Mechanisms of Phosphate Sorption on Soil Components with High Phosphate Retention Capacity

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To cope with the phosphorus deficiency problem of soils in Japan, phosphorus fertilizers have been heavily applied. However, from the viewpoint of minimizing phosphorus eutrophication of lakes and ponds, and saving phosphate resources as well as maximizing crop yield, reassessment of phosphorus application method will be needed. In search of better understanding of the mechanisms of phosphate sorption on soils and of more effective and detailed phosphorus management in soils than ever, basic studies are being continued.

This paper presents our recent results of the research on the mechanisms of phosphate sorption on soil components with high phosphate retention capacity. Materials used as a model of the soil components are synthetic goethite, alumina gel, silica-alumina gel and clay fractions of Kanuma-tsuchi and Miso-tsuchi (weathered pumice). Detection and identification of phosphate sorption products by diffuse reflectance infrared (DRIR) spectroscopy, and material balance associated with phosphate sorption are dealt with.

Phosphate adsorbed on goethite[5]

To obtain infrared spectra of phosphate adsorbed on goethite, differential diffuse reflectance method was employed. DRIR spectra were obtained on a Fourier-transform infrared spectrophotometer interfaced to an integrating sphere for diffuse reflectance measurement. Differential spectra were obtained by subtracting the spectrum of goethite from that of a phosphated goethite using a computer equipped with the spectrometer. An advantage to use diffuse reflectance method is that the background absorption bands of goethite can easily be eliminated from the differential spectrum.

In the spectra of the phosphate sorbed on goethite, a few absorption bands related to P–O stretching vibration between 1000 and 1200 cm^{-1} were observed as shown in Fig. 1. The positions of these bands varied with the change of pH. At pH 3.3, two bands, one at 1170–1180 cm^{-1} and the other at 1010–1015 cm^{-1}, were observed. With increasing pH, these bands gradually diminished and instead, another set of absorption bands appeared at 1120–1130 cm^{-1} and 1040–1050 cm^{-1}. Absorption bands of 1170–1180 cm^{-1} and 1010–1015 cm^{-1} were assigned to P=O and P–O–(Fe) stretching vibration, respectively and the absorption bands of 1120–1130 cm^{-1} and 1040–1050 cm^{-1} to P–O_2^- and P–O–(Fe) stretching vibration according to Parfitt et al.[8] With the pH changing from 3.3 to 11.9, one step of the structural change of adsorbed phosphate occurred. Under similar pH conditions, though the absorption maxima increased with the amount of phosphate adsorption, the positions of the absorption bands became less obvious at lower surface coverage with phosphate.

On the other hand, Na^+ and Cl^- adsorptions

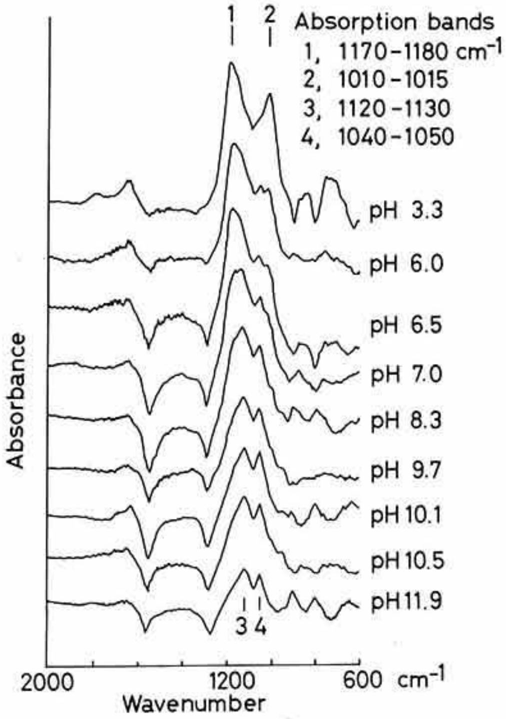


Fig. 1. Diffuse reflectance infrared spectra of phosphate adsorbed on geothite

of goethite with and without phosphate were measured under the same condition as the preparation of the samples used for obtaining the infrared spectra. In order to construct the dissociation curve of phosphate adsorbed on goethite, [the amount of Na^+ adsorption (Na^+ads.) due to dissociation of phosphate on goethite]/[the amount of phosphate adsorbed (Pads.)] was estimated as follows.

Na^+ads. due to dissociation of phosphate on goethite/Pads. = (Na^+ads. of phosphated goethite–Na^+ads. of goethite at the same pH)/Pads. ....(1)

The results were plotted in Fig. 2. This curve was closely related to the spectral change of phosphate on goethite with pH. Thus, at pH 3.3, phosphate adsorbed on goethite exists in the protonated form, at pH 6.7, it exists in the nearly half dissociated form and at a pH higher than 10, it exists in the completely dissociated form in 0.01 M NaCl.

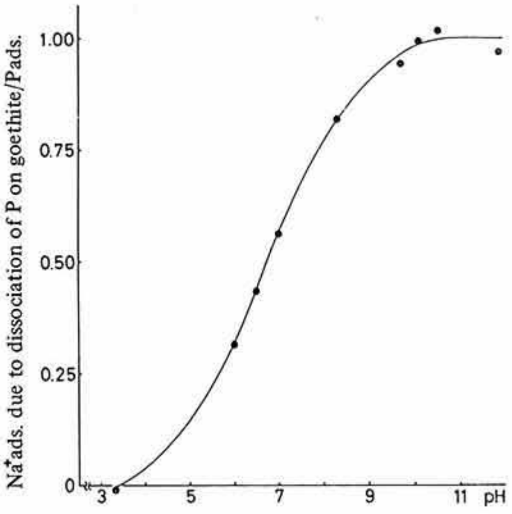
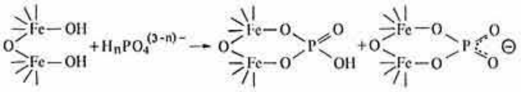


Fig. 2. Na adsorption property of phosphate adsorbed on goethite in 0.01 M NaCl

Phosphoric acid dissociates in three steps in aqueous solution, the dissociation constants being $pK'_1=2.18$, $pK'_2=6.93$ and $pK'_3=12.2$ (corrected to ionic strength=0.01). In the case of phosphate adsorbed on goethite, only a one-step dissociation over the pH range from 3.3 to 11.9 was shown indicating that the other two dissociative groups are blocked. This result is compatible with the idea of the bridging binuclear structure of the phosphate adsorbed on goethite proposed by Parfitt et al.[8] and is represented by the following formula.



Phosphate sorbed on alumina gel[6]

Parfitt et al.[7] reported that the infrared spectra of phosphate sorbed on alumina gel, measured by a transmission method, was obscured by absorption bands of the gel. However, the differential diffuse reflectance method was also successful in obtaining the infrared absorption spectra of phosphate sorbed on

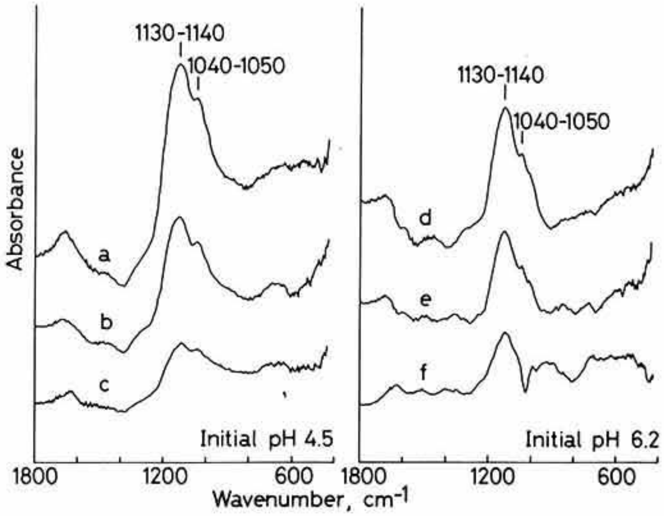


Fig. 3. Diffuse reflectance infrared spectra of phosphate sorbed on alumina gel
a, 1020; b, 611; c, 208; d, 914; e, 615; f, 206 × 10^{-6} mole P/g.

alumina gel. But, with an increase in pH value, the intensities for X-ray diffraction peaks and infrared absorption bands for bayerite* increased. Accordingly, subtraction of an DRIR spectrum of alumina gel from that of phosphated alumina gel was carried out between the gels showing almost the same peak intensities of X-ray diffraction for bayerite.

Absorption bands assigned to P–O stretching vibration of phosphate sorbed on alumina gel were observed at 1130–1140 cm^{-1} as a strong absorption band and at 1040–1050 cm^{-1} as a small peak (Fig. 3). The positions of these absorption bands were little affected by the change in pH and the amount of phosphate sorbed. Absorbance of these bands increased with an increase in the amount of phosphate sorbed. These spectra were different from those of $H_2PO_4^-$ and HPO_4^{2-} in aqueous solution[2] despite the fact that these ions are major phosphate species in solution under the pH conditions employed. These spectra are also different from those of NaH_2PO_4, Na_2HPO_4,[2] $Al(H_2PO_4)_3$ and taranakite[1] which have strong and complicated absorption bands at 900–1300 cm^{-1}, though the reaction mixture contained sodium and aluminum.

The spectra of phosphate sorbed on alumina gel are close to that of aluminium phosphate gel[3] in two respects: (i) the positions and compactness of the absorption bands due to P–O stretching vibration; (ii) little spectral change with suspension pH. A slight spectral change with pH in the spectra of aluminium phosphate gel was that an absorption shoulder at around 1250 cm^{-1} appeared in the spectrum at pH 3.4 and it disappeared with an increase in pH. Thus, the state of phosphate sorbed on alumina gel is similar to that of aluminium phosphate gel. The sorption product of phosphate on alumina gel was amorphous to X-ray diffraction.

Na^+ and Cl^- adsorption properties of alumina gel tended to shift to those of aluminium phosphate gel with phosphate sorption. With an increasing amount of phosphate sorption, the amount of Cl^- adsorption decreased, while the amount of Na^+ adsorption increased and the pH at which amounts of Na^+ and Cl^-

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* Bayerite=$Al(OH)_3$, polymorph of gibbsite.

adsorption were equal shifted to a lower value. The decrease of Cl^- adsorption is almost equal to the amount of phosphate sorbed when the amount of phosphate sorbed is small. These results on ion adsorption properties suggest that phosphate exchanges with positively charged aquo and/or hydroxo ligands on the surface of alumina gel. It was deduced that the initial reaction of phosphate with alumina gel is ligand exchange and the adsorbed phosphate is readily converted to a state similar to aluminium phosphate gel. Phosphate retention capacity, measured at 0.05 M of final phosphate concentration and at about pH 7, per unit surface (B.E.T.) area of alumina gel was much larger than that of goethite. This also suggests that phosphate can react not only with aluminium on the surface but also with that at the inner part of alumina gel.

Material balance associated with phosphate sorption[4]

Phosphate sorption on soil components with high phosphate retention capacity is associated with sorption and desorption of various chemical species. The material balance of all the chemical species associated with the phosphate sorption reaction on clay fraction of Kanuma-tsuchi and Miso-tsuchi, silica alumina gel and synthetic goethite was investigated by adjusting the initial pH to 4.0, 5.0, 6.0 and 7.0 in 0.1 M NaCl. Phosphate sorption decreased with increasing initial pH. During phosphate sorption, the suspension pH rose, adsorption of Cl^- decreased, adsorption of Na^+ increased, silicate was released and Al in solution was precipitated. With increasing initial pH, the amount of apparent released OH^- increased, the amount of Na^+ adsorption increased and the amount of released silicate decreased. These material balance associated with phosphate sorption is shown schematically in Fig. 4 where the increase in positive charge of the solid phase including adsorbed ions was chosen as plus. By applying the electroneutrality condition to the process of phosphate sorption, the sum of the plus should be balanced with that of the minus. Thus, regarding the charge,

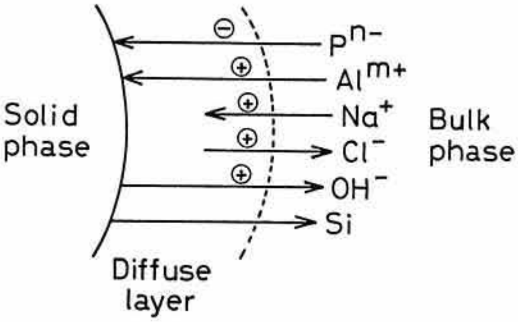

Fig. 4. Schematic diagram of the material balance associated with phosphate sorption

Sorbed P = Apparent released OH + Desorbed Cl + Adsorbed Na + Precipitated Al ....(2)

There is no confirmed relationship between the ionic composition of sorbing phosphate and that of phosphate remaining in the bulk solution. In the calculation of the total charge of sorbed phosphate, two assumptions were tentatively made: (i) there is no selective sorption among the ionic species of phosphate; (ii) the ionic species composition of sorbed phosphate is approximated by that of phosphate in the bulk solution at the mean value of the initial and final H^+ activity. In the case of goethite, the same calculation was carried out, by omitting the term involving Al from Equation (2). The values of the charge balance obtained by the right-hand side of Equation (2)/the left-hand side of Equation (2) were 0.79–0.97 for Kanuma-tsuchi, Miso-tsuchi and goethite and 0.75–0.85 for silica-alumina gel. In the case of goethite and alumina gel in 0.01 M NaCl[5,6] solution at pH 3.1 and 4.5, respectively, where the amount of apparent released OH, that of adsorbed Na and that of precipitated Al in Equation (2) were very small and phosphate species was mostly $H_2PO_4^-$, the amount of sorbed phosphate was nearly equal to that of desorbed Cl^-. The increment of Na^+ adsorption associated with phosphate sorption corresponds to the increment of cation exchange capacity due to heavy dressing with phosphorus fertilizers.

Remaining problems

Regarding the composition of aluminium phosphate gel as a sorption product on alumina gel, various P/Al ratios may be possible. The P/Al ratio may also vary in a gel particle; the ratio at the surface may be higher than that at the inner part. The relationship between Na^+ adsorption properties and infrared spectra of phosphate sorbed on alumina gel was obscure. It is also necessary to elucidate these problems.

Studies on detection and identification of phosphate sorption product on silica-alumina gel, iron gel, clay fraction of Kanuma-tsuchi and Miso-tsuchi, and various soils using differential diffuse reflectance infrared spectroscopy are now under way.

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