

Investigation of As(III) Sorption by Sand and Alumina under Anoxic Conditions

Seungyeol Lee^{1,2}, Minji Park¹, and Hoon Young Jeong^{1,*}

¹Department of Geological Sciences, BK21 School of Earth and Environmental Systems, Pusan National University, Busan 46241, South Korea

²NASA Johnson Space Center & Lunar and Planetary Institute, Houston, TX 77058, United States of America

Abstract: Under anoxic conditions, this study investigated removal of dissolved As(III) by Si and Al oxides including natural sand, chemically washed sand (silica), alumina, and activated alumina. Despite the similar surface area, natural sand showed greater extents of As(III) sorption than chemically washed sand. This was likely due to the high reactivity of Fe(oxyhydr)oxide impurities on the surface of natural sand. For both sands, As(III) sorption was the greatest at pH 7.1, in agreement with the weakly dissociating tendency of arsenous acid. Also, the least sorption was observed at pH 9.6. At basic pH, elevated silicate, which originated from the dissolution of silica in sands, would compete with As(III) for sorption. Due to the highest surface area, activated alumina was found to quantitatively immobilize the initially added As(III) (6.0×10^{-7} – 2.0×10^{-5} M). Alumina showed As(III) sorption compared to or greater than chemically washed sand, although the former had less than 6% of the surface of area the latter. The greater reactivity of alumina than chemically washed sand can be explained by using the shared charge of oxygen.

Keywords: arsenite, sand, alumina, sorption isotherm, shared charge of oxygen

Introduction

Increasing arsenic contamination threatens human health (e.g., skin and lung cancers) and ecosystems (e.g., catastrophic changes in microbial communities) on both regional and global scales (Abdul et al., 2015; Chen et al., 2015; Smedley and Kinniburgh, 2002). For example, more than 70 million people are at risk from drinking arsenic-contaminated waters in Bangladesh and India (Ahmed et al., 2004; Bhattacharya et al., 2002). The mobility and toxicity of arsenic are controlled by the oxidation state and chemical form (Hao et al., 2018). Arsenite (As(III)) and arsenate (As(V)) are the two dominant oxidation states of arsenic in soil and aquatic systems (Tian et al., 2021). While As(III) is stable in anoxic groundwater and

sediments, As(V) is dominant in oxic environments (Ferguson and Gavis, 1972). Since As(III) is more mobile and toxic than As(V), it is challenging to immobilize As(III) under anoxic conditions (Yamauchi and Fowler, 1994).

To date, Fe sulfides including mackinawite (FeS) and pyrite (FeS₂) have been largely evaluated as adsorbents to immobilize As(III) under anoxic conditions (Farquhar et al., 2002; Han et al., 2011; Jeong et al., 2010; Xie et al., 2016). Although these reduced minerals are common in anoxic sediments (Burton et al., 2009), this is not always the case. Under sulfur-deficient anoxic conditions, although ferric (oxyhydr) oxides undergo reductive dissolution (Goldhaber and Kaplan, 1974), Fe sulfides is not saturated. In this scenario, Si and Al oxides may play a significant role in controlling the mobility of As(III) due to their common occurrence (Park et al., 2022). Nonetheless, only a limited studies have addressed As(III) sorption by these oxides (Ferguson and Anderson, 1973; Khan et al., 2021; Masue et al., 2007; Zhao et al., 2018). Even for them, anoxic conditions were not maintained, thus causing the experimental artifact that As(III) may

*Corresponding author: hjeong@pusan.ac.kr
Tel: +82-51-510-2249

be oxidized by reaction with the atmospheric oxygen (Jeong et al., 2010) or its adsorption is suppressed by competition with the carbonate species originating from the atmosphere (Brechtbuhl et al., 2012).

Taken together, this study aimed to investigate As(III) sorption by natural sand, chemically washed sand (silica), alumina, and activated alumina under anoxic conditions. Given the pH-dependent behavior, As(III) sorption was examined at pH 4.7(\pm 0.1), 7.1(\pm 0.1), and 9.6(\pm 0.1). This study allows one to compare the reactivity of the aforementioned adsorbents toward As(III) sorption on the basis of surface area and inherent reactivity. Also, it may help predict the environmental fate of As(III) under anoxic groundwater and sediments.

Materials and Methods

Preparation and characterization of adsorbents

Natural sand (Hama Industry, Korea), synthetic alumina (Al_2O_3 , Metal Chem. Tech., Korea), and activated alumina (Acros organics) were sieved to collect a size fraction of 106–150 μm . Subsequently, these particles were repeatedly rinsed with deionized water to remove water-soluble species. Since no intensive washing was performed, natural sand contained mineral impurities (e.g., Fe (oxyhydr)oxides) besides silica (Park et al., 2018). Thus, a portion of natural sand was also chemically washed by using a sequence of 1 M $\text{Na}_2\text{S}_2\text{O}_4$ solutions to remove Fe and Mn oxides, 12 M HCl solutions to dissolve other minerals such as carbonates and phosphates, and 10% H_2O_2 solutions to oxidize organic matter (Kunze and Dixon, 1986). By X-ray diffraction, the chemically washed sand was composed of quartz (α - SiO_2) (Park et al., 2018). As a result, four different adsorbents were used for As(III) sorption experiments. Prior to As(III) sorption experiments, these materials were allowed to sit for at least one day inside a glovebox (Coy Inc., Grass Lake, MI) with an atmospheric composition of \sim 5% H_2 in N_2 . The oxygen concentration inside the glove box was maintained below 1 ppm.

By N_2 gas adsorption on a specific surface area

analyzer (TriStar II 3020, Micromeritics Instrument Co.), the surface areas were measured for natural sand, chemically washed sand (silica), alumina, and activated alumina. Also, to observe the surface texture, the aforementioned materials were coated with Pt films after being placed on conductive carbon tapes. Then, they were analyzed by a scanning electron microscope (SEM, HITACHI 6853-H) at voltages of 5–15 kV in the Busan Center of Korea Basic Science Institute.

As(III) sorption experiments

If not otherwise specified, all experiments were performed inside the glovebox to maintain anoxic conditions. All solutions were prepared by using the deoxygenated water that had been purged with N_2 gas ($>$ 99.999%). As(III) sorption experiments were conducted by using 15 mL centrifuge tubes. One gram of adsorbents were weighed into the centrifuge tubes. Then, 2 mL of 0.5 M acetate, morpholinopropanesulfonate (MOPS), or N,N,N',N'-tetraethylethlenediamine (TEEN) buffer solutions were added to reach the target pH at 4.7(\pm 0.1), 7.1(\pm 0.1), and 9.6(\pm 0.1). These buffers were chosen based on their weak complexation with metal ions (Buerge and Hug, 1997; Yu et al., 1997) and redox inertness (Buerge and Hug, 1998; Kirsch et al., 1998). Subsequently, As(III) stock solutions, NaCl solutions, and deoxygenated water were added together to the tubes to obtain the solid-to-solution ratio at 0.1 g/mL, the initial As(III) concentration at 6.0×10^{-7} – 2.0×10^{-5} M, the buffer concentration at 0.1 M, and the ionic strength at 0.2 M. The resultant batches were agitated on a shaker at room temperature for three days, which was found to be sufficient to reach the equilibrium state (Wolthers et al., 2005). After the 3-day reaction period, aliquots of the suspensions were filtered with 0.2 μm nylon filters. After acidified with 5% HNO_3 solutions, the filtrates were analyzed for dissolved As(III) concentration on an inductively coupled plasma optical emission spectroscopy (ICP-OES; HORIBA Jobin Yvon ULTIMA 2C). The analytical errors associated with dissolved As(III) concentration were close to the detection limit (e.g., $\sim 2.5 \times 10^{-8}$ M).

Results and Discussion

Properties of adsorbents

By N₂ adsorption, the specific surface area was measured to be 1.13(±0.01) m²/g for natural sand, 0.952(±0.004) m²/g for chemically washed sand (silica), 0.057(±0.001) m²/g for alumina, and 158.9(±1.3) m²/g for activated alumina. Notably, chemically washed sand had a little lower surface area than natural sand. The lower surface area of the former would result from the removal of mineral impurities by intensive chemical washing. Also, the highest surface area of activated alumina would be contributed to by its rugged surfaces.

Figure 1 shows the SEM images of four adsorbents before they were reacted with dissolved As(III). The surface of natural sand is covered by small-sized

particles (e.g., 1–10 μm). On the other hand, chemically washed sand is free of such particles since these particles may have been removed from natural sand by chemical treatment (Park et al., 2022). Consistent with XRD analysis (Park et al., 2018), chemically washed sand exhibits the crystal habit of quartz. A marked difference is noted between alumina and activated alumina. While alumina is characterized by smooth surfaces, activated alumina has rough surfaces. This accounts for the significantly different surface areas between them.

As(III) sorption by natural sand and chemically washed sand

In Fig. 2, As(III) sorption isotherms, plots of solid-phase As(III) concentrations versus dissolved As(III) concentrations, are compared between natural sand

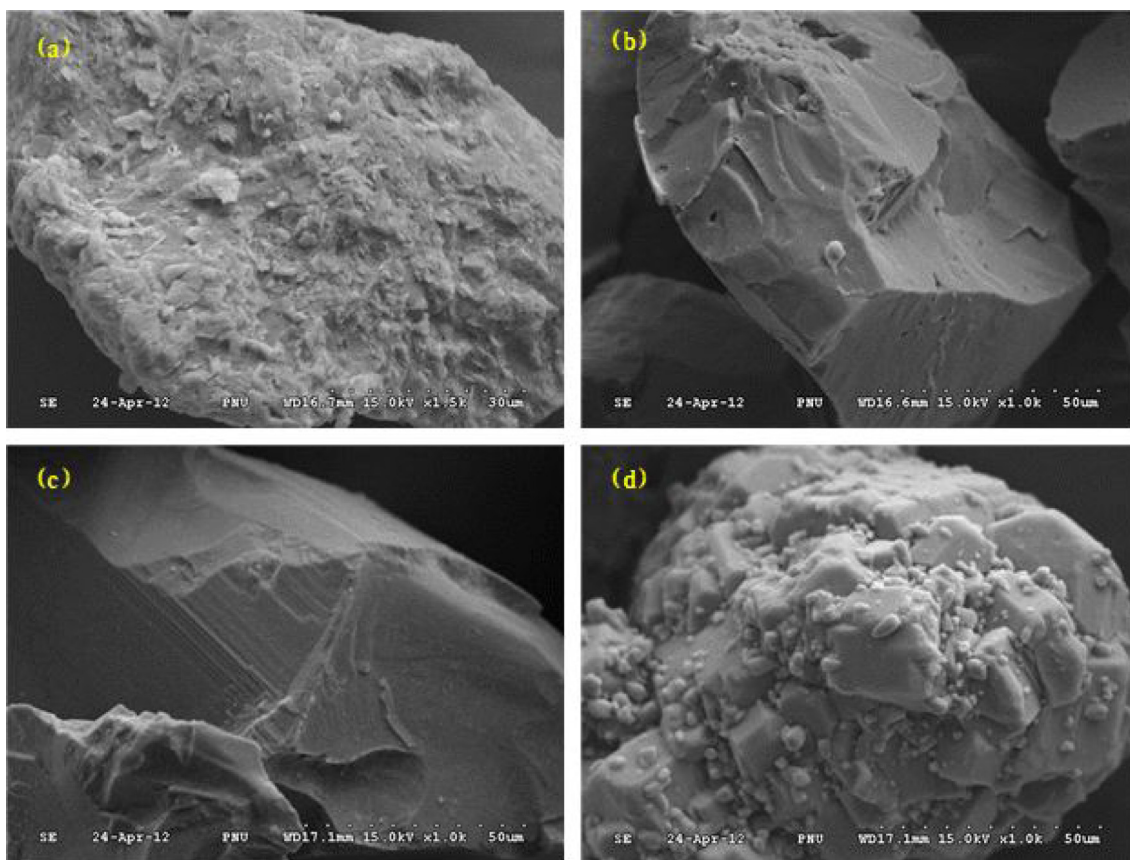


Fig. 1. Scanning electron microscope (SEM) images of unreacted adsorbents: natural sand (a), chemically washed sand (b), alumina (c), and activated alumina (d).

and chemically washed sand (silica). When interpreting sorption isotherms, it should be noted that the closer the data become to y-axis (i.e., the higher solid-phase concentrations become relative to dissolved concentrations), the greater sorption is expected. Regardless of pH, natural sand shows much greater As(III) sorption than chemically washed sand. This is rather surprising given the marginal difference in their surface areas ($1.13(\pm 0.01) \text{ m}^2/\text{g}$ for natural sand versus $0.952(\pm 0.004) \text{ m}^2/\text{g}$ for chemically washed sand). By acid extraction, the natural sand examined here was found to contain a significant amount of Fe, with magnetite (Fe_3O_4) accounting for $\sim 30\%$ of the total Fe (Park et al., 2018). Often, the sorption reactivity of minerals can be evaluated by using the shared charge of oxygen, the ratio of metal valence to coordination number; the lower shared charge a mineral has, the more strongly

it adsorbs (McBride, 1994). The shared charge of oxygen is $+4/4$ for silica, $+3/6$ for ferric (oxyhydr)oxides, and $+2/6$ for ferrous (hydr)oxides (McBride, 1994). This suggests that Fe-bearing minerals can adsorb As(III) more strongly than silica. Consequently, the Fe mineral impurities on the surface of natural sand should have provided the enhanced As(III) sorption capacity. Similar results have been reported for As(III) sorption by Fe oxide-coated sand (Lombi et al., 1999) and Cr(VI) sorption by natural sand (Park et al., 2018).

For natural sand, the extent of As(III) sorption increases in the order of $\text{pH } 9.6 < \text{pH } 4.7 < \text{pH } 7.1$. Similarly, chemically washed sand exhibits the greatest sorption at pH 7.1. Since arsenous acid (H_3AsO_3) is a weak acid, its anionic forms (H_2AsO_3^- and HAsO_3^{2-}), which are more strongly adsorbed than the undis-

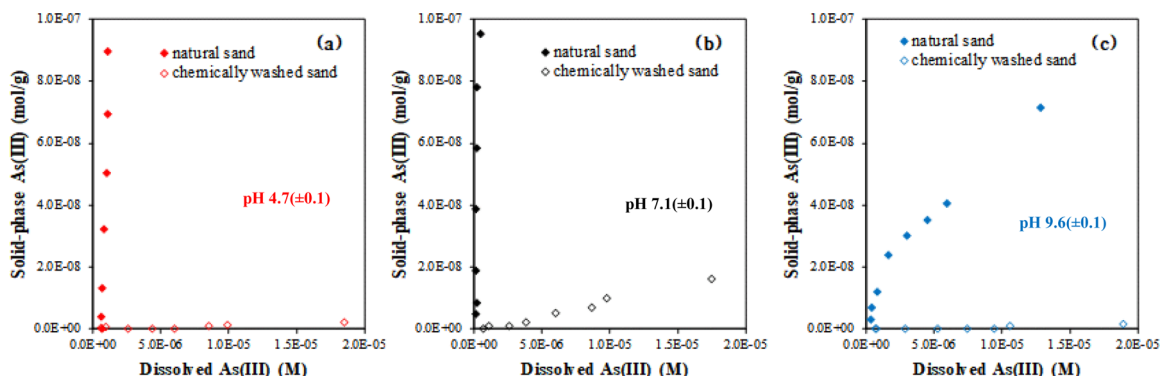


Fig. 2. As(III) sorption isotherms by natural sand and chemically washed sand at pH $4.7(\pm 0.1)$ (a), $7.1(\pm 0.1)$ (b), and $9.6(\pm 0.1)$ (c).

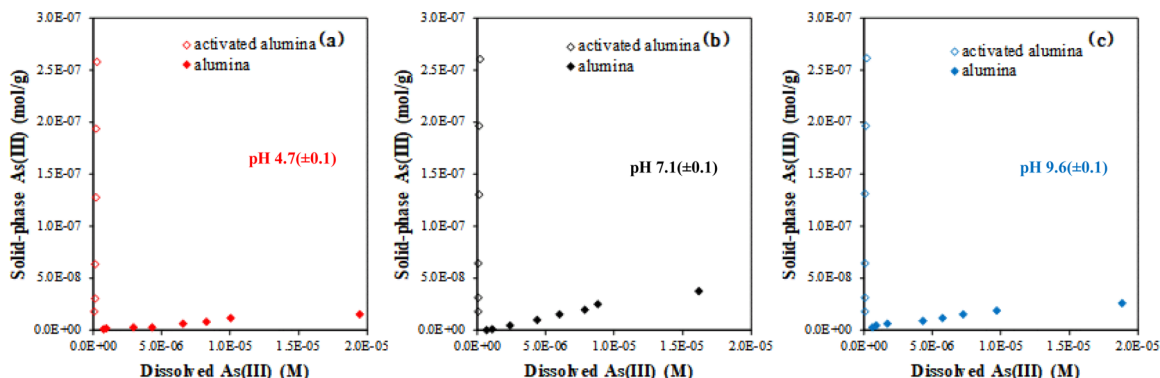


Fig. 3. As(III) sorption isotherms by alumina and activated alumina at pH $4.7(\pm 0.1)$ (a), $7.1(\pm 0.1)$ (b), and $9.6(\pm 0.1)$ (c).

sociated, acidic form, are not significant until neutral pH (Gong et al., 2002). However, as pH increases, the mineral surfaces become negatively charged such as to be less effective for adsorbing anions (McBride, 1994). Due to these opposing effects, the optimal adsorption of As(III) is generally encountered at circumneutral pH (Wei et al., 2016). On the other hand, the adsorption of arsenate, a conjugated base of a stronger acid (H_3AsO_4), occurs at acidic pH (Wei et al., 2016).

As(III) sorption by alumina and activated alumina

In Fig. 3, As(III) sorption isotherms are compared between alumina and activated alumina. Due to the extremely high surface area ($158.9(\pm 1.3) \text{ m}^2/\text{g}$), activated alumina can quantitatively immobilize the initial added As(III) under all pH conditions. On the other hand, alumina shows a limited As(III) sorption capacity. Similar to natural sand and chemically washed sand, alumina has the greatest As(III) sorption at pH 7.1. Nonetheless, As(III) sorption by alumina is greater at pH 9.6 than pH 4.7, in contrast to the cases by natural sand and chemically washed sand. Previously, silicate was shown to inhibit As(III) sorption and promote its desorption (Luxton et al., 2008). Since silica becomes highly soluble at basic pH (Wilhelm and Kind, 2015), the lowest As(III) sorption at pH 9.6 by both sand adsorbents may have resulted from the increased dissolved silicates (e.g., $\text{Si}(\text{OH})_4^0$, $\text{SiO}(\text{OH})_3^-$, $\text{SiO}_2(\text{OH})_2^{2-}$, etc) under such a pH condition.

Considering that the scale of y-axis in Fig. 3 is three time larger than that in Fig. 2, As(III) sorption by alumina is comparable to or greater than that by chemically washed sand. This is interesting because the former possessed less than 6% of the surface area of the latter. Since the shared change of oxygen is +3/6 for alumina and +4/4 for silica, the surface of alumina is expected to be more reactive than that of silica (McBride, 1994). As discussed above, the dissolved silicate produced via dissolution of silica may also have competed As(III) for adsorption (Luxton et al., 2008).

Conclusions

Under anoxic conditions, As(III) sorption capacity was compared among natural sand, chemically washed sand, alumina, and activated alumina. The sorption capacity of adsorbents was found to be mainly determined by both surface area and inherent reactivity. Compared to chemically washed sand (silica), natural sand showed the greater sorption capacity due to the presence of Fe-bearing impurities, which provided a stronger affinity for As(III) than silica. Also, the greater sorption by alumina than chemically washed sand was in line with the stronger affinity of the former for As(III). In this study, the shared charge of oxygen was demonstrated to be a useful parameter in estimating the inherent reactivity of (oxyhydr)oxide phases. Besides, the greatest sorption capacity by activated alumina resulted from the highest surface area. This study suggests that the mobility of As(III) under anoxic conditions can be effectively reduced in highly weathered regions enriched with SiO_2 and Al_2O_3 .

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