrow \text{Ca}_2\text{SiO}_4 + 4\text{H}_2\text{O} \quad (21)$$

$$3\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 6\text{OH}^- \rightarrow \text{Ca}_3\text{SiO}_3(\text{OH})_4 + 3\text{H}_2\text{O} \rightarrow \text{Ca}_3\text{SiO}_5 + 5\text{H}_2\text{O} \quad (22)$$

$$4\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 8\text{OH}^- \rightarrow \text{Ca}_4\text{SiO}_4(\text{OH})_4 + 4\text{H}_2\text{O} \rightarrow \text{Ca}_4\text{SiO}_6 + 6\text{H}_2\text{O} \quad (23)$$

Assuming that one Ca atom is chemically bonded to two O atoms and that one Si atom is chemically bonded to four O atoms, the formation of calcium silicate species with a Ca/Si molar ratio of 0.5–4 is stoichiometrically conceivable, as shown by Equations (19)–(23). In addition, when $H_3SiO_4^-$ is assumed to be the reactive silicic acid species, "H_4SiO_4" on the left side of the above formulas must be replaced with "$H_3SiO_4^- + H^+$". In addition to the above reactions, the silicic acid species in the solution may be adsorbed upon reacting

with the OH groups on the adsorbent surface, as shown in Equation (24); this reaction is essentially a dehydration–condensation reaction:

$$\text{Solid-O-Ca-OH} + H_4SiO_4 \rightarrow \text{Solid-O-Ca-O-Si(OH)}_3 + H_2O. \quad (24)$$

4.4.2. Estimation of Calcium Silicate Species Formed

As described at the beginning of Section 4.4, C_{Ca} in mg/L converted into molar units is denoted as M_{Ca}, mmol/L. The value of M_{Ca} at $C_{Si\text{-}T0}$ = 0 mg/L is denoted as M_{Ca0}, and the difference between M_{Ca0} and M_{Ca}, $M_{Ca0} - M_{Ca}$, is denoted as ΔM_{Ca}. Similarly, for $C_{Si\text{-}T}$, the value of $M_{Si\text{-}T}$ at $C_{Si\text{-}T0}$ = 0 mg/L is denoted as $M_{Si\text{-}T0}$, and the difference between $M_{Si\text{-}T0}$ and $M_{Si\text{-}T}$, $M_{Si\text{-}T0} - M_{Si\text{-}T}$, is denoted as $\Delta M_{Si\text{-}T}$. Figure 7 shows the plots of ΔM_{Ca} against $\Delta M_{Si\text{-}T}$. In addition, Table 10 shows the values of $\Delta M_{Ca}/\Delta M_{Si\text{-}T}$ corresponding to the plot lines.

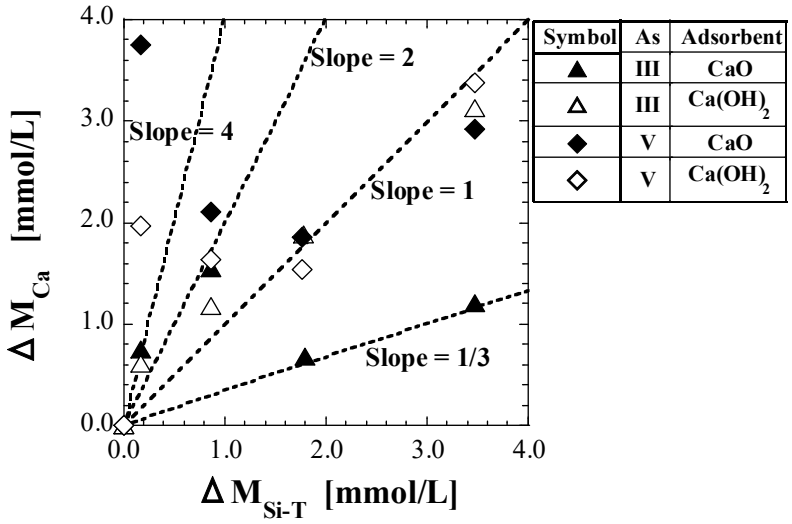


Figure 7. Plot of ΔM_{Ca} against $\Delta M_{Si\text{-}T}$.

Table 10. Values of $\Delta M_{Ca}/\Delta M_{Si\text{-}T}$.

			$C_{Si\text{-}T0}$ [mg/L]			
No.	**Adsorbent**	**As(valence)**	**5**	**25**	**50**	**100**
(1)	CaO	As(III)	4.43	1.79	0.38	0.35
(2)	$Ca(OH)_2$	As(III)	3.58	1.35	1.05	0.90
(3) [1]	CaO	As(V)	22.1	2.42	1.05	0.84
(4) [1]	$Ca(OH)_2$	As(V)	11.6	1.89	0.87	0.97

[1] The values of No. (3) and (4) were obtained by Sugita et al., 2018 [41].

If the only cause of the decrease in both M_{Ca} and $M_{Si\text{-}T}$ was the production of the calcium silicate species caused by a reaction between Ca^{2+} leached from the spent adsorbent and the silicic acid species in the solution, the value of $\Delta M_{Ca}/\Delta M_{Si\text{-}T}$ should be between 0.5 and 4, based on Equations (19)−(23). Most of $\Delta M_{Ca}/\Delta M_{Si\text{-}T}$ were found to be in the range 0.5–4, as shown in Table 10. For As(III), because the values of $\Delta M_{Ca}/\Delta M_{Si\text{-}T}$ at $C_{Si\text{-}T0}$ = 5 mg/L are approximately 4 for both CaO and $Ca(OH)_2$, the average composition of the calcium silicate species produced can be estimated to be Ca_4SiO_6. In addition, because the values at $C_{Si\text{-}T0}$ = 25 mg/L were approximately 1.5, the coexistence of Ca_2SiO_4 and $CaSiO_3$ could be estimated. Furthermore, because the values at $C_{Si\text{-}T0}$ = 50 and 100 mg/L for $Ca(OH)_2$ are approximately 1, the average composition of the calcium silicate species produced can be estimated to be $CaSiO_3$. On the other hand, the values at $C_{Si\text{-}T0}$ = 50 and 100 mg/L for CaO are 0.3–0.4, which is close to 1/3. This implies that $CaSi_3O_7$ has a chemical composition, and the hydration form can be represented as "$Si(OH)_3$O-Ca-O-

$Si(OH)2O\text{-}Si(OH)_3$." To produce this calcium silicate species, the polymerization of silicic acid must have occurred. However, as there was no significant difference in pH and $C_{Si\text{-}T0}$ compared to the other test conditions, it may not be theoretically conceivable that the polymerization of silicic acid occurred only in the set of As(III) and CaO. Therefore, CaO, reactions in which only silicic acid species decrease in the solution without decreasing Ca^{2+} concentration should be considered.

Replacing the hydration reaction of CaO with that of the surface layer of the adsorbent, Equation (17) can be rewritten as Equation (25):

$$\text{Solid-O-Ca-O-Ca-O-Solid} + H_2O \rightarrow \text{Solid-O-Ca-OH} + \text{HO-Ca-O-Solid}. \quad (25)$$

Assuming that the adsorption of silicic acid species on the spent adsorbent of CaO occurs after the reaction of Equation (25), there is essentially no mechanistic difference between the reaction of CaO with silicic acid species and reaction of $Ca(OH)_2$ with silicic acid species. However, as mentioned above, for CaO there must be some reaction in which only silicic acid species decrease without decreasing the concentration of Ca^{2+} in the solution. Therefore, assuming the mechanisms by which silicic acid species react directly with unhydrated CaO seems to be more appropriate. Equations (26) and (27) are proposed as the reaction of silicic acid species with a solid surface layer of CaO:

$$\text{Solid-O-Ca-O-Ca-O-Solid} + H_4SiO_4 \rightarrow \text{Solid-O-Ca-O-Si(OH)}_3 + \text{HO-Ca-O-Solid} \quad (26)$$

$$\text{Solid-O-Ca-O-Ca-O-Solid} + H_4SiO_4 \rightarrow \text{Solid-O-Ca-O-Si(OH)}_2\text{O-Solid} + Ca^{2+} + 2OH^{-}. \quad (27)$$

According to the reaction shown in Equation (26), the silicic acid species in the solution are directly adsorbed on the surface layer of the CaO adsorbent without reacting with Ca^{2+} in the solution. According to the reaction shown in Equation (27), the silicic acid species are adsorbed with the release of Ca^{2+} from the surface of the adsorbent.

Similar discussions on As(V) have been reported in detail in a previous study [41]. The values of $\Delta M_{Ca}/\Delta M_{Si\text{-}T}$ at $C_{Si\text{-}T0}$ = 5 mg/L for As(V) were significantly different from those for As(III) and greatly exceeded 4, at more than 20 for CaO and more than 10 for $Ca(OH)_2$, as shown in Table 10. In the test solvent containing silicic acid, the leaching of Ca and As might be inhibited to some extent by adsorbing the silicic acid species directly on the surface of the spent adsorbents and covering them. In low Si-normalized concentrations (approximately 5 mg/L), the proportion of Ca being inhibited by the direct adsorption of silicic acid was inferred to be larger than the proportion of Ca^{2+} that was consumed with silicic acid in the production of calcium silicate species [41].

Because the values of $\Delta M_{Ca}/\Delta M_{Si\text{-}T}$ are different between As(III) and As(V), as shown in Figure 7 and Table 10, the differences in the coordination number and dissociation constants of As may be considered to have some effect on the mechanisms of silicic acid adsorption on the adsorbent surface as well as on calcium silicate formation; however, such effects are currently unknown.

4.4.3. Effects of Silicic Acid on Leaching Behavior of As(III)

As in Section 4.4.1, C_{AS} in mg/L converted into molar units is denoted as M_{AS}, mmol/L, the value of M_{AS} at $C_{Si\text{-}T0}$ = 0 mg/L is denoted as M_{AS0}, and the difference between M_{AS0} and M_{AS} ($M_{AS0} - M_{AS}$) is denoted as ΔM_{AS}. Figure 8 shows a semi-logarithmic plot of ΔM_{AS} against $\Delta M_{Si\text{-}T}$.

For As(V), as shown in Figure 8, both CaO and $Ca(OH)_2$ appear to present a proportional relationship between ΔM_{AS} and the logarithmic value of $\Delta M_{Si\text{-}T}$. The proportional relationships in Figure 8 are represented by the following equation:

$$\Delta M_{AS} = A \times \log \Delta M_{Si\text{-}T} + B \quad (28)$$

where A and B are the slopes and intercepts of the lines, respectively. Equation (28) indicates that ΔM_{AS} increases with increasing $\Delta M_{Si\text{-}T}$.

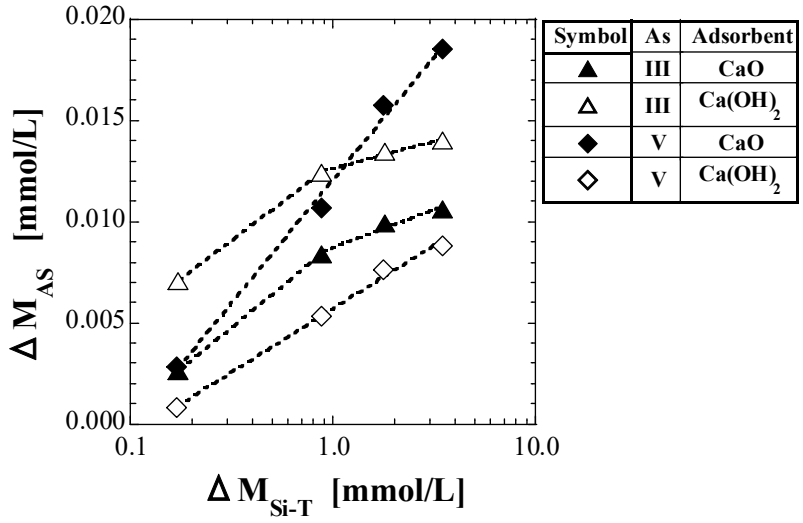


Figure 8. Plot of ΔM_{AS} against $\Delta M_{Si\text{-}T}$.

In a previous study on As(V) [41], the As which leached from the spent adsorbent with As(V) into the solution was speculated to be incorporated in place of some silicic acid species during the formation of calcium silicate species. A similar reaction is considered to have occurred in the current study with As(III); however, both the approximate curves of CaO and $Ca(OH)_2$ for As(III) appear to have a change in slope at around $\Delta M_{Si\text{-}T}$ = 1 mmol/L. The value of $C_{Si\text{-}T0}$ corresponding to $\Delta M_{Si\text{-}T}$ = 1 mmol/L in this study was approximately 25 mg/L. Therefore, it is considered that the proportion of As incorporated instead of silicate species during the production of calcium silicate species changed depending on whether $C_{Si\text{-}T0}$ was higher or lower than 25 mg/L. The values of *A* and *B* obtained using Equation (28) are listed in Tables 11 and 12, respectively.

Table 11. Values of *A* obtained using Equation (28).

			$C_{Si\text{-}T0}$ [mg/L]	
No.	**Adsorbent**	**As(valence)**	**5–25**	**25–100**
(1)	CaO	As(III)	0.00817	0.00377
(2)	$Ca(OH)_2$	As(III)	0.00755	0.00267
(3) [1]	CaO	As(V)	0.0122	
(4) [1]	$Ca(OH)_2$	As(V)	0.00628	

[1] The values of No. (3) and (4) were obtained by Sugita et al., 2018 [41].

Table 12. Values of *B* obtained using Equation (28).

			$C_{Si\text{-}T0}$ [mg/L]	
No.	**Adsorbent**	**As(valence)**	**5–25**	**25–100**
(1)	CaO	As(III)	0.00888	0.00873
(2)	$Ca(OH)_2$	As(III)	0.0129	0.0126
(3) [1]	CaO	As(V)	0.0121	
(4) [1]	$Ca(OH)_2$	As(V)	0.00571	

[1] The values of No. (3) and (4) were obtained by Sugita et al., 2018 [41].

Because the pH of leachate from cementitious solidification materials is generally highly alkaline, there is a concern that the reaction represented by Equation (13) may promote the leaching of As from spent adsorbents. In addition, because a large amount of Ca is leached from spent Ca-based adsorbents, the spent Ca-based adsorbents with As(III)

are considered to have an environmental stability as low as those with As(V). However, assuming that the leachate from soil and cementitious solidification materials contains a large amount of silicate and Ca components in advance, the leaching of Ca components from spent Ca-based adsorbents is likely to be inhibited, and thus the environmental stability of the spent adsorbents may be enhanced, as reported in a previous study [41].

5. Conclusions

After being used to purify As-contaminated water, the spent adsorbents contained a large amount of As. When spent adsorbents are discarded in the environment without proper treatment, secondary environmental pollution may be caused by the leaching of As. In a previous study [41], the effects of silicic acid on the environmental stability of spent Ca-based adsorbents with arsenate were reported. In this study, the effects of silicic acid on the environmental stability of spent Ca-based adsorbents with arsenite were examined.

Similar to the case of spent Ca-based adsorbents with arsenate, those with arsenite were strongly affected by silicic acid in the solution, and the amount of As leaching apparently decreased with increasing initial silicic acid concentration. The As concentration in the eluate, which was around 1 in the absence of silicic acid, decreased to less than 0.1 mg/L when the initial Si-normalized concentration was 100 mg/L. The corresponding inhibitory mechanism of silicic acid on As leaching was determined to primarily involve re-immobilization via incorporation of the As leached from the spent adsorbents during the production of the calcium silicate species. In addition, in the solution containing silicic acid the As leaching ratio was clearly lower for the spent Ca-based adsorbents with arsenite than for those with arsenate. The As leaching ratios of CaO and $Ca(OH)_2$ under the initial Si-normalized concentration of 100 mg/L were 3.78 and 1.94% for arsenate, respectively, while they were each less than 0.7% for arsenite. Thus, the spent adsorbents with arsenite demonstrate higher environmental stability than those with arsenate.

This study revealed that the environmental stability of spent Ca-based adsorbents differs depending on the valence of the adsorbed As. Future analyses should utilize chemical equilibrium models to further develop and validate the results presented here.

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References

1. van Geen, A.; Zheng, Y.; Cheng, Z.; Aziz, Z.; Horneman, A.; Dhar, R.K.; Mailloux, B.; Stute, M.; Weinman, B.; Good-bred, S.; et al. A transect of groundwater and sediment properties in Araihazar, Bangladesh: Further evidence of decoupling be-tween As and Fe mobilization. *Chem. Geol.* **2006**, *228*, 85–96. [CrossRef]
2. Harvey, C.F.; Ashfaque, K.N.; Yu, W.; Badruzzaman, A.B.M.; Ali, M.A.; Oates, P.M.; Michael, H.A.; Neumann, R.B.; Beckie, R.; Islam, S.; et al. Groundwater dynamics and arsenic contamination in Bangladesh. *Chem. Geol.* **2006**, *228*, 112–136. [CrossRef]
3. Senanayake, N.; Mukherji, A. Irrigating with arsenic contaminated groundwater in West Bengal and Bangladesh: A review of interventions for mitigating adverse health and crop outcomes. *Agric. Water Manag.* **2014**, *135*, 90–99. [CrossRef]
4. Khan, K.M.; Parvez, F.; Zoeller, R.T.; Hocevar, B.A.; Kamendulis, L.M.; Rohlman, D.; Eunus, M.; Graziano, J. Thyroid hormones and neurobehavioral functions among adolescents chronically exposed to groundwater with geogenic arsenic in Bangladesh. *Sci. Total Environ.* **2019**, *678*, 278–287. [CrossRef]

5. Huq, M.E.; Fahad, S.; Shao, Z.; Sarven, M.S.; Khan, I.A.; Alam, M.; Saeed, M.; Ullah, H.; Adnan, M.; Saud, S.; et al. Arsenic in a groundwater environment in Bangladesh: Occurrence and mobilization. *J. Environ. Manag.* **2020**, *262*, 110318. [CrossRef]
6. Shahid, M.; Niazi, N.K.; Dumat, C.; Naidu, R.; Khalid, S.; Rahman, M.M.; Bibi, I. A meta-analysis of the distribution, sources and health risks of arsenic-contaminated groundwater in Pakistan. *Environ. Poll.* **2018**, *242*, 307–319. [CrossRef]
7. Malik, A.; Parvaiz, A.; Mushtaq, N.; Hussain, I.; Javed, T.; Rehman, H.U.; Farooqi, A. Characterization and role of derived dissolved organic matter on arsenic mobilization in alluvial aquifers of Punjab, Pakistan. *Chemosphere* **2020**, *251*, 126374. [CrossRef]
8. Hamidian, A.H.; Razeghi, N.; Zhang, Y.; Yang, M. Spatial distribution of arsenic in groundwater of Iran, a review. *J. Geochem. Explor.* **2019**, *201*, 88–98. [CrossRef]
9. Chakraborti, D.; Das, B.; Rahman, M.M.; Nayak, B.; Pal, A.; Sengupta, M.K.; Ahamed, S.; Hossain, M.A.; Chowdhury, U.K.; Biswas, B.K.; et al. Arsenic in groundwater of the Kolkata Municipal Corporation (KMC), India: Critical review and modes of mitigation. *Chemosphere* **2017**, *180*, 437–447. [CrossRef]
10. Bhowmick, S.; Pramanik, S.; Singh, P.; Mondal, P.; Chatterjee, D.; Nriagu, J. Arsenic in groundwater of West Bengal, India: A review of human health risks and assessment of possible intervention options. *Sci. Total Environ.* **2018**, *612*, 148–169. [CrossRef] [PubMed]
11. Bindal, S.; Singh, C.K. Predicting groundwater arsenic contamination: Regions at risk in highest populated state of India. *Water Res.* **2019**, *159*, 65–76. [CrossRef] [PubMed]
12. Chandrajith, R.; Diyabalanage, S.; Dissanayake, C.B. Geogenic fluoride and arsenic in groundwater of Sri Lanka and its implications to community health. *Groundw. Sustain. Dev.* **2020**, *10*, 100359. [CrossRef]
13. Hoang, T.H.; Bang, S.; Kim, K.-W.; Nguyen, M.H.; Dang, D.M. Arsenic in groundwater and sediment in the Mekong River delta, Vietnam. *Environ. Poll.* **2010**, *158*, 2648–2658. [CrossRef]
14. Stopelli, E.; Duyen, V.T.; Mai, T.T.; Tran, P.T.K.; Viet, P.H.; Lightfoot, A.; Kipfer, R.; Schneider, M.; Eiche, E.; Kontny, A.; et al. Spatial and temporal evolution of groundwater arsenic contamination in the Red River delta, Vietnam: Interplay of mobilisation and retardation processes. *Sci. Total Environ.* **2020**, *717*, 137143. [CrossRef] [PubMed]
15. Richards, L.A.; Magnone, D.; Sültenfuß, J.; Chambers, L.; Bryant, C.; Boyce, A.J.; van Dongen, B.E.; Ballentine, C.J.; Sovann, C.; Uhlemann, S.; et al. Dual in-aquifer and near surface processes drive arsenic mobilization in Cambodian groundwaters. *Sci. Total Environ.* **2019**, *659*, 699–714. [CrossRef] [PubMed]
16. Wen, D.; Zhang, F.; Zhang, E.; Wang, C.; Han, S.; Zheng, Y. Arsenic, fluoride and iodine in groundwater of China. *J. Geochem. Explor.* **2013**, *135*, 1–21. [CrossRef]
17. Guo, H.; Wen, D.; Liu, Z.; Jia, Y.; Guo, Q. A review of high arsenic groundwater in Mainland and Taiwan, China: Distribution, characteristics and geochemical processes. *Appl. Geochem.* **2014**, *41*, 196–217. [CrossRef]
18. Zhang, L.; Qin, X.; Tang, J.; Liu, W.; Yang, H. Review of arsenic geochemical characteristics and its significance on arsenic pollution studies in karst groundwater, South-west China. *Appl. Geochem.* **2017**, *77*, 80–88. [CrossRef]
19. Mariño, E.E.; Ávila, G.T.; Bhattacharya, P.; Schulz, C.J. The occurrence of arsenic and other trace elements in groundwaters of the southwestern Chaco-Pampean plain, Argentina. *J. S. Am. Earth Sci.* **2020**, *100*, 102547. [CrossRef]
20. Alcaine, A.A.; Schulz, C.; Bundschuh, J.; Jacks, G.; Thunvik, R.; Gustafsson, J.-P.; Mörth, C.-M.; Sracek, O.; Ahmada, A.; Bhattacharya, P. Hydrogeochemical controls on the mobility of arsenic, fluoride and other geogenic co-contaminants in the shallow aquifers of northeastern La Pampa Province in Argentina. *Sci. Total Environ.* **2020**, *715*, 136671. [CrossRef] [PubMed]
21. Machado, I.; Falchi, L.; Bühl, V.; Mañay, N. Arsenic levels in groundwater and its correlation with relevant inorganic parameters in Uruguay: A medical geology perspective. *Sci. Total Environ.* **2020**, *721*, 137787. [CrossRef] [PubMed]
22. Navarro, O.; González, J.; Júnez-Ferreira, H.E.; Bautista, C.-F.; Cardona, A. Correlation of Arsenic and Fluoride in the Groundwater for Human Consumption in a Semiarid Region of Mexico. *Procedia Eng.* **2017**, *186*, 333–340. [CrossRef]
23. Gómez-Hernández, A.; Rodríguez, R.; Río, A.L.; Ruiz-Huerta, E.A.; Armienta, M.A.; Dávila-Harris, P.; Sen-Gupta, B.; Delgado-Rodríguez, O.; Ríos, A.D.A.; Martínez-Villegas, N. Alluvial and gypsum karst geological transition favors spreading arsenic contamination in Matehuala, Mexico. *Sci. Total Environ* **2020**, *707*, 135340. [CrossRef]
24. Bretzler, A.; Lalanne, F.; Nikiema, J.; Podgorski, J.; Pfenninger, N.; Berg, M.; Schirmer, M. Groundwater arsenic contamination in Burkina Faso, West Africa: Predicting and verifying regions at risk. *Sci. Total Environ.* **2017**, *584–585*, 958–970. [CrossRef] [PubMed]
25. Abiye, T.A.; Bhattacharya, P. Arsenic concentration in groundwater: Archetypal study from South Africa. *Groundw. Sustain. Dev.* **2019**, *9*, 100246. [CrossRef]
26. Podgorski, J.; Berg, M. Global threat of arsenic in groundwater. *Science* **2020**, *368*, 845–850. [CrossRef] [PubMed]
27. Shaji, E.; Santosh, M.; Sarath, K.V.; Prakash, P.; Deepch, V.; Divy, B.V. Arsenic contamination of groundwater: A global synopsis with focus on the Indian Peninsula. *Geosci. Front.* **2021**, *13*, 101079. [CrossRef]
28. Jadhav, S.V.; Bringas, E.; Yadav, G.D.; Rathod, V.K.; Ortiz, I.; Marathe, K.V. Arsenic and fluoride contaminated groundwaters: A review of current technologies for contaminants removal. *J. Environ. Manag.* **2015**, *162*, 306–325. [CrossRef]
29. Sarkar, A.; Paul, B. The global menace of arsenic and its conventional remediation-A critical review. *Chemosphere* **2016**, *158*, 37–49. [CrossRef]
30. Ghosh, S.; Debsarkar, A.; Dutta, A. Technology alter-natives for decontamination of arsenic-rich groundwater—A critical review, Environ. *Technol. Innov.* **2019**, *13*, 277–303. [CrossRef]

31. Kumar, R.; Patel, M.; Singh, P.; Bundschuh, J.; Pittman, C.U., Jr.; Trakal, L.; Mohan, D. Emerging technologies for arsenic removal from drinking water in rural and peri-urban areas: Methods, experience from, and options for Latin America. *Sci. Total Environ.* **2019**, *694*, 133427. [CrossRef] [PubMed]
32. Opiso, E.M.; Sato, T.; Morimoto, K.; Asai, A.; Anraku, S.; Numako, C.; Yoneda, T. Incorporation of arsenic during the formation of Mg-bearing minerals at alkaline condition. *Miner. Eng.* **2010**, *23*, 230–237. [CrossRef]
33. Park, Y.Y.; Tran, T.; Lee, Y.H.; Nam, Y., II; Senanayake, G.; Kim, M.J. Selective removal of arsenic(V) from a molybdate plant liquor by precipitation of magnesium arsenate. *Hydrometallurgy* **2010**, *104*, 290–297. [CrossRef]
34. Tresintsi, S.; Simeonidis, K.; Katsikini, M.; Paloura, E.C.; Bantsis, G.; Mitrakas, M. A novel approach for arsenic adsorbents regeneration using MgO. *J. Hazard. Mater.* **2014**, *265*, 217–225. [CrossRef] [PubMed]
35. Camacho, J.; Wee, H.-Y.; Kramer, T.A.; Autenrieth, R. Arsenic stabilization on water treatment residuals by calcium addition. *J. Hazard. Mater.* **2009**, *165*, 599–603. [CrossRef] [PubMed]
36. Montes-Hernandeza, G.; Concha-Lozan, N.; Renard, F.; Quirico, E. Removal of oxyanions from synthetic wastewater via carbonation process of calcium hydroxide: Applied and fundamental aspects. *J. Hazard. Mater.* **2009**, *166*, 788–795. [CrossRef]
37. Olyaie, E.; Banejad, H.; Afkhami, A.; Rahmani, A.; Khodaveisi, J. Development of a cost-effective technique to remove the arsenic contamination from aqueous solutions by calcium peroxide nanoparticles. *Sep. Purif. Technol.* **2012**, *95*, 10–15. [CrossRef]
38. Hua, C.-Y.; Lo, S.-L.; Kuan, W.-H. High concentration of arsenate removal by electrocoagulation with calcium. *Sep. Purif. Technol.* **2014**, *126*, 7–14. [CrossRef]
39. Sugita, H.; Oguma, T.; Zhang, M.; Hara, J.; Takahashi, S. Environmental stability of spent magnesium-based and calcium-based arsenic adsorbents-Effects of soils. *J. Jpn. Soc. Civ. Eng. Ser. G Environ. Res.* **2016**, *72*, 437–448. [CrossRef]
40. Sugita, H.; Oguma, T.; Zhang, M.; Hara, J.; Kawabe, Y. Effects of silicic acid on environmental stability of spent magnesium-based arsenic adsorbents. *J. Jpn. Soc. Civ. Eng. Ser. G Environ. Res.* **2017**, *73*, 407–418. [CrossRef]
41. Sugita, H.; Oguma, T.; Zhang, M.; Hara, J.; Kawabe, Y. Effects of silicic acid on environmental stability of spent calcium-based arsenic adsorbents. *J. Jpn. Soc. Civ. Eng. Ser. G Environ. Res.* **2018**, *74*, 493–502. [CrossRef]
42. Sugita, H.; Oguma, T.; Hara, J.; Zhang, M.; Kawabe, Y. Effects of solution pH on spent Mg-based and Ca-based adsorbents -leaching behavior of arsenite and arsenate acids. *Jpn. Geotech. J.* **2020**, *15*, 441–453. [CrossRef]
43. The Chemical Society of Japan (CSJ). *Kagaku Binran (Handbook of Chemistry), Pure Chemistry II*, 4th ed.; Maruzen: Tokyo, Japan, 1993; p. 317.