Competitive Adsorption of Oxalate and Phosphate on Allophane at Low Concentration

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COMPETITIVE ADSORPTION OF OXALATE AND PHOSPHATE ON ALLOPHANE AT LOW CONCENTRATION

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ABSTRACT

The adsorption of an anion such as oxalate and phosphate at low concentration by soils is important because their contents in the soils are usually low. The adsorption of oxalate and phosphate on allophane at initial concentrations up to 200 μM showed that the amount of adsorption of phosphate was higher than that of oxalate, while the adsorption energy of oxalate estimated by the Freundlich parameter n was higher than that of phosphate. The high adsorption energy for oxalate was also suggested by molecular orbital calculations, where changes in the total energy of the adsorption reactions of oxalate were compared with that of phosphate. The amount of adsorption of oxalate or phosphate increased with raising the concentration of the background electrolyte (i.e. NaCl). This was ascribed to development of anion exchange site on allophane under the high concentration of NaCl. The amount of adsorption of oxalate coexisting with 200 μM of phosphate decreased as compared to that of oxalate alone. However, the adsorption strength of oxalate estimated by the Langmuir K and Freundlich n parameters was enhanced by the coexisting phosphate. For the adsorption of phosphate in coexisting oxalate, oxalate also had the effect on the adsorption strength of phosphate. Especially for the adsorption of oxalate, it was clearly observed that the amounts of Si and Al released from allophane with the adsorption abruptly increased at the equilibrium oxalate concentration of about 100 μM. This means that, at the equilibrium concentration, the adsorption schema of oxalate changed from the ligand exchange reaction between hydroxyl group and oxalate to the replacement reaction of silicate with oxalate. The critical equilibrium concentration shifted to about 70 μM with the addition of 200 μM phosphate. This indicates that the coexisting phosphate also consumed hydroxyls (Al–OH) leading oxalate to begin replacement with silicate at lower equilibrium concentration. It is concluded that, at low concentration, coexisting phosphate affect not only amount and strength but also mechanism of the adsorption of oxalate, and vice versa.

Key words: allophane, oxalate, phosphate, competitive adsorption, low concentration

INTRODUCTION

Phosphate is an essential nutrient element for plant growth and has great importance from agronomic and environmental aspects; adsorption of phosphate by soils and soil constituents has been the subject of extensive reviews (Parfitt, 1978; Guppy et al., 2005). This anion is easily adsorbed on allophonic soils (Pardo and Guadalix, 1990; Beck et al., 1999) and very strongly adsorbed on the natural nano-ball allophane (Johan et al., 1997). Phosphorus is less abundant in soils than nitrogen and potassium, and total phosphorus in surface soils varies from 1.6 to 48.3 mmol kg⁻¹, and total P content in a soil has little or no relation to the availability of phosphorus to plants (Brady and Weil, 2002).

Low-molecular-weight organic acids such as formic, acetic, oxalic, citric and malic acids are often produced in soils from the decomposition of organic matter, root exudates, and microbial metabolites (Fox and Comerford, 1990; Xu et al., 2003). Among many biomolecules recognized in soils, oxalate plays an important role in many ecosystems, in both well-drained and poorly drained soils (Vedy and Bruckert, 1982). For many organisms, oxalate is a metabolic end product (Cromack et al., 1979). Organic acids have capacity to complex metals in solution, and the degree of complexation depends on: (a) number and proximity of carboxyl and hydroxyl groups of the organic acid, (b) concentration of the organic acid, (c) type of the surface sites, and (d) pH and ionic strength of the soil solution. Oxalate anion is known to easily adsorb on the natural nanoball allophane (Hanudin et al., 1999).

Allophane is a main component of volcanic ash soils and podzols, and a series name of naturally occurring hydrous aluminum silicate with various chemical compositions (Wada and Harward, 1974). Previously, the aluminum silicate had not been believed to have definite morphology and structure.
However, Kitagawa (1971) and Henmi and Wada (1976) found that allophane, at least separated from volcanic ash soils and weathered pumice grains, had definite hollow spherical morphology (nano-ball with external diameter between 3.5 and 5.0 nm). The chemical composition varies from 0.5 to 1.0 with respect to Si/Al atomic ratio. The wall structure of the nano-ball allophane has been proposed as aluminum-nesosilicate structure composed of the curved gibbsite sheet with monomeric SiO$_4$ tetrahedra attached to it.

To investigate the competitive adsorption of oxalate and phosphate on soil components is important to understand the behavior of the biomolecules in soil environments and their availability for plants. The study on the competitive adsorption between phosphate and organic ligands has received attention from many researchers. For example, the competitive adsorption was investigated onto a tropical soil (Lopez-Hernandez et al., 1986), synthetic clay minerals and oxides (Violante and Gianfreda, 1993, 1995), spodosols (Bhatti et al., 1998), and acid soil (Hu et al., 2001). Jara et al. (2006) studied the competitive adsorption of phosphate with oxalate on the synthetic and natural allophanic soil (allophanic material content of 42%). A review (Guppy et al., 2005) on the competitive adsorption between phosphate and the low-molecular-weight organic acids in soils showed that the previous studies were usually carried out at high initial concentrations (1–100 mM), and the resultant amounts of adsorption were much higher than those found in soils. Therefore, objective of this study was to investigate adsorption and competitive adsorption of oxalate and phosphate on the nano-ball allophane at lower initial concentrations than 1 mM. Because the adsorption experiments are conducted under such low oxalate and phosphate concentrations, the effect of NaCl concentration as a background electrolyte on the adsorption was also examined. Analysis of the adsorption mechanism was carried out by using the recent information about detailed morphology and chemical structure of the wall of the aluminum silicate (Abidin et al., 2007). Figure 1a shows whole structure of the allophane unit particle, and Fig. 1b represents the schematic arrangement of atoms at the pore region of the particle, where oxalate and phosphate are mainly adsorbed.

MATERIALS AND METHODS

Pumice grains containing the nano-ball allophane were collected from a volcanic ash soil near Mt. Daisen in Tottori prefecture, Japan. In order to obtain the pure nano-ball allophane that is free from contaminants such as volcanic glass, opaline silica and imogolite, only the inner portion of the pumice grains was used (Henmi and Wada, 1976). The fraction with diameter of less than 0.2 μm was collected by centrifugation after ultrasonification at 28 kHz and dispersion at pH 4. The collected sample was flocculated by saturated NaCl solution and washed with water, then stored as suspension of pH 6 in 10 mM NaCl. The prepared allophane was subjected to X-ray diffractometry, infrared spectroscopy and thermal analysis, and was proven to be free from the above-mentioned contaminants. The Si/Al ratio of allophane used was determined as 0.67 by the acid oxalate method (Higashi and Ikeda, 1974), and content of the other metals except for Na was negligible.

The allophane used belongs to the low Si/Al type (Henmi and Wada, 1976).

Adsorption experiments of oxalate and phosphate were carried out with 25 mL of the allophane suspension (containing 100 mg of allophane on the basis of drying up allophane at 105°C in an oven) in a 250 mL polypropylene centrifuge bottle. Oxalate (Na$_2$C$_2$O$_4$) or phosphate (NaH$_2$PO$_4$) solution was
mixed with NaCl solution and water, and pH was adjusted to 6.0 by HCl or NaOH solution; oxalate or phosphate concentration of the prepared solution was 0 to 2.67 mM, and the concentration of NaCl was 13.3 mM. The pH value of 6.0 was selected because the zero point of salt effect on this allophane was 6.0 (Johan et al., 1999). To the centrifuge bottle containing 25 mL of the allophane suspension, 75 mL of the prepared solution was added to give initial oxalate or phosphate concentration of 0 to 2 mM and NaCl concentration of 10 mM. The adsorption experiment of oxalate (or phosphate) at initial concentrations of 0 to 200 mM were conducted in the absence or presence of 200 mM of phosphate (or oxalate). The oxalate or phosphate adsorption experiment at the low concentration (0 to 200 mM) was also conducted with 0 and 100 mM NaCl, in addition to with 10 mM NaCl.

The mixture was shaken for 24 h, and then centrifuged at 59000 m s⁻² for 15 min. Supernatant was analyzed colorimetrically for phosphate by the ascorbic molybdate method (Murphy and Riley, 1962), by the K₃MnO₄ titration method for oxalate, and by atomic absorption spectrophotometer for Si and Al. The oxalate did not interfere with phosphate determination at the concentrations. The amounts of adsorption of oxalate and phosphate were calculated from the difference between initial and final concentrations.

An anion exchange capacity (AEC) of allophane used at the equilibrium pH 6.0 was determined by adsorption of Na⁺ and Cl⁻ to allophane to use 10 or 100 mM of NaCl solution. The allophane suspension was washed 3 times with 100 mL of 10 or 100 mM NaCl solution at pH 6, and equilibrated with the solution. After the final centrifugation, volume of the entrained NaCl solution was determined by mass measurement. Then the residue was washed 3 times with 100 mL of 1 M NH₄NO₃ solution to extract Cl in the system. AEC was calculated as the difference between Cl extracted and entrained.

Molecular orbital calculation was performed by Gaussian03 Revision D.01 program with ONIOM method (Frisch et al., 2004), where B3LYP/6-31G(d,p) and HF/3-21G basis functions were applied for adsorption region and other region of the allophane model cluster, respectively.

RESULTS AND DISCUSSION

**Adsorption isotherms of oxalate and phosphate**

Adsorption isotherms of oxalate and phosphate on allophane at pH 6.0 and at initial concentrations from 200 to 2000 μM are shown in Fig. 2. The amount of adsorption of phosphate was always higher than that of oxalate; this is consistent with the previous studies (Violante and Gianfreda, 1993; Violante et al., 1996; Jara et al., 2006). The amount of adsorption of phosphate depended on the concentration of the system. The adsorption of oxalate and phosphate was calculated from the difference between initial and final concentrations.

**Effect of background NaCl concentration**

It is considered that 10 mM of NaCl as the background electrolyte may affect the adsorption of phosphate or oxalate. Especially, the background electrolyte might have some effects on adsorption of phosphate until 8 μM of the equilibrium concentration. To confirm this, adsorption experiments of phosphate with 0 and 100 mM NaCl solutions were conducted, and the results are shown in Fig. 4b. The starting point of the adsorption of phosphate shifted little from 8 μM (Fig. 4b). These results indicate that the coexisting chloride anion do not compete with the phosphate anion toward allophane. Therefore the reason why phosphate did not adsorbed at equilibrium concentration of less than 8 μM remains in question, and further study is necessary to clarify this phenomenon.

Adsorption of phosphate was influenced unexpectedly by...
the background electrolyte. The adsorption of phosphate increased with elevating the concentration of the background electrolyte. That cause may be due to increase in the anion exchange sites on allophane (Al–OH₂⁻). It is known that cation and anion exchange capacities of allophane samples at a constant pH increase with increasing ionic strength of the bulk solution (Okamura and Wada, 1983). The AEC value of the allophane at equilibrium pH of 6 was 100 and 170 μmol g⁻¹ in 10 and 100 mM, respectively. Therefore, high concentration of NaCl developed much anion exchange site, Al–OH₂⁻Cl⁻, and then phosphate anion was attracted toward the positive charge of the Al–OH₂⁻ to replace Cl⁻. The similar trend was observed for the adsorption of oxalate. However, the adsorption of oxalate with 100 mM NaCl was lower than that with 10 mM NaCl (Fig. 4a). This may be due to decrease in the activity coefficient of divalent oxalate ion: the activity coefficient of oxalate ion was calculated as 0.67 in 10 mM NaCl, and 0.42 in 10 mM NaCl, by using the extended Debye-Hückel equation. These results are very important in soil solution chemistry, indicating that high concentration of Cl⁻ and also probably NO₃⁻ in soils never prevents adsorption of phosphate and low-molecular-weight organic anions. The high concentrations of the monovalent anions, in fact, accelerate adsorption of oxalate and phosphate on the variable charged soil components.

Analysis with the Langmuir and Freundlich equations

The adsorption data of oxalate and phosphate in Fig. 3 are plotted according to linear form of the Langmuir equation below,

\[
\frac{C}{X} = \frac{1}{X_m K} + \frac{C}{X_m}
\]

where \(X\) = adsorption amount of oxalate or phosphate (μmol g⁻¹), \(K\) = a constant related to the binding energy (L μmol⁻¹), \(X_m\) = maximum adsorption of oxalate or phosphate (μmol
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FIG. 5. Langmuir plots for adsorption of (a) oxalate and (b) phosphate in the absence and presence of 200 µM of the counterpart.

FIG. 6. Freundlich plots for adsorption of (a) oxalate and (b) phosphate in the absence and presence of 200 µM of the counterpart.

g⁻¹), and C = equilibrium concentration of oxalate or phosphate (µmol L⁻¹). Adsorption of oxalate or phosphate was plotted according to the equation (1) (Fig. 5). The adsorption of oxalate was satisfied well with the equation (1) in Fig. 5a. On the other hand, adsorption of phosphate did not correspond to the equation (1) as shown in Fig. 5b. These suggested that oxalate was adsorbed on surface aluminol groups of the allophane sample very strongly, and the adsorption energy of oxalate was assumed to be greater than that of phosphate.

This assumption was supported by fitting the adsorption data in Fig. 3 to logarithm form of the Freundlich equation below,

\[ \log X = \log k + \frac{1}{n} \log C \]

where X = adsorption amount of oxalate or phosphate (µmol g⁻¹), and C = equilibrium concentration of oxalate or phosphate (µmol L⁻¹), whereas k and n are empirical constants. The n is related to the adsorption strength, and k to both the strength and amount of adsorption. The Freundlich plots for adsorptions of oxalate and phosphate are shown in Fig. 6, and in both cases, data points fitted the linear form of the equation (2). Table 1 summarizes the Langmuir parameters obtained for the adsorption of oxalate, and the Freundlich parameters for adsorptions of oxalate and phosphate. When we compared the Freundlich parameters between adsorptions of oxalate and phosphate, the parameter n related to the adsorption energy of oxalate is higher than that of phosphate. The parameter k related to both strength and amount of adsorption of oxalate is also higher than that of phosphate.
Analysis by molecular orbital method

The adsorption strength of the two anions on aluminol groups of the nano-ball allophane were also estimated by the molecular orbital method, where changes in the total energy of the following adsorption reaction equations were calculated.

\[
\text{allophane} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{allophane-C}_2\text{O}_4{}^{2-} + \text{OH}^-(3)
\]

\[
\text{allophane} + \text{HPO}_4^{2-} \rightarrow \text{allophane-HPO}_4{}^{2-} + \text{OH}^- (4)
\]

In these adsorptions, we assumed a simple monodentate ligand exchange reaction between Al-OH of allophane and the anions. Change in the total energy is given by subtracting sum of the total energy of the reactants from that of the products. The calculated values were \(-360 \text{ kJ mol}^{-1}\) for adsorption of oxalate and \(-330 \text{ kJ mol}^{-1}\) for adsorption of phosphate. That means that the adsorption energy of oxalate was stronger than that of phosphate.

Competitive adsorption of oxalate and phosphate

Results of the competitive adsorption experiments between oxalate and phosphate on allophane used are plotted in Fig. 3. The adsorption of oxalate or phosphate was evidently depressed by the competitor (i.e. phosphate or oxalate). When the amount of adsorption of oxalate with initial concentration of 200 \(\mu\text{M}\) was plotted to coexisting phosphate concentrations, the adsorption of oxalate decreased almost linearly with increasing coexisting phosphate concentration. Similarly, increasing coexisting oxalate linearly depressed the adsorption of 200 \(\mu\text{M}\) phosphate.

We adopted the competitive adsorption data of oxalate and phosphate with coexisting 200 \(\mu\text{M}\) of the counterparts to the Langmuir and Freundlich equation (Figs. 5 and 6). The adsorption of phosphate with 200 \(\mu\text{M}\) of oxalate did not fit to linear form of the Langmuir equation as well as the adsorption of phosphate without oxalate as the competitor (Fig. 5b). The Langmuir parameters obtained for the adsorption of oxalate, and the Freundlich parameters for adsorptions of oxalate and phosphate are given in Table 1.

The calculated Langmuir \(X_m\) value for the adsorption of oxalate decreased with the coexistence of 200 \(\mu\text{M}\) phosphate, from 115 to 83 \(\mu\text{mol g}^{-1}\) (Table 1), and this corresponds to about 32% reduction. On the other hand, with the addition of phosphate, Langmuir K value for the adsorption of oxalate increased from 0.09 to 0.13 \(\mu\text{mol}^{-1}\), indicating increasing adsorption energy of oxalate onto allophane. Similar results were obtained from the Freundlich parameters for the adsorption of oxalate and phosphate in Table 1. The above described changes in the Langmuir and Freundlich parameters indicate that the addition of phosphate (or oxalate), though adsorption strength of oxalate (or phosphate) increases by the coexisting phosphate (or oxalate). The increase in the adsorption strength may be due to simultaneous adsorption of the both anions onto the surface of allophane. For example, when oxalate is added to allophane, the oxalate begins to adsorb on accessible sites of allophane, and next, on adsorption sites with less accessibility. The coexisting phosphate might impose a part of the oxalate to adsorb on the less accessible site, and the resulting adsorption strength increased. Detailed discussion on the above mentioned two kinds of adsorption site is made below.

Figure 7 shows the amounts of Si and Al released from allophane after the adsorption of oxalate (or phosphate) with and without coexisting 200 \(\mu\text{M}\) phosphate (or oxalate). The release of Si and Al increased with elevating adsorption of oxalate and phosphate. When we compared the adsorption of oxalate to that of phosphate, much Si and Al were released for oxalate: oxalate has an ability to dissolve low crystallinity silicate minerals such as allophane (Higashi and Ikeda, 1974). In the case of adsorption of oxalate without phosphate, the release of Si or Al abruptly increased at around adsorption of 100 \(\mu\text{mol g}^{-1}\) (Fig. 7). This indicates that, at the low oxalate concentration, oxalate adsorbed on allophane mainly by simple adsorption onto the aluminol group; oxalate might be adsorbed by replacement of Si with increasing amount of adsorption of oxalate, as suggested by Hanudin et al. (1999). The release of Al may be due to dissolution as aluminum oxalate complexes, and also due to induced effect of the Si dissolution which partially destroyed the nano-ball allophane structure (Abidin et al., 2005).

With the addition of 200 \(\mu\text{M}\) of phosphate to the adsorption of oxalate, the abrupt increase of the release of Si and Al occurred at low adsorption as compared with no phosphate addition (70 \(\mu\text{M}\); Fig. 7). The adsorption mechanism of oxalate, that is to say the replacement of Si with oxalate, started from the low amount of adsorption of oxalate, because the aluminol group as the adsorption site of oxalate was occupied by phosphate. For the adsorption of phosphate with 200 \(\mu\text{M}\) of oxalate, the sudden release of Si was observed from about 120 mmol g\(^{-1}\) of adsorption (Fig. 7). In adsorption of oxalate (or phosphate) including phosphate (or oxalate) as the competitor, each of the competing anions will affect not only amount and energy of adsorption of oxalate (or phosphate), but also the mechanism of adsorption of oxalate (or phosphate).

CONCLUSIONS

At low initial concentrations up to 200 \(\mu\text{M}\), the amount of adsorption of phosphate on the nano-ball allophane was higher than that of oxalate, but the adsorption strength of oxalate was higher than that of phosphate. High concentration of the monovalent anion such as chloride has shown to enhance the adsorption of oxalate and phosphate, may be due to forming of anion exchange site, Al-OH\(\text{Cl}^+\), on allophane. The adsorption mechanism of the anions was firstly the ligand exchange with hydroxyl, and then would change to the...
replacement reaction with Si. In binary system of the two anions, coexistence of the counterpart depressed the amount of adsorption, but enhanced the adsorption strength. It is notable that the coexistence also affected the adsorption mechanism of the counterpart.

REFERENCES


