

Residence time effects on arsenate sorption on an allophanic Andosol

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Abstract

The mobility and bioavailability of As in agricultural soils are controlled by sorption onto minerals. The effect of the residence time on the reaction between arsenate and allophanic Andosol, a typical agricultural soil in Japan, remains unclear. Therefore, we investigated the reaction between arsenate and allophanic Andosol and its components allophane and ferrihydrite over several months, based on the desorption experiment and X-ray diffraction (XRD) measurements in the long-term sorption experiment. The reaction between arsenate and three sorbents continued for approximately 150 d. The XRD patterns of allophane and ferrihydrite that reacted with arsenate did not change during the long-term sorption experiments under near-neutral pH conditions, suggesting negligible formation of surface precipitation. Furthermore, the irreversibility of arsenate sorption onto allophanic Andosol

and allophane increased with extended residence time. These results suggested that the slow sorption of arsenate onto the materials could be ascribed to internal diffusion.

Keywords: Arsenic, Allophane, Ferrihydrite, Sorption kinetics, Internal diffusion

1. Introduction

Arsenic (As) is a ubiquitous and harmful element in the environment. Continuous intake of As through contaminated food and drinking water could cause chronic poisoning and cancer (Mandal and Suzuki, 2002; Sarkar and Paul, 2016). Arsenic contamination of irrigation water and agricultural soils remains a serious global problem. High levels of As contamination are frequently observed in Himalayan catchments [e.g., Bangladesh, Cambodia, China, Nepal, Vietnam, and West Bengal (India)] (Shaji et al., 2021; Smedley and Kinniburgh, 2002). In Bangladesh, irrigation using As-contaminated groundwater caused soil contamination (Dittmar et al., 2007; Saha and Ali., 2007). Arsenic contamination is also found in the Circum-Pacific region (e.g., Chile, Japan, New Zealand, the United States, and Taiwan) (Shaji et al., 2021; Smedley and Kinniburgh, 2002). In such volcanic regions, As contamination of irrigation water could occur accidentally because of volcanic eruptions (Hama et al., 2023).

The sorption controls the mobility and bioavailability of As in agricultural soils. Allophanic Andosol, which covers a wide range of agricultural lands in volcanic regions, has high sorption capacity for arsenate (Sato et al., 2023) because it is rich in short-range order

minerals such as allophane and ferrihydrite (Parfitt, 2009; Takahashi, 2020; Takahashi and Dahlgren, 2016). Arsenate forms inner-sphere complexes on minerals (Ladeira et al., 2001; Sherman and Randall, 2003). Generally, arsenate sorption is affected by soil pH, soil organic matter, and competitive ions such as phosphate (Sato et al., 2023; Violante and Pigna, 2002; Weng, van Riemsdijk, and Hiemstra, 2009). Furthermore, residence time (reaction time) is an important factor because arsenate sorption is a time-dependent phenomenon. Arsenate sorption is characterized by a rapid reaction, followed by a slow reaction (Arai, Sparks, and Davis, 2005; Arai and Sparks, 2002; O'Reilly, Strawn, and Sparks, 2001). The longer the residence time, the more arsenate would be sorbed onto the soil. Three main mechanisms control the sorption kinetics, namely (i) film diffusion between the bulk solution and the solid surface, (ii) internal diffusion into the particle, and (iii) adsorption–desorption equilibrium (Landrot and Sparks, 2023; Wang and Guo, 2020; Willett, Chartres, and Nguyen, 1988). Internal diffusion particularly contributes to the irreversibility of arsenate sorption (Landrot and Sparks, 2023; Barrow, 1983). As arsenate is believed to remain for a long time in the field, the effect of residence time on arsenate sorption should be considered in risk assessments of arsenate contamination in agriculture. However, to our knowledge, no studies have evaluated the residence time effects on arsenate sorption onto allophanic Andosol or allophane.

Therefore, the objective of this study is to evaluate the effect of residence time on the sorption of arsenate onto allophanic Andosol. Long-term sorption and desorption experiments were conducted using allophanic Andosol. The same experiments were

conducted using synthesized allophane and ferrihydrite, the most important sorbents in allophanic Andosol.

2. Materials and Methods

2.1. Soil sample properties

Soil sample was collected from the surface layer (0–15 cm) of the experimental field of the Kyushu-Okinawa Agricultural Research Center, National Agriculture and Food Research Organization, in Miyazaki Prefecture, Japan (N31°45'18", E131°01'02"). This soil sample was classified as an allophanic Andosol (Matsuyama et al., 2005). The soil sample was air-dried, ground, and sieved through a 2-mm mesh. Soil pH (pH_{H₂O}) was determined using a pH meter with a soil/solution ratio of 1:2.5. The amounts of acid-oxalate-extractable Al (Al_{ox}), Fe (Fe_{ox}), Si (Si_{ox}), citrate-dithionite-extractable Fe (Fe_{cd}), and pyrophosphate-extractable Al (Al_p) and Fe (Fe_p) were determined using a method described by Blakemore, Searle, and Daly (1981). The method is explained in detail in a previous study (Sato et al., 2023). The values of Al_{ox}, Fe_{ox}, and Si_{ox} represent the fractions of poorly crystalline and non-crystalline minerals; Fe_{cd} represents the fractions of iron oxides; and Al_p and Fe_p represent the fractions of Al/Fe-humus complexes. The soil properties are summarized in Table 1 (Sato et al., 2023). The low values of Al_p/Al_{ox} (0.13) and Fe_p/Fe_{ox} (0.12) suggests that the content of Al/Fe-humus complexes was much less than those of allophane and ferrihydrite. In other words, allophane and ferrihydrite can be the most important minerals acting as sorbent for arsenate in the soil sample.

2.2. Allophane and ferrihydrite synthesis

Allophane and ferrihydrite were synthesized following the methods of Ohashi et al. (2002) and Schwertmann and Cornell (2000), respectively. Both samples were freeze-dried and finely ground, followed by X-ray diffraction (XRD) measurements (Ultima IV, Rigaku Co., Ltd., Japan). The XRD patterns were characteristic of allophane and ferrihydrite (Fig. 1) (Ohashi et al., 2002; Schwertmann and Cornell, 2000). Ferrihydrite is usually named according to the number of its XRD peaks. The XRD patterns showed two peaks, suggesting two-line ferrihydrite was synthesized.

2.3. Residence time effects on arsenate sorption

The soil sample (0.8 g) was mixed with 40 mL of 0.1 mol L⁻¹ NaNO₃ solution in a 50 mL polyethylene tube. The synthesized allophane and ferrihydrite (2 g) was mixed with 1000 mL of 0.1 mol L⁻¹ NaNO₃ solution in 1000 mL glass bottle. Suspensions of allophanic Andosol (20 g L⁻¹), allophane (2 g L⁻¹), and ferrihydrite (2 g L⁻¹) were pre-equilibrated at pH 6.7, before arsenate solutions were added. To achieve an initial arsenate concentration of 2 mmol L⁻¹, 400 mmol L⁻¹ Na₂HAsO₄ · 7H₂O solution was added to the suspensions. After adding arsenate, the suspension pH was adjusted manually to 6.7 ± 0.2 daily for up to 1 week. Thereafter, the pH of the suspension was periodically adjusted to pH 6.7 ± 0.2. The suspensions were shaken for 4–237 d. These kinetic experiments for arsenate sorption were conducted at 25 °C. After shaking, suspensions of allophane and ferrihydrite (40 mL) were collected from the glass bottle. The suspensions of allophanic Andosol, allophane, and ferrihydrite were centrifuged to separate the supernatant from the residual solids. The

supernatant solution was filtered through a 0.22- μm filter. The Eh value of the solutions was measured, confirming that the experiments were conducted under oxic conditions (approximately 450 mV). Therefore, it was assumed that the reductive transformation of arsenate into arsenite was negligible. The final As concentration in the solution was measured by Inductively Coupled Plasma Optical emission spectroscopy (ICP-OES; ICPE-9000, Shimadzu Corporation, Japan). The amounts of As sorbed onto allophanic Andosol, allophane, and ferrihydrite were calculated from the differences between the concentrations in the initial and final solutions. The wet pastes (i.e., the residual solid after centrifugation) of the allophane and ferrihydrite were washed with distilled water, followed by air-drying at 25 °C. Air-dried allophane and ferrihydrite were ground finely, after which XRD measurements were conducted.

Furthermore, wet pastes of allophanic Andosol and allophane were used for subsequent desorption experiments. However, a desorption experiment was not conducted for ferrihydrite because the residual ferrihydrite solid was unstable, even after centrifugation. The irreversibility of arsenate sorbed onto allophanic Andosol and allophane was investigated using the replenishment method described by Arai and Sparks (2002), with arsenate desorbed by repeatedly adding the solution. In the current study, the desorption procedure was repeated thirteen times—one with NaNO_3 and twelve with phosphate. A solution (40 mL) of 0.1 mol L^{-1} NaNO_3 was added to the wet paste after the kinetic experiments. The suspensions were shaken for 1.5 h under adjusted pH (6.7 ± 0.2) and constant temperature (25 °C). The solution containing the desorbed As and the solid still containing the sorbed As were separated by centrifugation. The amount of As first desorbed

with the NaNO_3 solution was estimated from the As concentration in the solution, which was measured by ICP-OES. Subsequently, a solution (40 mL) of 2 mmol L^{-1} phosphate with 0.1 mol L^{-1} NaNO_3 was added to the residual solid. The suspensions were shaken for 24 h under identical conditions. The desorption of As by the phosphate solution was repeated 12 times. The amount of As desorbed from the phosphate solution was estimated in the same manner as that for the first desorption. All experiments were performed in singlicate.

3. Results and Discussion

3.1. Sorption kinetics of arsenate

The sorption kinetics of arsenate on allophanic Andosol, allophane, and ferrihydrite are shown in Fig. 2. Rapid reactions were observed in the arsenate sorption onto allophanic Andosol, allophane, and ferrihydrite. The amount of arsenate sorbed onto allophanic Andosol was 52.4 mmol kg^{-1} within 4 d, corresponding to 70% of the sorbed arsenate within 149 d. Similarly, compared with arsenate sorption within 150 d, 62% (293 mmol kg^{-1}) and 86% (824 mmol kg^{-1}) of arsenate were sorbed onto allophane and ferrihydrite within 4 d, respectively. Slow sorption followed rapid sorption. The sorption of arsenate onto allophanic Andosol, allophane, and ferrihydrite continued for approximately 150 d. Slow sorption of arsenate was observed in other minerals such as and aluminum oxide and goethite (Arai and Sparks, 2002; O'Reilly, Strawn, and Sparks, 2001). However, the sorption in our study was more slowly than previously reported. Arai, Sparks, and Davis (2005) reported that arsenate completely sorbed onto allophane within 30 d when allophane was prepared without freeze-drying. The difference from previous studies may be due to aggregation of the minerals because allophane

and ferrihydrite can aggregate irreversibly in freeze-drying procedure (Karube, 2004; Scheinost et al., 2001). Scheinost et al. (2001) reported that the sorption of Pb onto ferrihydrite was slowed down by the drying procedure. In addition, Barrow (1983) revealed that slow sorption of phosphate was caused by intra-particle diffusion. Therefore, the slow sorption of arsenate can be due to internal diffusion into on the aggregated minerals. Furthermore, the slow sorption of arsenate on allophanic Andosols can be ascribed to internal diffusion because allophanic Andosols contain submicron-scale aggregates (Asano and Wagai, 2014).

3.2. XRD pattern change in sorption kinetics

3.2.1. Allophane

Surface precipitation can lead to slow sorption of arsenate on solids (Jia et al. 2006; Jiang et al., 2015). However, the XRD patterns of allophane reacting with arsenate (Fig. 1a) did not show peaks at $2\theta = 26^\circ$ or 28.8° , which are typical for poorly crystalline AlAsO_4 (Haraguchi et al., 2013; Pantuzzo, Santos, and Ciminelli, 2014). This finding suggested that surface precipitation had hardly formed with the increased residence time in our experimental conditions, i.e., lower molar ratio of As to Al ($\text{As/Al} = 0.13$) and near-neutral pH ($\text{pH} = 6.7$). Similar results have been reported previously (Arai, Sparks, and Davis, 2005; Haraguchi et al., 2013). Haraguchi et al. (2013) reported that surface precipitation was not detected by XRD, although poorly crystalline Al hydroxides had reacted with higher concentrations of arsenate ($\text{As/Al} = 5.0$). Using extended X-ray absorption fine structure (EXAFS) analysis, Arai, Sparks, and Davis (2005) revealed that the mechanism of arsenate adsorption on

allophane remained unchanged for 11 months without surface precipitation. We also confirmed that no significant change was observed by solid-state ^{31}P NMR in the molecular environment of sorbed phosphate (an analog of arsenate) on allophane for 237 d (Sato et al., forthcoming).

3.2.2. Ferrihydrite

The XRD patterns indicating ferrihydrite reaction with arsenate (Fig.1b) did not show peaks at $2\theta = 28^\circ$ and 58° , which are typical for poorly crystalline FeAsO_4 (Jia et al., 2006), suggesting that surface precipitation was hardly formed with increased residence time. Using EXAFS analysis, O'Reilly, Strawn, and Sparks (2001) showed that the molecular environment of arsenate sorbed onto goethite does not change with increased residence time. In contrast, Jia et al. (2006) reported that significant amounts of surface precipitation of FeAsO_4 occurred when arsenate was sorbed onto ferrihydrite with a higher molar ratio of As to Fe ($\text{As/Fe} > 0.125$) under acidic conditions. The difference in the results was ascribed to the difference in experimental conditions, as our experiments were conducted under mild conditions, namely lower As loading ($\text{As/Fe} = 0.093$) and near-neutral pH ($\text{pH} = 6.7$). The Fe^{3+} released from ferrihydrite was not sufficient to form surface precipitation (Ler and Stanforth, 2003; Jiang et al., 2015). However, we should pay attention that XRD cannot detect low concentrations of surface precipitates (Li et al., 2013).

3.3. Irreversibility of arsenate sorption onto allophanic Andosol and allophane

The desorption ratios of arsenate sorbed on allophanic Andosol and allophane are shown in Fig. 3. The desorption ratio decreases with increased residence time. The desorption ratio in the allophanic Andosol system decreased from 71% (residence time = 6 d) to 59% (149 d), whereas that in the allophane system decreased from 77% (6 d) to 61% (149 d). These results indicated that the irreversibility of arsenate sorption on allophanic Andosol and allophane was enhanced by extending the residence time. The effect of residence time on the irreversibility of arsenate sorption was also observed in $\gamma\text{-Al}_2\text{O}_3$ (Arai and Sparks, 2002), clay minerals (Lin and Puls, 2000), or soils (Lombi, Wenzel, and Sletten, 1999). Physical stabilization by internal diffusion (Markis et al., 2004) and chemical stabilization by surface precipitation (Arai and Sparks, 2002; Opiso, Sato, and Yoneda, 2009) play important roles in the effect of residence time. Our results indicated that the irreversibility of arsenate sorption could be ascribed mainly to physical stabilization with the time-dependent diffusion of arsenate into the aggregates of allophanic Andosol and allophane.

4. Conclusion

Arsenate sorption onto allophanic Andosol, synthesized allophane, and ferrihydrite continued for approximately 150 d. The sorption–desorption hysteresis of the sorbed arsenate increased with prolonged residence time. Because no significant change was observed in the XRD pattern during sorption kinetics, it could be concluded that the internal diffusion of arsenate into the aggregated material is a key factor in the irreversibility of arsenate sorption.

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Figure and Table captions

Table 1. Soil sample properties of allophanic Andosol.

Figure 1. XRD patterns of (a) allophane and (b) two-line ferrihydrite unreacted (0 d) and reacted with arsenate. Samples were prepared at pH 6.7 with initial arsenate concentration of 2 mmol L⁻¹ for the indicated time. The suspension density is 2 g L⁻¹.

Figure 2. Arsenate sorption kinetics of (a) allophanic Andosol, (b) allophane, and (c) ferrihydrite. Suspension density is 2 g L⁻¹ for allophane and ferrihydrite and 20 g L⁻¹ for allophanic Andosol. The initial arsenate concentration was 2 mmol L⁻¹ at pH 6.7.

Figure 3. Effects of residence time on the ratio of total desorbable arsenate to sorption arsenate from (a) allophanic Andosol and (b) allophane against 2 mmol L⁻¹ phosphate. Before the desorption experiment for arsenate-reacted allophanic Andosol and allophane, samples were prepared under the following reaction conditions: pH 6.7, suspension density = 20 g L⁻¹ for allophanic Andosol and = 2 g L⁻¹ for allophane, initial arsenate concentration = 2 mmol L⁻¹, and residence time = indicated time.

Table 1. Soil sample properties of allophanic Andosol.

Soil	pH (H ₂ O)	OM [†]	Al _{ox}	Fe _{ox}	Si _{ox}	Fe _{ed}	Al _p	Fe _p
		g kg ⁻¹			mmol kg ⁻¹			
Allophanic Andosol	5.41	38.6	1135	192	371	191	153	23

[†]Soil Organic matter.

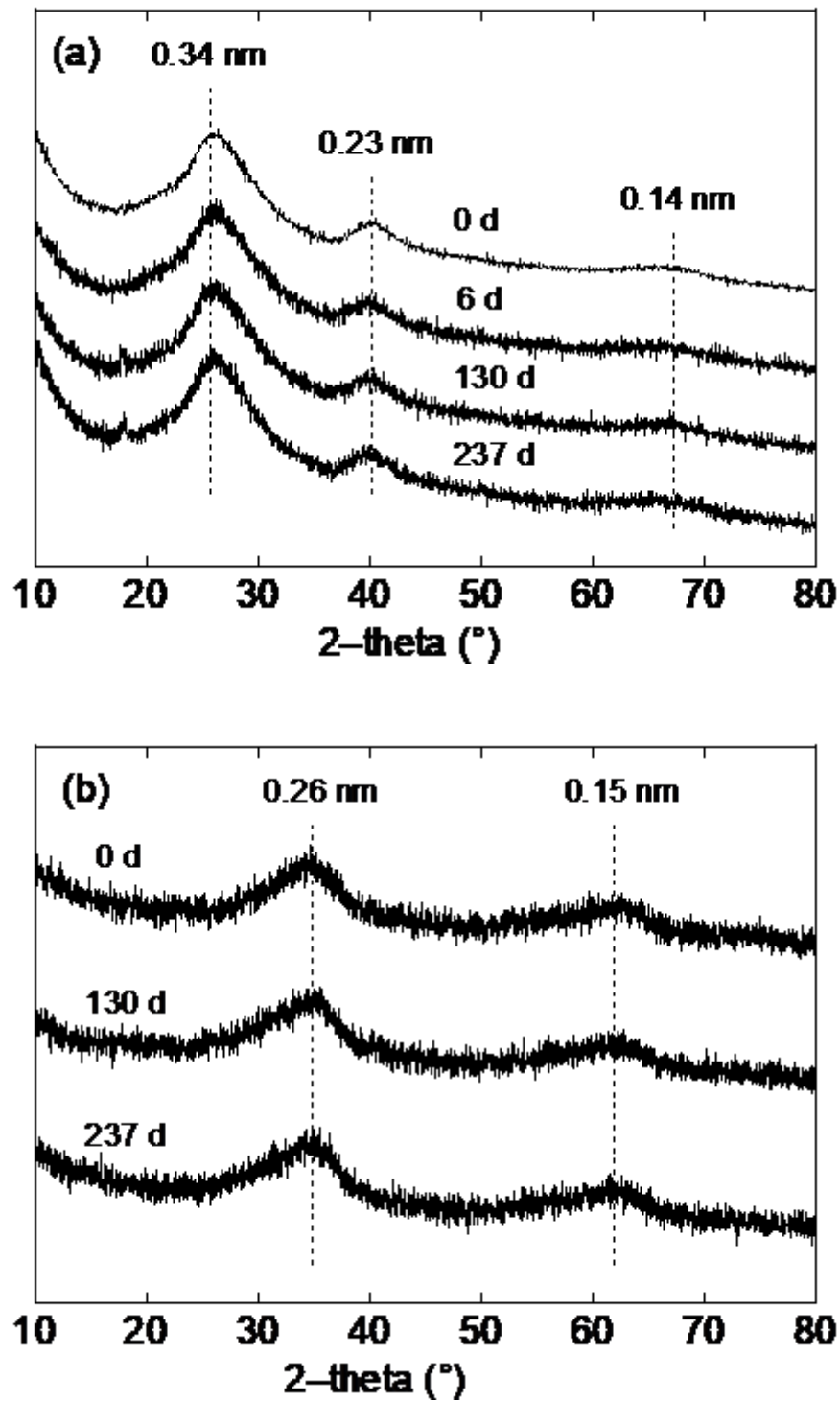


Figure 1. XRD patterns of (a) allophane and (b) two-line ferrihydrite unreacted (0 d) and reacted with arsenate. Samples were prepared at pH 6.7 with initial arsenate concentration of 2 mmol L^{-1} for the indicated time. The suspension density is 2 g L^{-1} .

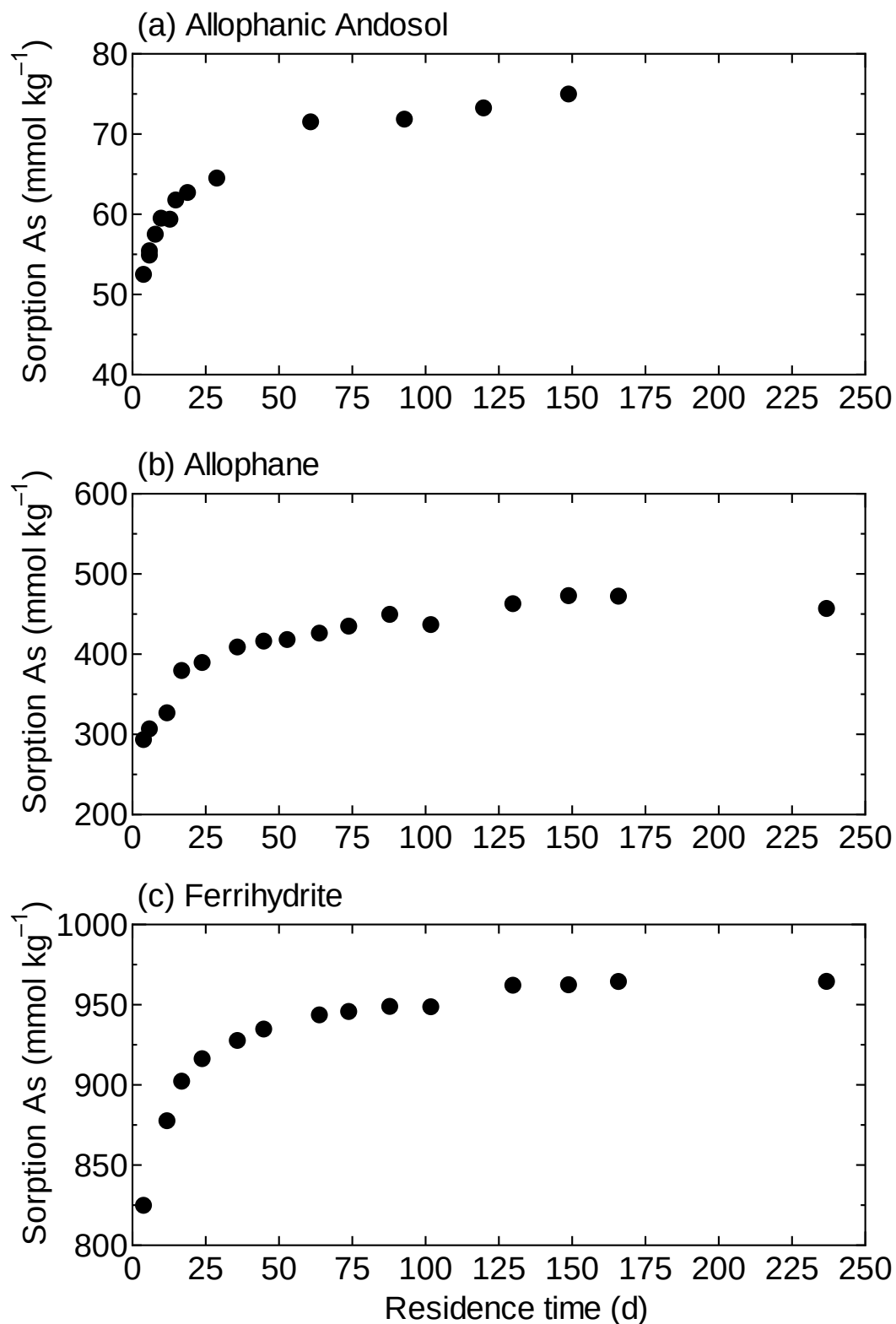


Figure 2. Arsenate sorption kinetics of (a) allophanic Andosol, (b) allophane, and (c) ferrihydrite. Suspension density is 2 g L⁻¹ for allophane and ferrihydrite and 20 g L⁻¹ for allophanic Andosol. The initial arsenate concentration was 2 mmol L⁻¹ at pH 6.7.

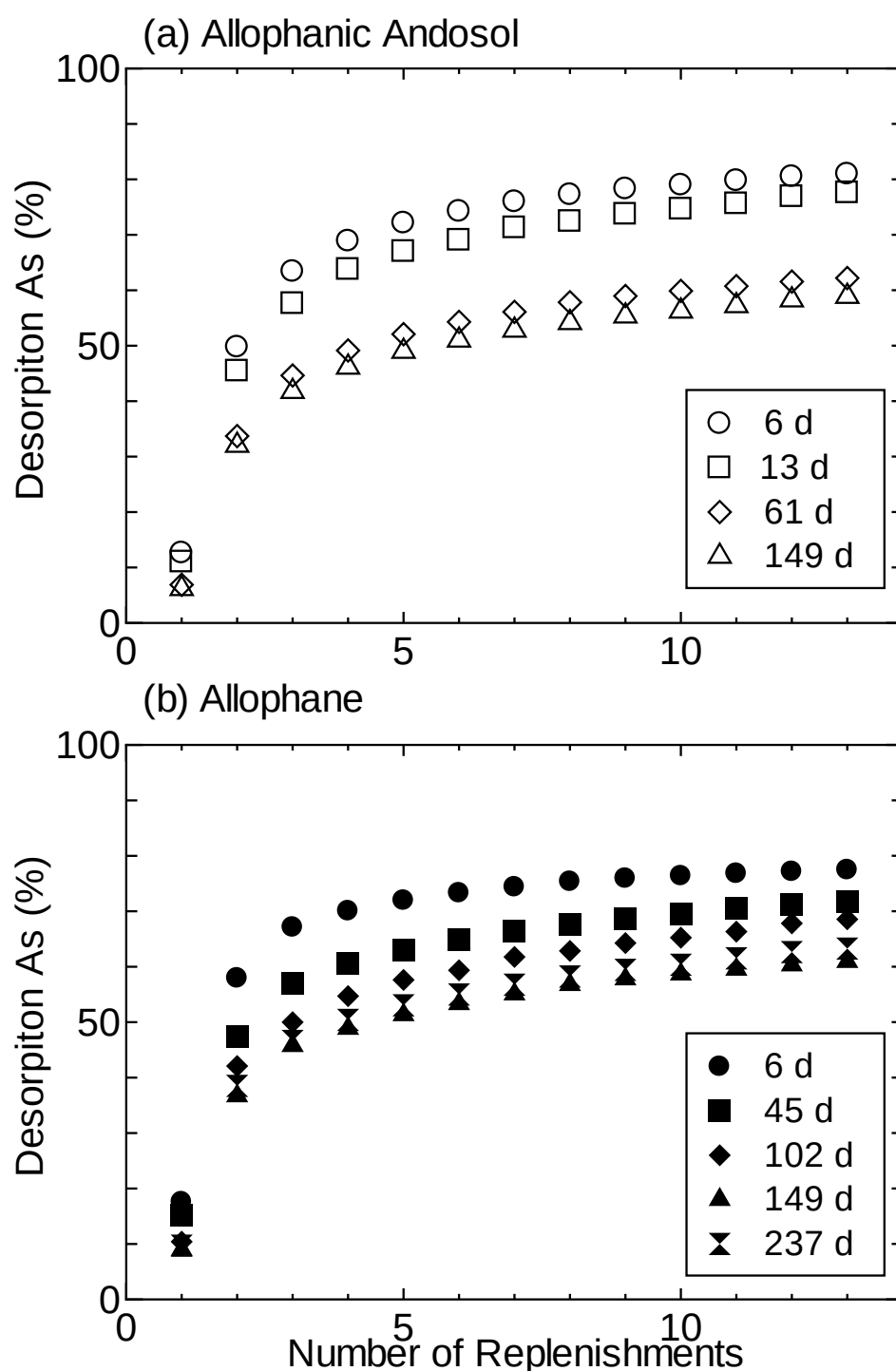


Figure 3. Effects of residence time on the ratio of total desorbable arsenate to sorption arsenate from (a) allophanic Andosol and (b) allophane against 2 mmol L^{-1} phosphate. Before the desorption experiment for arsenate-reacted allophanic Andosol and allophane, samples were prepared under the following reaction conditions: pH 6.7, suspension density = 20 g L^{-1} for allophanic Andosol and = 2 g L^{-1} for allophane, initial arsenate concentration = 2 mmol L^{-1} , and residence time = indicated time.