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Effects of Soils on Environmental Stability of Spent Mg-Based and Ca-Based Adsorbents Containing Arsenite

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Abstract: Spent adsorbents used in As removal treatment may re-leach As. In this study, the effects of soil on spent Mg-based and Ca-based adsorbents were investigated. The spent adsorbents containing arsenite (As(III)) were prepared by adsorbing As(III) on MgO, Mg(OH)₂, CaO, and Ca(OH)₂ powder reagents. Kuroboku soil (Ku), yellow-brown forest soil (YF), Kanuma soil (Ka), river sand (RS), and mountain sand (MS) were used as soil samples. The As leaching ratio was examined in coexistence with soil via shaking tests, and the results were compared with those of a previous study on adsorbents containing arsenate (As(V)). The environmental stability of the spent adsorbents was found to vary greatly depending on the combination of the As valence, adsorbent type, and soil type. However, regardless of the adsorbent or soil type, the spent adsorbents containing As(III) were more likely to leach As than those containing As(V). Additionally, the As leaching ratio was generally lower in Ku and YF and higher in Ka, RS, and MS. For environmentally friendly and sustainable As removal treatment, disposal, and management, the selection of MgO as the adsorbent and treatment involving the oxidation treatment of As(III) to As(V) before adsorbing As onto adsorbents are recommended.

Keywords: arsenic pollution; leaching ratio; adsorbent; disposal; environmental stability; environmentally sustainable treatment; magnesium oxide; magnesium hydroxide; calcium oxide; calcium hydroxide



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1. Introduction

Arsenic (As) is generally widely known as an element with extremely high toxicity to the human body. The World Health Organization (WHO) has set a provisional value for As at 0.01 mg/L in its guidelines for drinking water quality [1]. The As contamination of groundwater occurs in many parts of the world, mainly in Asia [2–19], Latin America [20–24], and Africa [25,26]. In some areas of these developing areas, many people directly use As-contaminated groundwater (well water) for drinking, resulting in significant health damage. Therefore, the purification of As-contaminated water is essential.

Typical purification methods for As-contaminated water have been introduced by Jadhav et al. [27], Sarkar and Paul [28], Ghosh et al. [29], and Kumar et al. [30], including co-precipitation methods, ion-exchange methods, adsorption methods, microfiltration methods, oxidation methods, and electrocoagulation methods. In developing countries, As treatment methods using inexpensive adsorbents may be recommended owing to economic and operational conditions. Among the adsorbents, Mg-based and Ca-based adsorbents are particularly suitable for arsenic removal [31–38]. Mg and Ca are unlikely to have any negative effects on the human body or the ecosystem. Therefore, both Mg-based and Ca-based adsorbents can be recommended as environmentally friendly and sustainable adsorbents.

However, the spent adsorbents recovered after being used in As-purification processes end up as As-rich waste. Therefore, the spent adsorbents need to be recovered, treated, and

managed appropriately. If the spent adsorbents are not appropriately treated or dumped untreated, they could re-leach As, causing secondary environmental contamination. Sugita et al. [39] examined the environmental stability of spent Mg-based and Ca-based adsorbents in coexistence with soil; the spent adsorbents were prepared by adsorbing arsenate, As(V); the effects of soil on As leaching from the spent adsorbents were evaluated via leaching tests. They found that the spent adsorbents based on MgO and Mg(OH)₂ exhibited high environmental stability because the As leaching ratios for all soil samples were low. Furthermore, a high risk of secondary environmental pollution was suggested owing to As re-leaching under sandy soil conditions. The aforementioned study focused only on As(V), and no similar study on arsenite, As(III), has been conducted thus far. As(III) is known to be more toxic than As(V); therefore, the leaching of As(III) from the spent adsorbents containing As(III) would cause serious environmental issues.

To bridge this knowledge gap, in this study, spent Mg- and Ca-based adsorbents containing As(III) were studied, and leaching tests with soils were performed. In these tests, the leaching behaviors of As, Mg, and Ca from the spent adsorbents was investigated. Subsequently, the effects of soil on the environmental stability of spent Mg-based and Ca-based adsorbents with As(III) were evaluated. Additionally, by comparing the data for the As(III) obtained in this study and for As(V) presented in a previous study [39], more environmentally friendly adsorbent selection and sustainable processing methods were suggested.

2. Materials and Methods

The reagents used in this study were purchased from FUJIFILM Wako Pure Chemical Corporation (formerly Wako Pure Chemical Industries, Ltd., 3-1-2 Doshomachi, Chuo-ku, Osaka, Japan), unless specified otherwise.

2.1. Adsorbents

In this study, two types of commercially available Mg reagents, MgO and Mg(OH)₂, and Ca reagents, CaO and Ca(OH)₂, were used as Mg- and Ca-based adsorbents, respectively. The purity (nominal) P (%), median particle size D_{p50} (μm), Brunauer–Emmett–Teller (BET) surface area S_{BET} (m^2/g), and Mg content α_{Mg} (%) or Ca content α_{Ca} (%) of these adsorbents are shown in Table 1. The data in Table 1 were taken from Sugita et al. [39].

Table 1. Purity (nominal), median particle size, BET surface area, and Mg and Ca contents of the four adsorbents used in this study.

| Adsorbent | P (%) | D_{p50} (μm) | S_{BET} (m^2/g) | α_{Mg} (%) | α_{Ca} (%) |
|---------------------|------------|--------------------------------|---|-----------------------------|-----------------------------|
| MgO | 98.0 | 1.54 | 4.3 | 59.1 | - |
| Mg(OH) ₂ | 99.9 | 4.13 | 22.0 | 40.6 | - |
| CaO | 99.6 | 19.6 | 2.7 | - | 71.2 |
| Ca(OH) ₂ | 98.9 | 41.7 | 14.3 | - | 53.5 |

P : nominal purity, D_{p50} : median particle diameter, S_{BET} : BET surface area, α_{Mg} : Mg content, and α_{Ca} : Ca content; data were taken from Sugita et al. (2016) [39].

2.2. Synthetic As-Contaminated Water

A powdered reagent of sodium arsenite (NaAsO₂, 90%) was dissolved in ion-exchange water, and a stock solution of As(III) (2000 mg-As/L) was prepared. A portion of each stock solution was diluted with ion-exchange water to prepare a 20 mg As/L solution. These solutions used synthetic As-contaminated water whose pH had been adjusted to near neutral by adding hydrochloric acid (HCl).

2.3. Preparation of Spent Adsorbents

Each unspent adsorbent (1 g) was weighed into a TPX beaker, and synthetic As-contaminated water (0.2 L) was added to the beaker and stirred with a magnetic stirrer at

approximately 500 rpm for approximately 24 h. Then, suction filtration was performed using a Teflon filter (pore size of 0.45 μm). The concentrations of As, Mg, and Ca in each filtrate were measured using inductively coupled plasma–mass spectrometry (ICP–MS) (7700X, Agilent Technologies, Inc., Santa Clara, CA, USA, or ICPM-8500, Shimadzu Co., Kyoto, Japan) and ICP–atomic emission spectrometry (ICP–AES) (SII SPS3500DD, Seiko Instruments Inc., Chiba, Japan). The calculation methods applied to determine data pertaining to each filtrate were similar to those employed in previous studies [39–41].

Table 2 lists the data in relation to the production of four types of spent adsorbents containing As(III); W_{AD} (g) is the amount of unspent adsorbent added to the synthetic As-contaminated water. V is the liquid volume (L) of the synthetic As-contaminated water. W_{AD}/V is the amount of the unspent adsorbent added per unit volume of As-contaminated water (g/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 (mg/L) of the As-contaminated water, C_{AS} is the As concentration of the filtrate, and R_{AS} is the As removal ratio, which was calculated as follows:

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

C_{Mg} and C_{Ca} in Table 2 refer to the Mg and Ca concentrations in the filtrate (mg/L), respectively, and β_{Mg} and β_{Ca} are the Mg and Ca leaching ratios (%), respectively, which are defined by the following equation:

$$\beta_X = C_X / ((W_{AD}/V) \times 1000 \times \alpha_X / 100) \times 100 \quad (2)$$

where C_X is C_{Mg} or C_{Ca} , α_X is α_{Mg} or α_{Ca} , and β_X is β_{Mg} or β_{Ca} . Note that in Equation (2), W_{AD}/V is multiplied times 1000 to make the units match.

The adsorbents containing As collected by the solid–liquid separation operation were dried at ~ 40 $^{\circ}\text{C}$ for approximately half a day in a constant-temperature dryer and then stored in a closed polypropylene bottle. The adsorbents containing As were used as “spent adsorbents” in the leaching tests, as described later. The calculation method of the As content of the spent adsorbents is outlined below.

The residual ratio of adsorbent γ (%) is defined by the following equation:

$$\gamma = 100 - \beta_X. \quad (3)$$

The amount of As adsorbed per unit mass of the adsorbent remaining as solid δ_{AS} (mg As/g) was calculated using the following equation:

$$\delta_{AS} = (C_{AS0} - C_{AS}) / (W_{AD}/V \times \gamma / 100). \quad (4)$$

The weighed value of a spent adsorbent was taken as the total value of the adsorbent and As adsorbed onto its surface. Then, the As content was determined per unit mass of the recovered spent adsorbent Q_{AS} (mg As/g) was determined using the following equation:

$$Q_{AS} = \delta_{AS} / (1 + \delta_{AS} / 1000). \quad (5)$$

In this study, $\delta_{AS} \approx Q_{AS}$ was assumed, because $\delta_{AS} \ll 1000$. The main reason that the Q_{AS} values of the spent Ca-based adsorbents were higher than those of the spent Mg-based adsorbents is the difference in β_X . The values of Q_{AS} in Table 2 were used to calculate the leaching ratio of As from each spent adsorbent, as described later.

Table 2. Data relating to the production of spent Mg-based and Ca-based adsorbents.

| No. | As(Valence) | Adsorbent | W_{AD}/V (g/L) | pH_0 | C_{AS0} (mg/L) | C_{AS} (mg/L) | C_{Mg} (mg/L) | C_{Ca} (mg/L) | R_{AS} (%) | β_{Mg} (%) | β_{Ca} (%) | Q_{AS} (mg/g) |
|------------------|-------------|---------------------|---------------------|--------|---------------------|--------------------|--------------------|--------------------|-----------------|---------------------|---------------------|--------------------|
| (1) ¹ | As(III) | MgO | 5.004 | 6.99 | 21.79 | 0.149 | 6.23 | - | 99.3 | 0.21 | - | 4.32 |
| (2) ¹ | As(III) | Mg(OH) ₂ | 5.007 | 7.10 | 21.85 | 1.013 | 7.80 | - | 95.4 | 0.38 | - | 4.16 |
| (3) ² | As(III) | CaO | 5.009 | 7.09 | 22.35 | 1.437 | - | 837 | 93.6 | - | 23.5 | 5.42 |
| (4) ² | As(III) | Ca(OH) ₂ | 5.009 | 7.09 | 22.73 | 1.378 | - | 858 | 93.9 | - | 32.0 | 6.23 |

¹ The data for Nos. (1) and (2) were taken from Sugita et al. [41]. ² The data for Nos. (3) and (4) were taken from Sugita et al. [40].

2.4. Soils

The following soils were selected for the leaching tests as representative of the soil characteristics of main Japanese soil types.

1. Kuroboku soil (Ku) is Andosols-type distinguished by the chemical properties of aluminum such as aluminum–humus complexes; volcanic ash soils rich in organic components and particularly common in Japan.
2. Yellow-brown forest soil (YF) is a slightly acidic and inorganic volcanic ash soil.
3. Kanuma soil (Ka) is an acidic soil formed from weathered pumice. It is high in allophane, which is a type of clay mineral made of hydrated aluminosilicate.
4. River sand (RS) is a sandy soil with a high silica content and an alkaline pH.
5. Mountain sand (MS) is a sandy soil with a high iron content and an alkaline pH.

The chemical compositions of the soils and water content (adsorbed and structured waters) were described in Sugita et al. [39]. Additionally, the experimental condition with no soil is denoted as NS.

The soil samples were sieved to a particle size of 0.5–2 mm for the leaching tests.

2.5. Leaching Tests (Shaking Tests)

Two types of water solvents were prepared with hydrochloric acid to simulate acid rain: ion-exchange water adjusted to approximately pH 7 and pH 4. Next, 0.08 g of spent adsorbent and 4 g of soil were weighed into a 50 mL centrifuge tube, 40 mL of the abovementioned water solvent was added, and the tube was sealed. The tube was shaken in a thermostatic shaker for 24 h (approximately 150–180 rpm, room temperature), followed by centrifugation for solid–liquid separation (4500 rpm, 20 min). The supernatant was filtered using a syringe filter (0.45 μ m), and the filtrate (leachate) was collected in a polypropylene bottle. The As, Mg, and Ca concentrations in the leachate were determined using ICP–MS and ICP–AES. Si and Fe were also measured in most of the leachates. Additionally, shaking tests with only-water solvent (without the spent adsorbent and soil) were conducted to check the change in solvent pH due to shaking. Leaching tests with only water solvent and soil (without the spent adsorbent) were also performed to check the pH of the leachate in the presence of only soil.

3. Results

3.1. pH of Leachate

The pH values of the leachate (pH_f) obtained from the leaching tests in this study are shown in Figure 1, where “Blank” refers to the leaching tests (or the shaking tests) without the spent adsorbent. As shown in Figure 1, almost no difference in pH_f was observed with variation in pH_0 , except for the Blank in the NS case (the shaking test with only water as a solvent). Therefore, under these test conditions, pH_f was influenced by the type of soil and adsorbent more than by pH_0 . In the leaching tests with only spent adsorbent without soil (NS), the pH_f values for the Ca-based adsorbents were higher than those for the Mg-based adsorbents, with pH_f following the order of Mg(OH)₂ \leq MgO $<$ CaO \approx Ca(OH)₂. In the leaching tests with only soil without spent adsorbent (Blank), the magnitude order of pH_f was Ku $<$ YF $<$ Ka $<$ RS $<$ MS. Moreover, in the leaching tests with both spent adsorbent

and soil, pH_f followed the order of Ku, YF, Ka < RS, MS, regardless of the type of the spent adsorbent.

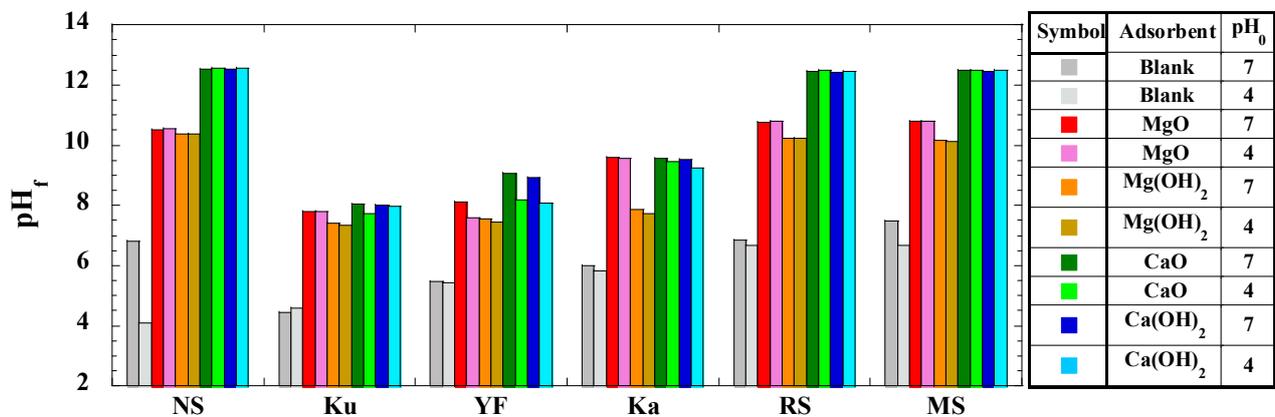


Figure 1. pH values of leachate versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

3.2. As Concentration in Leachate

The As concentrations in the leachate, C_{AS} (mg/L), obtained from the leaching tests in this study are shown in Figure 2.

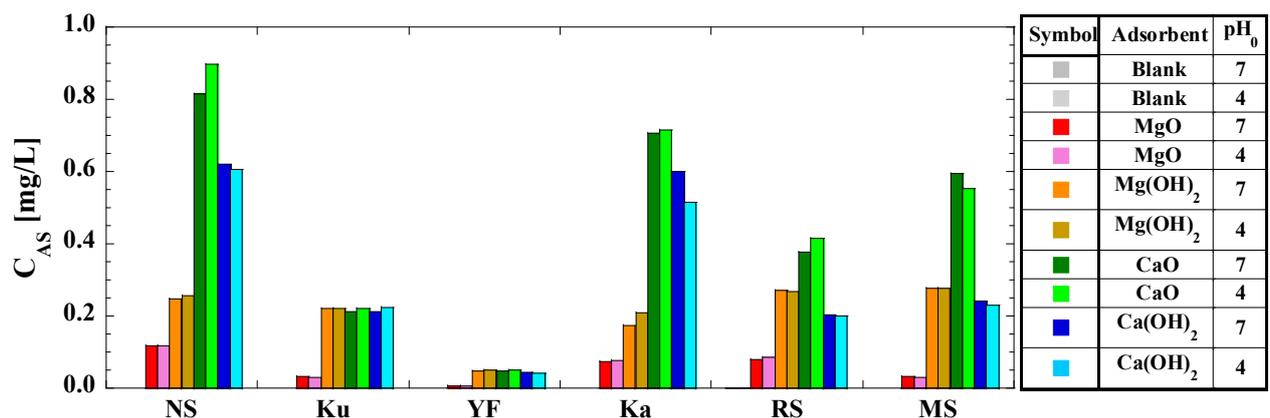


Figure 2. As concentration in leachate versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

In the leachate from only soil without the spent adsorbent, a small amount of As was evident only in the leachate in RS (approximately 0.001 mg/L); no As was detected in the leachates of the other soils. For the spent adsorbents containing As(III), no significant difference in C_{AS} due to pH_0 was observed (Figure 2). Focusing on each soil in Figure 2, C_{AS} follows the order MgO \ll Mg(OH)₂ \approx Ca(OH)₂ \approx CaO in Ku; MgO < Ca(OH)₂ \leq Mg(OH)₂, CaO in YF; MgO < Mg(OH)₂ \ll Ca(OH)₂ < CaO in NS and Ka; and MgO \ll Ca(OH)₂ < Mg(OH)₂ < CaO in RS and MS. Focusing on each spent adsorbent in Figure 2, C_{AS} follows the order YF < Ku \leq MS < Ka < RS < NS for MgO; YF < Ka < Ku \leq NS \leq RS \leq MS for Mg(OH)₂; YF < Ku < RS < MS < Ka < NS for CaO; and YF < RS \leq Ku \leq MS < Ka < NS for Ca(OH)₂.

3.3. Mg Concentration in Leachate

The Mg concentrations in the leachate, C_{Mg} (mg/L), obtained from the leaching tests in this study are shown in Figure 3. The C_{Mg} values for the spent Ca-based adsorbents are not included in this figure because they were not measured.

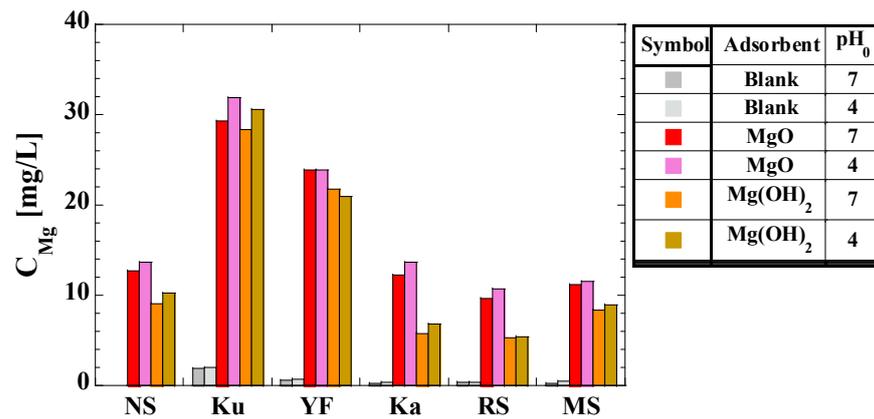


Figure 3. Mg concentration in leachate versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

In the leaching tests without spent adsorbent (Blank), the C_{Mg} values were approximately 2 mg/L in Ku and less than 1 mg/L in the other soils. These values were significantly lower than those observed for the spent Mg-based adsorbents. Therefore, it could be concluded that most of the Mg ions detected in the leachate were derived from the Mg-based adsorbents. In Figure 3, some differences exist in C_{Mg} between $pH_0 = 4$ and 7 in some cases, but no significant difference is apparent for most cases. Therefore, the effects of pH_0 on C_{Mg} seem to be relatively weak, similar to those of pH_f . Furthermore, in Figure 3, comparing the C_{Mg} values among the NS cases, $Mg(OH)_2 < MgO$, and this tendency is different from the abovementioned tendency of C_{AS} . Additionally, the C_{Mg} values obtained from testing the different soil types follow the order $Ka, RS, MS \leq NS \ll YF < Ku$.

3.4. Ca Concentration in Leachate

The Ca concentrations in the leachate, C_{Ca} (mg/L), obtained from the leaching tests in this study are shown in Figure 4. The C_{Ca} values for the spent Mg-based adsorbents are not included in this figure because they were not measured.

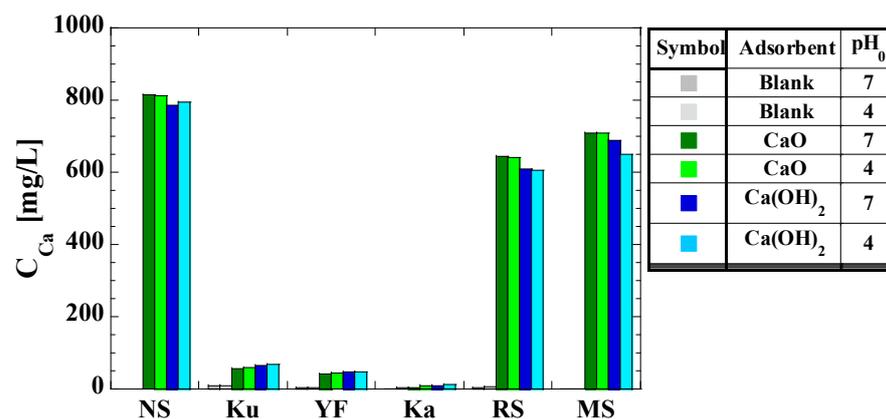


Figure 4. Ca concentration in leachate versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

In the leaching tests without the spent adsorbent (Blank), the C_{Ca} values were approximately 9 mg/L in Ku and less than 3 mg/L in the other soils. These values were much lower than those in the leaching tests with the spent Ca-based adsorbents. Therefore, it could be concluded that most of the Ca ions detected in the leachate derived from the Ca-based adsorbents. For the spent adsorbents containing As(III), as shown in Figure 4, a slight difference existed in C_{Ca} between $pH_0 = 7$ and 4.

3.5. Si Concentration in Leachate

The Si concentrations in the leachate, C_{Si} (mg/L), obtained from the leaching tests in this study are shown in Figure 5.

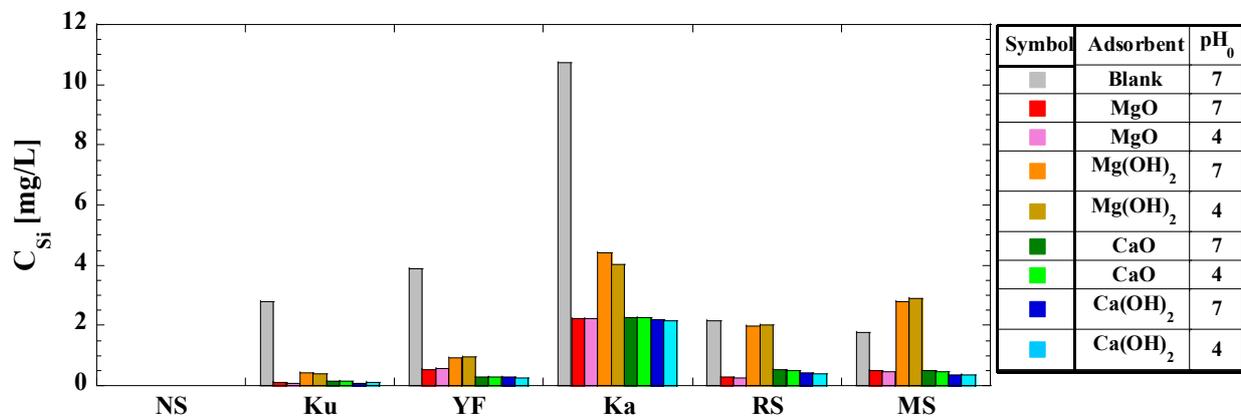


Figure 5. Si concentration in leachate versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

No difference in C_{Si} was observed depending on pH_0 , similar to C_{AS} , C_{Mg} , and C_{Ca} . Comparing the data in the leaching tests with only soil without the spent adsorbent, C_{Si} followed the order $MS < RS < Ku < YF < Ka$. In the leaching tests with both spent Mg-based adsorbent and soil, C_{Si} followed the order $MgO < Mg(OH)_2$ among the Mg-based adsorbents and $Ku < YF < MS \leq RS < Ka$ among the soils. Additionally, in RS and MS, the C_{Si} values were higher when the spent $Mg(OH)_2$ adsorbent and soil coexisted than in the only-soil case. However, the C_{Si} values in all the soils were lower when the Ca-based adsorbent and soil coexisted than in the only-soil case, and C_{Si} followed the order $Ku < YF < RS \approx MS < Ka$. Additionally, a slight difference in C_{Si} existed between CaO and $Ca(OH)_2$. Furthermore, comparisons between the different spent adsorbents revealed that C_{Si} followed the order $MgO < CaO \approx Ca(OH)_2 < Mg(OH)_2$.

3.6. Fe Concentration in Leachate

The Fe concentration in the leachate, C_{Fe} (mg/L), was measured in all tests. In the leaching tests with only soil without the spent adsorbent, Fe was detected only in RS and MS (0.10–0.24 mg/L). In the leaching tests with both spent adsorbent and soil, most of the C_{Fe} values for Ka were slightly over 0.01 mg/L, whereas those for the other soils were significantly below 0.01 mg/L.

4. Discussion

4.1. As Leaching Ratio

In this study, the As leaching ratio, E_{AS} (%), was calculated as follows:

$$E_{AS} = C_{AS} / (Q_{AS} \times W_{SP} / V) \times 100 \quad (6)$$

where the additional concentration of the spent adsorbent in the leaching tests was W_{SP} / V (g/L).

The E_{AS} values obtained from the above equation are shown in Figure 6 for each spent adsorbent type and initial pH value.

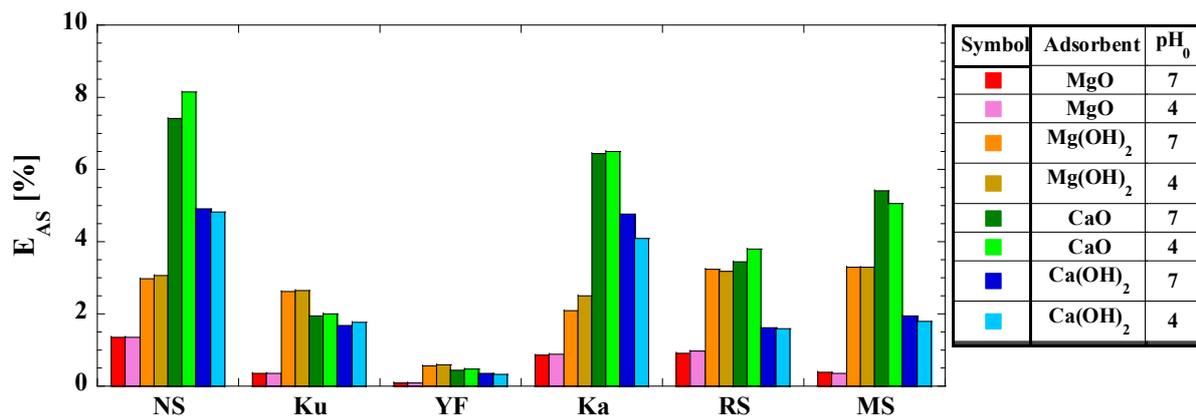


Figure 6. As leaching ratio versus soil: NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

E_{AS} followed various orders depending on the soil type: $MgO < Ca(OH)_2 \leq CaO < Mg(OH)_2$ for Ku and YF; $MgO < Mg(OH)_2 < Ca(OH)_2 < CaO$ for Ka; $MgO < Ca(OH)_2 < Mg(OH)_2 < CaO$ for RS and MS. Although the ease of leaching As from the adsorbent differed depending on soil type, Figure 6 demonstrates that the spent MgO adsorbent had the lowest E_{AS} value for all soils.

Additionally, overall, the E_{AS} values shown in Figure 6 are clearly higher than for those containing As(V) reported in a previous study [39]. Therefore, the risk of As leaching in soil is higher for spent adsorbents containing As(III) than for those containing As(V). From the above results, it can be concluded that the environmental stability of spent adsorbents largely depends on the As valence as well as the type of adsorbent and soil.

4.2. Dissolved Forms of As in Leachate

The As(III) in the spent Mg- and Ca-based adsorbents is presumed to be adsorbed (immobilized) on the solid surface as “Solid-Mg-O-As(OH)₂” and “Solid-Ca-O-As(OH)₂”, respectively [40,41]. In addition, the reactions in which As(III) is desorbed from the adsorbent surface in a neutral or an alkaline solution are expressed by the following equations.

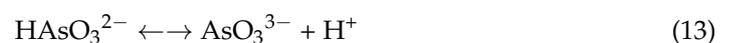
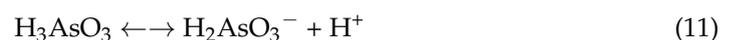
For the Mg-based adsorbents:



For the Ca-based adsorbents:



The dissolved forms of As(III) leached from the spent adsorbent containing As(III) are represented by the following dissociation reactions for arsenous acid:



where the acid dissociation constants of arsenous acid are $pK_{a1} = 9.1$, $pK_{a2} = 12.1$, and $pK_{a3} = 13.4$ (25 °C) [42], and the abundances of the dissolved arsenous acid species are determined by the following:

$$\frac{[\text{H}_2\text{AsO}_3^-]}{[\text{H}_3\text{AsO}_3]} = 10 \exp(pH_f - pK_{a1}) \quad (14)$$

$$[\text{HAsO}_3^{2-}]/[\text{H}_2\text{AsO}_3^-] = 10 \exp(\text{pH}_f - \text{p}K_{a2}) \quad (15)$$

$$[\text{AsO}_3^{3-}]/[\text{HAsO}_3^{2-}] = 10 \exp(\text{pH}_f - \text{p}K_{a3}). \quad (16)$$

The main dissolved forms in each leachate estimated using the above equations are shown in Table 3. No classification based on pH_0 is included in Table 3 because a slight difference in pH_f was observed between $\text{pH}_0 = 7$ and 4, indicating a small difference in the abundance ratio among arsenous acid species based on pH_f . In addition, when two forms are listed in a column, the one on the left is dominant.

Table 3. Dissolved forms of As leached from Mg- and Ca-based adsorbents containing As(III).

| Soil | Blank | MgO | Mg(OH) ₂ | CaO | Ca(OH) ₂ |
|------|---------------------------------|--|--|--|--|
| NS | H ₃ AsO ₃ | H ₂ AsO ₃ ⁻ | H ₂ AsO ₃ ⁻ | HAsO ₃ ²⁻ , H ₂ AsO ₃ ⁻ | HAsO ₃ ²⁻ , H ₂ AsO ₃ ⁻ |
| Ku | H ₃ AsO ₃ | H ₃ AsO ₃ | H ₃ AsO ₃ | H ₃ AsO ₃ | H ₃ AsO ₃ |
| YF | H ₃ AsO ₃ | H ₃ AsO ₃ | H ₃ AsO ₃ | H ₃ AsO ₃ , H ₂ AsO ₃ ⁻ | H ₃ AsO ₃ , H ₂ AsO ₃ ⁻ |
| Ka | H ₃ AsO ₃ | H ₂ AsO ₃ ⁻ , H ₃ AsO ₃ | H ₃ AsO ₃ | H ₂ AsO ₃ ⁻ , H ₃ AsO ₃ | H ₂ AsO ₃ ⁻ , H ₃ AsO ₃ |
| RS | H ₃ AsO ₃ | H ₂ AsO ₃ ⁻ | H ₂ AsO ₃ ⁻ | HAsO ₃ ²⁻ , H ₂ AsO ₃ ⁻ | HAsO ₃ ²⁻ , H ₂ AsO ₃ ⁻ |
| MS | H ₃ AsO ₃ | H ₂ AsO ₃ ⁻ | H ₂ AsO ₃ ⁻ | HAsO ₃ ²⁻ , H ₂ AsO ₃ ⁻ | HAsO ₃ ²⁻ , H ₂ AsO ₃ ⁻ |

NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

As shown in Table 3, for Blank, the main dissolved form of arsenite in all leachates is estimated to be H₃AsO₃. Also, in Ku, the main dissolved form is estimated to be H₃AsO₃, regardless of the type of the spent adsorbent. In YF, the main dissolved form is H₃AsO₃ for the spent Mg-based adsorbents; in addition to H₃AsO₃, H₂AsO₃⁻ is estimated to be present in non-negligible amounts for the spent Ca-based adsorbents. In Ka, the main dissolved form is estimated to be H₃AsO₃ for Mg(OH)₂, whereas more H₂AsO₃⁻ than H₃AsO₃ is present for MgO, CaO, and Ca(OH)₂. In both RS and MS, the main dissolved form is estimated to be H₂AsO₃⁻ for the spent Mg-based adsorbents, and more HAsO₃²⁻ than H₂AsO₃⁻ is present for the Ca-based adsorbents.

4.3. Mg and Ca Leaching Ratios

In this study, the Mg and Ca leaching ratios, E_{Mg} (%) and E_{Ca} (%), were calculated as follows:

$$E_X = C_X / ((W_{\text{SP}}/V) \times 1000 \times \alpha_X / 100) \times 100 \quad (17)$$

where E_X is E_{Mg} or E_{Ca} .

Equation (17) is essentially the same as Equation (2). The E_{Mg} and E_{Ca} values obtained from Equation (17) for each adsorbent type and initial pH value are shown in Figure 7a,b, respectively.

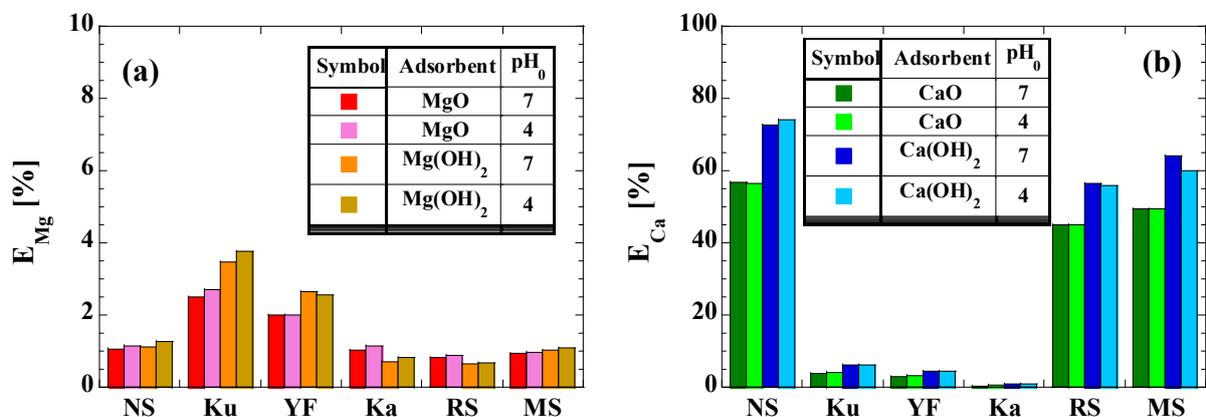


Figure 7. Mg and Ca leaching ratios versus soil: (a) spent Mg-based adsorbents; (b) spent Ca-based adsorbents. NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

The E_{Mg} values in NS were clearly higher than those in Ku and YF, being almost equal to those in RS and MS. In Ka, the E_{Mg} values were comparable to those in NS. Moreover, as shown in Figure 7b, the E_{Ca} values were slightly lower in RS and MS than in NS but were significantly lower in Ku, YF, and Ka than in NS. Both E_{Mg} and E_{Ca} were the lowest in YF.

The residual ratio of each spent adsorbent after the leaching test was calculated by subtracting each value of E_{Mg} or E_{Ca} from 100. In all the soils tested in this study, the residual ratios of the spent Mg-based adsorbents were over 96%. However, although the residual ratios of the Ca-based adsorbents reached over 93% in Ku, YF, and Ka, they were less than $\approx 60\%$ in RS and MS. Therefore, the environmental stability of spent Ca-based adsorbents was significantly reduced in sandy soils.

4.4. Effects of Silicic Acid Leached from Soils

In the only-soil leaching tests without the spent adsorbent (Blank at $pH_0 = 7$), Si components of more than 1.7 mg/L were leached from the soil in all soils, as shown in Figure 5. Although Si was not measured during the leaching test with only soil without the spent adsorbent at $pH_0 = 4$ (Blank at $pH_0 = 4$), Si components were expected to be leached to the same extent as in the Blank at $pH_0 = 7$. Previous studies have reported that the leaching behavior of As from spent Mg- and Ca-based adsorbents can be significantly influenced by the Si components present in a solvent [40,41]. These reports revealed that the presence of silicic acid slightly decreases the As leaching amount for spent Mg-based adsorbents containing As(III) [41]. They also reported that, for spent Ca-based adsorbents, the As leaching amount decreased with increasing initial silicic acid concentration [40].

In this study, to examine the effects of the Si components (silicic acid species) leached from soil, the C_{Si} value for the Blank (without adsorbent) in each soil was defined as the hypothetical initial Si concentration, C_{Si0} . In addition, due to the lack of C_{Si} data for the Blank at $pH_0 = 4$ in this study, only data at $pH_0 = 7$ were considered in this study. C_{Si0} increased in the order $NS < MS \leq RS < Ku < YF \ll Ka$. The E_{AS} values obtained from each leaching test are plotted in Figure 8 against C_{Si0} for each soil. Figure 8a,b correspond to the spent Mg- and Ca-based adsorbents, respectively.

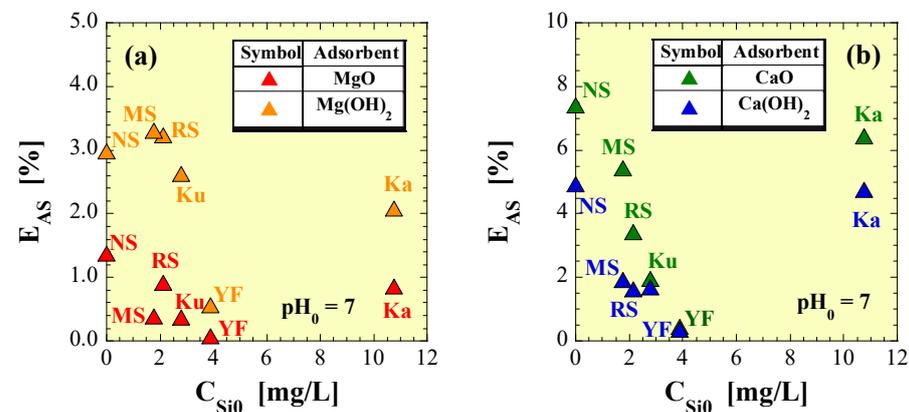


Figure 8. As leaching ratios versus hypothetical initial Si concentration: (a) spent Mg-based adsorbents; (b) spent Ca-based adsorbents. NS, no soil; Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

As shown in Figure 8a, for As(III)-Mg(OH)₂, the E_{AS} values of MS and RS were slightly higher than that of NS, whereas the values in Ku, YF, and Ka were lower than that of NS. In particular, the E_{AS} value of YF was approximately one-fifth of that of NS, which is extremely low. Additionally, for As(III)-MgO, the E_{AS} values in all soils were lower than that in NS. The above findings demonstrate that for the Mg-based adsorbent containing As(III), the presence of silicic acid tended to lower E_{AS} overall, except in the cases of RS and MS for Mg(OH)₂. According to the above, for As(III)-MgO and As(III)-Mg(OH)₂, the

effects of C_{Si0} on E_{AS} in the presence of soil in this study are in agreement with previous reports using silicic acid solutions [41].

As shown in Figure 8b, for the spent Ca-based adsorbents, E_{AS} tended to decrease as C_{Si0} increases, except in the plots of Ka. The E_{AS} values in Ka are slightly lower than those in NS for the spent Ca-based adsorbents containing As(III). Therefore, for the spent Ca-based adsorbents containing As(III), except for the Ka data, the effects of C_{Si0} on E_{AS} in the presence of soil in this study are in agreement with those reported in previous studies [40]. Additionally, $Ca(OH)_2$ evidently has higher environmental stability than CaO, because overall the E_{AS} values were lower for $Ca(OH)_2$ than for CaO. Furthermore, based on the test results, it seems reasonable to assume that the spent Ca-based adsorbents reduced the E_{AS} when coexisting with soil.

The results of this study demonstrate that, with the exception of some data, the As leaching from spent adsorbents is more likely to be reduced when the spent adsorbents coexist with soils than when soils are not present. This result introduces several possibilities, including (i) readsorption of As onto the spent adsorbent, (ii) adsorption of As onto the soil, (iii) incorporation of As in the process in which the Mg or Ca ions leached from the base material of the adsorbents produce magnesium or calcium hydroxide, and (iv) the incorporation of As in the process in which the silicic acid ions react with Mg or Ca ions leached from the base material of the adsorbent to produce magnesium or calcium silicate.

To verify these hypotheses, 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). Thus, C_{Si} in mg/L converted to molar units is denoted as M_{Si} , mmol/L. The value of C_{Si} for the Blank is denoted as M_{Si0} . The difference between M_{Si0} and M_{Si} , $M_{Si0} - M_{Si}$, is denoted as ΔM_{Si} . The ΔM_{Si} value is assumed to be the amount consumed for the formation of silicates or the adsorption on the spent adsorbent surface. Similarly, C_{Mg} , C_{Ca} , and C_{AS} in mg/L converted to molar units are denoted as M_{Mg} , M_{Ca} , in M_{AS} in mmol/L, respectively. Mg, Ca, and As may be leached from both the spent adsorbent and soil. Therefore, the values of M_{Mg} , M_{Ca} , and M_{AS} for the Blank are denoted as $M_{Mg(Blank)}$, $M_{Ca(Blank)}$, and $M_{AS(Blank)}$, respectively, and their values in NS are denoted as $M_{Mg(NS)}$, $M_{Ca(NS)}$, and $M_{AS(NS)}$, respectively. Furthermore, $M_{Mg(NS)} + M_{Mg(Blank)}$, $M_{Ca(NS)} + M_{Ca(Blank)}$, and $M_{AS(NS)} + M_{AS(Blank)}$ are denoted as M_{Mg0} , M_{Ca0} , and M_{AS0} , respectively. $M_{Mg0} - M_{Mg}$ and $M_{Ca0} - M_{Ca}$ are denoted as ΔM_{Mg} and ΔM_{Ca} , respectively. ΔM_{Mg} and ΔM_{Ca} are assumed to correspond to the amounts consumed in their silicate formation and directly adsorbed on the soil. Also, ΔM_{Mg} and ΔM_{Ca} do not include the amount readsorbed onto the spent adsorbents and the amount consumed due to Mg and Ca hydroxide formation, because ΔM_{Mg} and ΔM_{Ca} are the values obtained by subtracting $M_{Mg(NS)}$ and $M_{Ca(NS)}$, respectively. $M_{AS0} - M_{AS}$ is denoted as ΔM_{AS} . ΔM_{AS} is assumed to correspond to the amounts incorporated in the process of forming Mg and Ca silicates and directly adsorbed on the soil. Furthermore, ΔM_{AS} does not include the amount readsorbed onto the spent adsorbents and the amount incorporated in the process of forming Mg or Ca hydroxides, because ΔM_{AS} is the value obtained by subtracting $M_{AS(NS)}$.

In some cases, the ΔM_{Si} , ΔM_{Mg} , and ΔM_{AS} values obtained in this study were negative. A negative value of ΔM_{Si} suggests that the amount of Si leached from the soil increases when it coexists with the spent adsorbent in relation to when only the soil is present. Negative values of ΔM_{Mg} and ΔM_{AS} indicate that the amount of Mg and As leached from the spent adsorbent increased when it coexisted with the soil in relation to those when only the spent adsorbent was present. Moreover, ΔM_{Ca} never takes a negative value, regardless of the soil type.

Figure 9a,b show the plots of ΔM_{Mg} for the spent Mg-based adsorbents and ΔM_{Ca} for the spent Ca-based adsorbents against ΔM_{Si} , respectively.

If the decreases in Si, Mg, and Ca in the presence of soil were caused only by the formation of magnesium silicate or calcium silicate species, positive correlations should be observed between ΔM_{Si} and ΔM_{Mg} or ΔM_{Ca} in Figure 9. As shown in Figure 9a, for

Ku and YF, a weak positive correlation appears, but both ΔM_{Si} and ΔM_{Mg} have negative values. Thus, the leaching amounts of both Si and Mg increased. For Ka, RS, and MS, no regular trend was observed in the fluctuation in ΔM_{Mg} with respect to that in ΔM_{Si} . In Figure 9b, no regular trend exists in the fluctuation in ΔM_{Ca} with respect to that in ΔM_{Si} . In both Figure 9a,b, no regular trend can be observed even when focusing on the type of adsorbents. However, focusing on the soil types indicates that data for the same type of soil are plotted in adjacent positions. Even for data corresponding to the same soil type, the relative positions plotted in Figure 9a,b are different. However, in both images, RS is plotted adjacent to MS, and Ku is plotted adjacent to YF, whereas Ka is plotted at a location separate from them. These findings suggest that the soil properties that affect the spent adsorbents were similar for Ku and YF and for RS and MS, whereas those for Ka were quite different from those for the other soils.

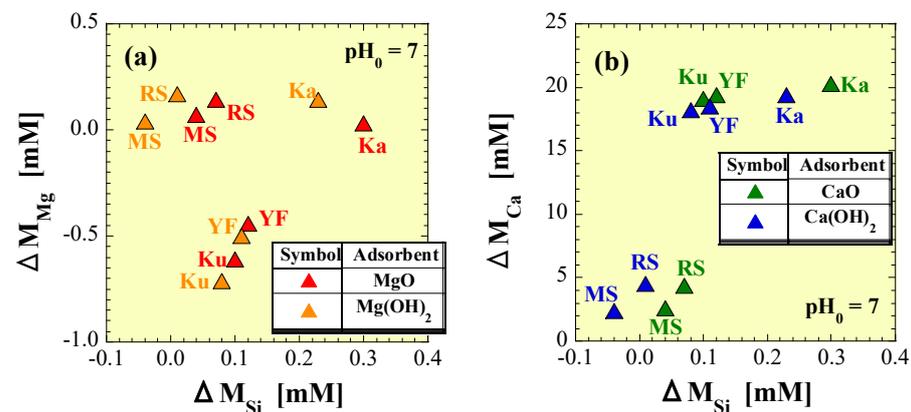


Figure 9. Plots of (a) ΔM_{Mg} for the spent Mg-based adsorbents and (b) ΔM_{Ca} for the spent Ca-based adsorbents against ΔM_{Si} . Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

The chemical composition of calcium silicate species is $Ca_xSiO_{(x+2)}$, where $x = 0.5\text{--}4$ [40], indicating that the Ca/Si molar ratio of the average composition of the calcium silicate species produced should be between 0.5 and 4. Similarly, the Mg/Si molar ratio of the average composition of the magnesium silicate species produced should be between 0.5 and 4. Tables 4 and 5 show the values of $\Delta M_{Mg}/\Delta M_{Si}$ and $\Delta M_{Ca}/\Delta M_{Si}$ determined based on the data in Figure 9. Additionally, if either ΔM_{Si} or ΔM_{Mg} or ΔM_{Ca} had a negative value, we assumed that neither magnesium nor calcium silicate was produced, and such a result was excluded. Tables 4 and 5 only present the ratios of the production amounts of silicates to the amounts of Mg and Ca adsorbed on the soil or to the amount of Si components adsorbed on the spent adsorbent; they do not indicate the produced amounts of silicates.

Table 4. Values of $\Delta M_{Mg}/\Delta M_{Si}$ for spent Mg-based adsorbents at $pH_0 = 7$.

| As | Adsorbent | Ku | YF | Ka | RS | MS |
|---------|---------------------|----|----|------|------|------|
| As(III) | MgO | - | - | 0.09 | 59.1 | - |
| As(III) | Mg(OH) ₂ | - | - | 22.0 | 2.05 | 1.58 |

Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

Table 5. Values of $\Delta M_{Ca}/\Delta M_{Si}$ for spent Ca-based adsorbents at $pH_0 = 7$.

| As | Adsorbent | Ku | YF | Ka | RS | MS |
|---------|---------------------|-----|-----|------|------|------|
| As(III) | CaO | 203 | 152 | 67.1 | 77.6 | 59.2 |
| As(III) | Ca(OH) ₂ | 190 | 144 | 66.6 | 75.3 | 48.7 |

Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

In Tables 4 and 5, the values exceeding four indicate a reduction in Mg or Ca beyond that consumed in silicate formation, which suggest that Mg and Ca leached from the spent adsorbent were directly adsorbed onto the soil. Conversely, values less than 0.5 indicate a reduction in Si beyond that consumed in the silicate formation, which suggest that silicic acid ions leached from the soil were directly adsorbed onto the spent adsorbent. As shown in Tables 4 and 5, the above analysis indicates that in Ku and YF, magnesium silicate was not produced for all Mg-based adsorbents. Additionally, for As(III)-MgO, magnesium silicate was not produced even in MS. Moreover, for the Ca-based adsorbents, calcium silicates could have been produced in all soils.

Subsequently, assuming that silicate was formed, the incorporation of As into the silicate was examined. The extreme (Mg or Ca)/Si composition molar ratios of the silicate species that can be produced are 0.5 and 4, as described above. Assuming the (Mg or Ca)/Si composition molar ratio of the generated silicate species is 0.5, if the value of $\Delta M_{\text{Si}} - (\Delta M_{\text{Mg}} \text{ or } \Delta M_{\text{Ca}}) \times 2$ is positive, the amount of $(\text{Mg or Ca})_{0.5}\text{SiO}_{2.5}$ produced is equal to $(\Delta M_{\text{Mg}} \text{ or } \Delta M_{\text{Ca}}) \times 2$, and, if negative, it is equal to ΔM_{Si} . Assuming that the (Mg or Ca)/Si composition molar ratio of the generated silicate species is four, if the value of $\Delta M_{\text{Si}} - (\Delta M_{\text{Mg}} \text{ or } \Delta M_{\text{Ca}}) \times 1/4$ is positive, the amount of $(\text{Mg or Ca})_4\text{SiO}_6$ produced is equal to $(\Delta M_{\text{Mg}} \text{ or } \Delta M_{\text{Ca}}) \times 1/4$, and if negative, it is equal to ΔM_{Si} .

The plots of ΔM_{AS} against the production amount of silicate estimated based on these assumptions are shown in Figures 10 and 11. Figure 10 is a plot of ΔM_{AS} against the estimated production amounts of (a) $\text{Mg}_{0.5}\text{SiO}_{2.5}$ and (b) Mg_4SiO_6 for the coexistence of the spent Mg-based adsorbents and soil. Figure 11 is a plot of ΔM_{AS} against the estimated production amounts of (a) $\text{Ca}_{0.5}\text{SiO}_{2.5}$ and (b) Ca_4SiO_6 for the coexistence of the spent Ca-based adsorbents and soil. However, Figure 11a,b are exactly the same data plots, because $M_{\text{Ca}0.5\text{SiO}2.5} = M_{\text{Ca}4\text{SiO}6} = \Delta M_{\text{Si}}$ was derived from the analysis based on the above assumptions.

In Figure 10a,b, no correlation can be observed between the produced amount of magnesium silicate species and ΔM_{AS} . However, because the amount of As leached from the spent Mg-based adsorbents was essentially low, even if the incorporation of As into the magnesium silicate species had occurred, it is possible that no clear trend could be observed.

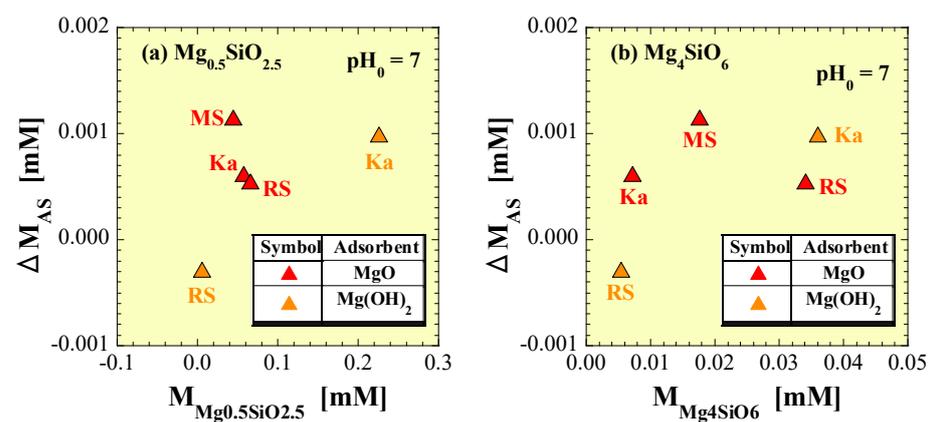


Figure 10. Plots of ΔM_{AS} against estimated production amounts of (a) $\text{Mg}_{0.5}\text{SiO}_{2.5}$ and (b) Mg_4SiO_6 for the coexistence of the spent Mg-based adsorbents and soil: Ka, Kanuma soil; RS, river sand; MS, mountain sand.

Comparing the values of ΔM_{AS} in soils of the same type with different estimated production amounts of calcium silicate species can afford the amount of As adsorbed on the soil and the ratio of As incorporated into calcium silicate. However, in this study, such an analysis could not be conducted, because data for same soil types with significantly different estimated production amounts of calcium silicate species could not be obtained. However, in Figure 11, focusing on the data plots in which the type of adsorbent is the same, a positive correlation appears between the produced amount of calcium silicate species

and ΔM_{AS} , except in the data plots of Ka. This result was attributed to the extremely low amount of As and the Ca ions leached from the spent adsorbents being directly adsorbed on Ka. The Ca ions were directly adsorbed before silicic acid ions were leached from Ka, forming calcium silicate species in situ. Additionally, CaO tends to have a slightly higher ΔM_{AS} than Ca(OH)_2 , which is attributed to the actual produced amount of calcium silicate species, which could be lower for Ca(OH)_2 than for CaO. In other words, the proportion of silicic acid adsorbed on the spent adsorbent is inferred to be higher for Ca(OH)_2 than for CaO.

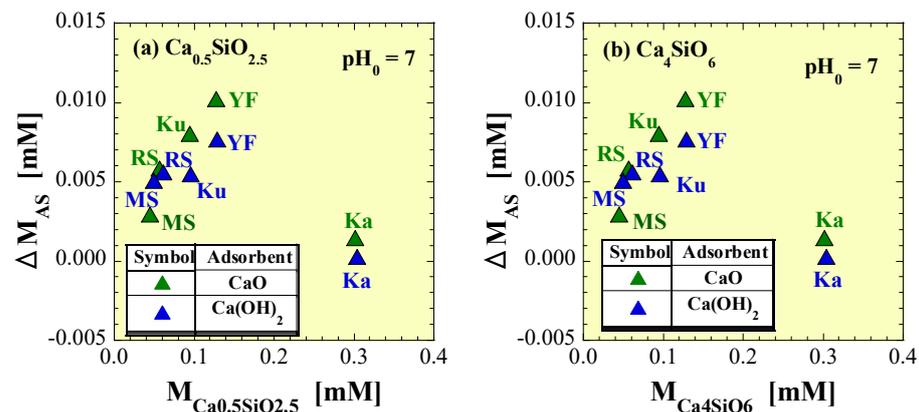


Figure 11. Plots of ΔM_{AS} against estimated production amounts of (a) $\text{Ca}_{0.5}\text{SiO}_{2.5}$ and (b) Ca_4SiO_6 for the coexistence of the spent Ca-based adsorbents and soil: Ku, Kuroboku soil; YF, yellow-brown forest soil; Ka, Kanuma soil; RS, river sand; MS, mountain sand.

4.5. Recommendations for Waste Disposal Considering Effects of Soil on Spent Adsorbents

As described in Section 4.4, in coexistence with soil, the effects of silicic acid species leached from the soil are thought to be quite significant. For Ca-based adsorbents in particular, the incorporation of As into the generated calcium silicate species is thought to prevent environmental pollution due to As leaching. However, the As adsorption capacity of the soil itself is assumed to contribute the most to the decline in E_{AS} , suggesting that the soil acts as a second adsorbent. If the soil itself has a high As adsorption capacity, most of the As leached from the spent adsorbents adsorbs onto the soil that is in contact with the spent adsorbents, which prevents the spread of As contamination over a wide area. Conversely, if the soil itself has a low As adsorption capacity, leached As does not readily adsorb onto the soil, and As contamination spreads over a wide area. Applying the abovementioned rationale to the soils tested in this study, Ku and YF are considered to exhibit the former behavior, and Ka, RS, and MS are considered to exhibit the latter. Thus, Ku and YF prevent the spread of As contamination, although the soil itself in contact with the spent sorbent is contaminated with As. Conversely, Ka, RS, and MS are less susceptible to contamination with As, but As contamination may spread over a wide area via soil pore water.

Furthermore, it may be possible to investigate the As adsorption capacity of individual soils and to use soils with a high As adsorption capacity as a natural adsorbent to prevent the spread of As contamination. However, the soil used as an As adsorption barrier must be risk-managed as As-contaminated soil, and trade-offs and risks must be considered to establish sustainable As treatment processes. Based on the premise that used adsorbents are appropriately processed and managed, examining the characteristics of the nearby soil when planning the location of a waste disposal site is very important to ensure sustainable safety, considering all steps from As purification using adsorbents to the disposal of spent adsorbents containing As.

Finally, among all the soils tested in this study, the spent adsorbents containing As(III) had lower environmental stability than those containing As(V) reported in a previous study [39]. This result indicates that oxidizing As(III) to As(V) before adsorbing As onto

adsorbents is advisable. Furthermore, MgO is strongly recommended as an adsorbent for As, because it exhibits high environmental stability for all soils.

5. Conclusions

Focusing on As(III), which is more toxic than As(V), leaching tests were conducted in this study involving four types of spent adsorbents containing As(III), five types of soil, and two types of ion-exchange water with different pH values. A slight difference was observed in E_{AS} due to solvent pH, whereas E_{AS} varied greatly depending on both type of adsorbent and type of soil. Focusing on the soil type, E_{AS} followed the order of $MgO \ll Mg(OH)_2 \approx Ca(OH)_2 \approx CaO$ in Ku, $MgO < Ca(OH)_2 \leq Mg(OH)_2$, CaO in YF, $MgO < Mg(OH)_2 \ll Ca(OH)_2 < CaO$ in NS and Ka, and $MgO \ll Ca(OH)_2 < Mg(OH)_2 < CaO$ in RS and MS. Focusing on the spent adsorbent type, E_{AS} followed the order of $YF < Ku \leq MS < Ka < RS < NS$ for MgO, $YF < Ka < Ku \leq NS \leq RS \leq MS$ for $Mg(OH)_2$, $YF < Ku < RS < MS < Ka < NS$ for CaO, and $YF < RS \leq Ku \leq MS < Ka < NS$ for $Ca(OH)_2$. For both the spent Mg-based and Ca-based adsorbents, the E_{AS} values were clearly higher for the spent adsorbents containing As(III) than for those containing As(V) reported in a previous study [39]. Therefore, the risk of As leaching in soil was evaluated as being higher for the spent adsorbents containing As(III) than for those containing As(V). Although the ease of leaching As from the adsorbent differed depending on the combination of soil type and As valence, the spent MgO adsorbent had the lowest E_{AS} in all the combinations. Finally, regarding environmentally friendly and sustainable As-removal treatment, disposal, and management, we recommend the following: (i) selection of MgO as an adsorbent and (ii) oxidation treatment of As(III) to As(V) before the step of adsorbing As onto adsorbents.

The amount of As leached from the used adsorbent is expected to vary depending on the ratio of the spent adsorbent to both soil and liquid. Therefore, as a near future challenge, it will be important to conduct leaching tests with these mixing ratios as experimental parameters. Additionally, to estimate the long-term stability of spent adsorbents, it will be necessary to investigate how the valence and state (mineralogy) of As incorporated into spent adsorbents change in soil.

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References

1. The World Health Organization (WHO). *Guidelines for Drinking-Water Quality*, 4th ed.; WHO: Tarxien, Malta, 2011; Arsenic; pp. 315–318; ISBN 978-92-4-154815-1. Available online: https://apps.who.int/iris/bitstream/handle/10665/44584/9789241548151_eng.pdf (accessed on 21 February 2024).
2. van Geen, A.; Zheng, Y.; Cheng, Z.; Aziz, Z.; Horneman, A.; Dhar, R.K.; Mailloux, B.; Stute, M.; Weinman, B.; Goodbred, S.; et al. A transect of groundwater and sediment properties in Araihasar, Bangladesh: Further evidence of decoupling between As and Fe mobilization. *Chem. Geol.* **2006**, *228*, 85–96. [CrossRef]
3. 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]

4. 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](#)]
5. 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](#)] [[PubMed](#)]
6. 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](#)] [[PubMed](#)]
7. 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. Pollut.* **2018**, *242*, 307–319. [[CrossRef](#)] [[PubMed](#)]
8. 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](#)]
9. 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](#)]
10. 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](#)]
11. 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](#)]
12. 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](#)]
13. 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](#)]
14. 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. Pollut.* **2010**, *158*, 2648–2658. [[CrossRef](#)] [[PubMed](#)]
15. Stopelli, E.; Duyen, V.T.; Mai, T.T.; Trang, 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](#)]
16. 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](#)]
17. 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](#)]
18. 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](#)]
19. 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](#)]
20. 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](#)]
21. Aullón Alcaine, 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](#)]
22. 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](#)]
23. 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](#)]
24. Gómez-Hernández, A.; Rodríguez, R.; Lara Del Río, A.; Ruiz-Huerta, E.A.; Armienta, M.A.; Dávila-Harris, P.; Sen-Gupta, B.; Delgado-Rodríguez, O.; Del Angel Ríos, A.; Martínez-Villegas, N. Alluvial and gypsum karst geological transition favors spreading arsenic contamination in Matehuala, Mexico. *Sci. Total Environ.* **2020**, *707*, 135340. [[CrossRef](#)] [[PubMed](#)]
25. 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](#)]
26. Abiye, T.A.; Bhattacharya, P. Arsenic concentration in groundwater: Archetypal study from South Africa. *Groundw. Sustain. Dev.* **2019**, *9*, 100246. [[CrossRef](#)]
27. 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](#)] [[PubMed](#)]
28. Sarkar, A.; Paul, B. The global menace of arsenic and its conventional remediation—A critical review. *Chemosphere* **2016**, *158*, 37–49. [[CrossRef](#)]
29. 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](#)]

30. 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](#)]
31. Park, Y.Y.; Tran, T.; Lee, Y.H.; Nam, Y.I., 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](#)]
32. 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](#)]
33. Yu, X.Y.; Luo, T.; Jia, Y.; Zhang, Y.X.; Liu, J.H.; Huang, X.J. Porous hierarchically micro-/nanostructured MgO: Morphology control and their excellent performance in As(III) and As(V) removal. *J. Phys. Chem. C* **2011**, *115*, 22242–22250. [[CrossRef](#)]
34. 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](#)]
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](#)]
36. Montes-Hernandez, G.; Concha-Lozano, 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. Olyae, 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. Hu, 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.; Hara, J.; Zhang, M.; Kawabe, Y. Effects of silicic acid on leaching behavior of arsenic from spent calcium-based adsorbents with arsenite. *Sustainability* **2021**, *13*, 12937. [[CrossRef](#)]
41. Sugita, H.; Oguma, T.; Hara, J.; Zhang, M.; Kawabe, Y. Effects of silicic acid on leaching behavior of arsenic from spent magnesium-based adsorbents containing arsenite. *Sustainability* **2022**, *14*, 4236. [[CrossRef](#)]
42. The Chemical Society of Japan (CSJ). *Kagaku Binran (Handbook of Chemistry), Pure Chemistry II*, 4th ed.; Maruzen: Tokyo, Japan, 1993; p. 317.

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