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ABSTRACT

Influence of phosphate sorption on dispersion of a Ferralsol

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INTRODUCTION

When a soil is dispersive, the soil permeability decreases and it sometimes induces erosion. The dispersed soil is transported in surface runoff. Subsurface leaching also occurs. In those cases, adsorbed nutrients are also conveyed and they sometimes cause water contamination. Because phosphate is an important limited resource, it must be used effectively.

Long-term fertilizer applications have been reported to cause increases in water stable aggregation, porosity, infiltration capacity and hydraulic conductivity and decreases in bulk density (Haynes and Naidu 1998). A number of workers have investigated the use of phosphoric acid as an agent for promoting aggregate stability in soils (e.g. Thien 1976; Yeoh and Oades 1981) where other phosphatic fertilizers have no effect (Haynes and Naidu 1998). On the other hand, other researchers have reported that phosphate sorption induces mobilization of colloids and colloidal phosphate, and phosphate accumulation in soils increases the risk of colloid-facilitated leaching of phosphate (Siemens 2004; Jianhong 2005; Scalenghe et al. 2007; Calero et al. 2008; Ilg et al. 2008). Shanmuganathan and Oades (1983), Lima et al. (2000), and Lagaly and Ziesmer (2003) have indicated that phosphate sorption increases the negative charge density of soils and it affects flocculation-dispersion phenomena. Penner and Lagaly (2001) have shown that salts with multivalent anions such as sulfates and phosphates increase the critical coagulation concentration for montmorillonite and kaolinite dispersions. Teo et al. (2009) have indicated that high enough phosphate concentration completely deflocculated the clay slurries. The phosphate concentrations in soils are generally low; however, near fertilized points, phosphate concentration may reach much higher values. Celi et al. (2000) found that high phosphate addition near fertilized particles have caused a compression of diffuse layer closer to oxide surface, leading increase of phosphate sorption due to reduction of the electrostatic repulsive forces. Therefore, understanding the influence of phosphate sorption under wide range of its concentrations on flocculation-dispersion is valuable as the fundamental study for preventing erosion and colloidal leaching with phosphate loss. In addition, because pH affects soil charge, it strongly influences the dispersion-flocculation of soils. Flocculation occurred near point of zero charge; the Al oxide was flocculated at pH > 9.5 and the iron oxide was flocculated between pH 6.0 and 8.2 (Goldberg and Glaubig 1987). The soil dispersed well and the permeability decreased well at pH 9 more than those at pH 6 for the montmorillonitic and the kaolinitic soil (Suarez et al. 1984). The allophanic andisol dispersed well and the permeability decreased well at pH < 5 and pH >10 (Nakagawa and Ishiguro 1994, Ishiguro and Nakajima 2000, Ishiguro 2005). Therefore, pH is one of the most important factors when we consider the influence of dispersion-flocculation

Electrokinetic methods are applied widely in colloid science to obtain the charge characteristics of the colloids as well as evaluation of colloidal stability by many authors (Ilg et al. 2008, Celi et al. 2000). Based on zeta potential, optical density and particle size, Ilg et al. (2008) concluded that the addition of phosphate caused mobilization of soil colloids when zeta potential was -20mV. Celi et al. (2000) indicated that increase of phosphate sorption on goethite made zeta potential more negative (-20mV to -37mV). Colloidal dispersion can be theoretically determined by using the DLVO theory in which the electric repulsive potential energy and the van der Waals attractive potential energy between the two colloidal particles are evaluated. When the electric repulsive potential energy becomes larger than the attractive potential energy when the two particles come closer, the particles disperse. By using the theory, Kobayashi et al. (2005) showed that stability of colloidal silica increases with decreasing ionic strength and increasing magnitude of particle charge. Although researches of soil dispersion influenced by phosphate sorption have been conducted, such a theoretical investigation has not been applied.

In this paper, the influence of phosphate sorption on soil dispersion was firstly evaluated by calculating repulsive potential energy. A Ferralsol, which is typical in rainy tropical regions and sorbs phosphate strongly, was used. The influence was systematically investigated under different pH and electrolyte concentration.

MATERIALS AND METHODS

Soil

Ferralsol was collected at a depth approximately 10cm from a rubber tree field in Nam Dong District, Thua Thien Hue Prefecture, Vietnam. The rubber trees had been planted for 15 years. All soil samples were air dried and sieved with a 2 mm sieve. The general physical and chemical properties are listed in Table 1. The organic matter content was determined by the method of Walkley and Black (1934). Exchangeable Al was extracted with 1 mol L-1 KCl. Total Al and Fe fractions were extracted with 0.1 mol L-1 sodium pyrophosphate. The CEC was determined by the ammonium acetate method (Sumner and Miller 1996). The crystalline clay minerals and their composition are listed in Table 2. The crystalline clays were identified by X-Ray powder diffraction method. The elemental or oxide contents of crystalline clays were measured by the X-Ray Fluorescence method.

Phosphate sorption experiment

The phosphate sorption at the prescribed pH (4, 5.5, 7, and 8.5) was determined by using a batch method. Phosphate was added as NaH2PO4. HNO3 and NaOH were used to adjust pH. The Na adsorption amount and that of NO3 at <10mmol L-1 NaH2PO4 added amount were also measured.

The experimental procedure was as follows:

1. About 3 g of the soil was equilibrated with 0.025 L of a 1 mmol L^{-1} or a 10 mmol L^{-1} $NaNO_3$ solution at the prescribed pH (4, 5.5, 7, 8.5) in a centrifuge tube. It was centrifuged, and the supernatant A was stored. The weight of (the centrifuge tube + the soil + the soil solution) was measured after discarding the supernatant.

2. A 0.025 L phosphate solution at different concentration (0, 0.03, 0.3, 3, 10, 30, 100 mmol L^{-1}) was added to the tube. The pH of the solution was adjusted if the pH changed. The tube was shaken for 24 hours. The final equilibrium electrolyte concentration was set at 1 $mmol_c$ L^{-1} or 10 $mmol_c$ L^{-1} with $NaNO_3$ when the adding phosphate concentration was smaller than that concentration. The final equilibrium electrolyte concentration became more than 1 $mmol_c$ L^{-1} or 10 $mmol_c$ L^{-1} when the adding phosphate concentration was larger than that concentration.

3. The tube was centrifuged and the supernatant B was stored. The weight of (the centrifuge tube + the soil + the soil solution) was measured after discarding the supernatant.

4. 0.03 L of a 100 mmol L^{-1} KCl solution was added to the tube. The tube was shaken for more than one hour and then, centrifuged and gathered the supernatant C. This was repeated 5 times.

5. The soil was oven dried and the weight was measured.

The phosphate concentrations of the supernatants (A, B, C) were measured by ascorbic acid method (Murphy and Riley 1962). Na concentrations of the supernatants (A, B, C) were measured by flame emission spectrometry. NO_3- concentrations were measured by using calorimetric method in a continuous-flow analytical system (Traccs 800, Bran+Lubbe, Norderstedt, Germany).

The phosphate sorption was calculated by subtracting the amount in the final soil solution in step 3 from the added amount. The Na and NO3 adsorptions were calculated by subtracting the amount remaining in the soil solution at the end of step 3 from the amount in the supernatant C.

Dispersion experiment

The soil and the solution under the same condition in the phosphate sorption experiment were shaken well and stood still for 3 hours. Then, 4 cm^3 of the supernatant was taken from 2 cm below the water surface. Its absorbance was measured using the light at 660 nm wavelength (UV-VIS Spectrophotometer 1240, Shimadzu Corporation, Japan).

Zeta potential measurement

The zeta potential was calculated from the measured electrophoretic mobility by using the Ohshima equation (Ohshima 2004; Kobayashi 2008), because the measurement condition satisfied $\kappa a > 30$, where κ is the inverse of Debye length expressed by the following Eq. 2, and a is the mean radius of the soil particles. In the mobility measurement, the mean radius of the soil particles was about 0.5 μm. The radius was measured with dynamic light scattering method. The measurement procedure was as follows.

1. The soil was prepared under the same solution condition at the end of step 3 in the phosphate sorption experiment. It was shaken well and soon the suspension was taken from 2 cm below the water surface.

2. The sampled suspension was stirred by ultrasonic waves for 30 seconds. One cm^3 of the suspension was diluted about 10,000 times by the same solution.

3. The zeta potential of the soil suspension

was obtained by measuring the mobility (Model 502, Nihon Rufuto).

THEORY OF ELECTRICAL REPULSIVE POTENTIAL ENERGY

The electrical repulsive potential energy between the soil clay particles were estimated in order to evaluate the behavior of soil dispersion and flocculation affected by phosphate sorption. The energy was calculated based on the zeta potential.
In the case of low surface potentials (|ψ|<25 mV), a potential at the distance x from the charged clay surface, ψ, can be estimated as follows:

$$\psi = \psi_s \exp(-\kappa x) \quad (1)$$

$$\kappa = \left(\frac{e^2 \sum_i z_i^2 n_i}{\varepsilon kT}\right)^{1/2} \quad (2)$$

$$n_i = 1000 M_{io} N_A \quad (3)$$

where ψs is the potential of the soil surface, e = 1.602x10-19 C is the elementary charge, z_i is the charge number of ion i, n_i is expressed as the number of ions per cubic meter, ε is the dielectric constant of the medium, Mio is the concentration of ion i in equilibrium solution (mol L^{-1}) and N_A is the Avogadro constant. In this calculation, a zeta potential is used instead of ψs in Eq. 1 in order to get the potential distribution from the plane of the zeta potential to the bulk solution.

In general case, the relationship between ψ and x are explained in the following equation 4 (Hiemenz 1986).

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{2kT}{\varepsilon} \sum_i n_{io} \left[\exp\left(\frac{-z_i e\psi}{kT}\right) - 1\right] \quad (4)$$

The following approximation solution can be derived from Eq. 4.

$$\Delta\psi = \left(\frac{2000RT}{\varepsilon}\right)^{0.5} \left(\sum_i M_{io} \left[\exp\left(\frac{-z_i e\psi}{kT}\right) - 1\right]\right)^{0.5} \Delta x \quad (5)$$

where Δψ is the small increment of the potential after the small increment of the distance Δx.

The concentration of ion i in the midpoint between two soil particles, Mi(x), at distance x from the zeta potential plane can be calculated with the following equation.

$$M_i(x) = M_{io} \exp\left(\frac{-z_i e\psi_m(x)}{kT}\right) \quad (6)$$

where ψm(x) is the potential at the midpoint at distance x from the zeta potential plane, which is obtained from the following equation.

$$\psi_m(x) = 2\psi(x) \quad (7)$$

where ψ(x) is the potential at distance x from the zeta potential plane when the soil particle exists alone. This is obtained from Eq. 1 or Eq. 5 and the zeta potential.

The electrical repulsive force between the particles, ΔP(x), is the osmotic pressure difference between the midpoint and the bulk solution.

$$\Delta P(x) = RT \sum (M_{o,i} - M_i(x)) \quad (8)$$

Therefore, the repulsive potential energy, Vζ, when the two particles approach from far distance $2b_2$ to the distance $2b_1$ between each zeta potential plane can be obtained by the following equation.

$$V_\zeta = -2 \int_{b_2}^{b_1} \Delta P(x)\, dx \quad (9)$$

V_ζ is derived to sum up 2ΔP(x)×Δx from b_1 to b_2 as shown in Eq. 9, where b_2 is the distance from the zeta potential plane to the boundary of the bulk solution (Bresler 1970, Iwata 1995, Ishiguro et al. 2003). Colloid dispersion-flocculation is determined by the peak value of the total potential energy (repulsive-attractive) between the colloid particles. We assume that the peak value rises at the distance between the zeta potential planes of the soil particles = 1 nm (i.e. b_1= 0.5 nm) with reference to the publications (Pashley 1981, Israelachvili 1982, Hiemenz 1986, The Clay Science Society of Japan 2009). We let the b_2 equal to $100\kappa^{-1}$ in the calculations. 0.1 κ^{-1} was used as the small increment of the distance Δx in calculation of Eq. 5 and 9. Because κa was larger than 30, the diffuse layer thickness was much smaller than the radii of the soil clays. Therefore, we evaluated the interaction by using this simple plate model. We used Eq. 9 because the measured conditions were not a z:z electrolyte. In this calculation, all of ions in the solution were considered in Eq. 8; since the valences of phosphate ions in solution change with pH, they were also included. The calculations were carried out by Microsoft Excel software.

RESULTS

Flocculation and dispersion of the soil suspension evaluated by absorbance

The obtained relationship between phosphate sorption and absorbance of the soil suspension is shown in Fig. 1(a). The absorbance corresponds with the dispersion. When the value is larger, the soil disperses. The largest value indicated 4 because that was the upper limit of the absorbance for the spectrophotometer. When the value is smaller, the soil flocculates. At pH 4, the soil suspension showed most flocculative compared with other pH. However, the peak of dispersion was observed at around 20 mmol P kg^{-1} sorption. At this pH, the increase of absorbance could be observed clearly after > 1.6 mmol P kg^{-1} sorption at 1.1 mmol L^{-1} equilibrium electrolyte concentration and after > 2.7 mmol P kg^{-1} sorption at 10 mmol L^{-1} equilibrium electrolyte concentration (Fig. 1(a) and 1(d)). At pH 5.5 for the initial $NaNO_3$ concentration of 1 mmol L^{-1} in step 1 in the phosphate sorption experiment, it was relatively flocculative at 0 mmol P kg^{-1} sorption (absorbance was 0.44). It became well dispersed after phosphate sorption. At pH 5.5 for the initial $NaNO_3$ concentration of 10 mmol L^{-1} in step 1 in the phosphate sorption experiment, it dispersed well as the phosphate sorption increased; it was well dispersed at around 15 mmol P kg^{-1} sorption. At pH 7 and pH 8.5, it dispersed well. At higher phosphate sorption, the absorbance became smaller. Increase of phosphate sorption corresponds to the increase of equilibrium electrolyte concentration at > 17 mmol P kg^{-1} sorption because phosphate was added as NaH_2PO_4.

The relationship between phosphate concentration and absorbance of the soil suspension is shown in Fig. 1(b). At pH 4, the peak dispersion was at 7.2-7.5 mmol P L^{-1}. At pH 5.5 for the initial $NaNO_3$ concentration of 10 mmol L^{-1} in step 1 in the phosphate sorption experiment, the influence of phosphate sorption was clear when the phosphate concentration was more than 0.001 mmol P L^{-1}. The soil also became well dispersed for the initial NaNO3 concentration of 1 mmol L^{-1} after phosphate sorption as mentioned above.

The relationships between Na adsorption, Na concentration, and absorbance of the soil suspension are shown in Fig. 1(c) and Fig. 1(d). Na concentration equals the equilibrium electrolyte concentration. At pH 5.5 the soil changed after phosphate sorption from relatively flocculative to well dispersive even at the same Na adsorption of 10 mmol Na kg^{-1} for the initial $NaNO_3$ concentration of 1 mmol L^{-1} and even at the slight increase from 30 to 38 mmol Na kg^{-1} for the initial NaNO3 concentration of 10 mmol L^{-1}. At these changes, the Na concentrations showed almost similar values. At pH 4 for the initial NaNO3 concentration of 10 mmol L^{-1}, Na adsorption increased from 8 mmol Na kg-1 to 20 mmol Na kg^{-1}, although the Na concentration kept almost the same value around 10 mmol L^{-1}. At higher Na concentration the absorbance became smaller. It was more flocculative at lower pH.

Zeta potential

The obtained relationship between absorbance of the soil suspension and the zeta potential is shown in Fig. 2(a). The soil dispersed well when the magnitude of the zeta potential increased. It was flocculative when the zeta potential was larger than -20 mV. It was well dispersive when the zeta potential was smaller than -25 mV. However, the data at pH 5.5 and the absorbance of 1.8, and the data at pH 8.5 and the absorbance of 3.6 deviated slightly from the other data, although their trend was similar. The zeta potential for the initial $NaNO_3$ concentration of 1 mmol L^{-1} and the equilibrium electrolyte concentration smaller than 10 mmol L^{-1} was smaller than that for the initial $NaNO_3$ concentration of 10 mmol L^{-1}, because the potential was shielded when the electrolyte concentration was larger.

The relationship between the phosphate sorption and the zeta potential is shown in Fig. 2(b). The magnitude of the zeta potential increased with the increase of the phosphate sorption until its peak value. The equilibrium electrolyte concentration increased with the increase of the phosphate sorption when the NaH_2PO_4 solution concentrations added in step 2 of the experiment were larger than the initial NaNO3 concentrations at step 1. The magnitude of the zeta potential decreased with increase of electrolyte concentration (also see in Fig. 2(d)) after its peak.

The relationship between the Na adsorption, the Na concentration and the zeta potential are shown in Fig. 2(c) and Fig. 2(d). The Na adsorption was larger at higher pH. The magnitude of the zeta potential was larger at higher pH. Even at the similar Na adsorption and Na concentration (·····1 mmol L^{-1} or ——10 mmol L^{-1} in Fig. 2) at their lower values, the magnitude of the zeta potential increased where the phosphate sorption increased as shown in Fig. 2(b).

Repulsive potential energy

The obtained relationship between the absorbance of the soil suspension and the repulsive potential energy is shown in Fig. 3(a). The absorbance

increased with the increase of the repulsive potential energy. It flocculated well when the repulsive potential energy was less than 0.064 μJ m^{-2} with absorbance <0.05. It dispersed well when the repulsive potential energy was larger than 0.3 μJ m^{-2} with absorbance =4. A slight spread was observed among the data between 0.069 μJ m^{-2} and 0.3 μJ m^{-2} where the soil suspension turned to dispersion/ flocculation. However, the overall correlation between the repulsive potential energy and the absorbance was well.

The relationship between the phosphate sorption and the repulsive potential energy is shown in Fig. 3(b). The repulsive potential energy increased with the increase of pH. It increased with the increase of phosphate sorption at lower phosphate sorption (4.5 to 20 mmol P kg^{-1}). After its peak, it decreased with the increase of the phosphate sorption, which corresponded with the increase of the equilibrium electrolyte concentration; it decreased when the equilibrium electrolyte concentration was equal to or larger than 10 mmolc L^{-1} (the thicker lines shown in Fig. 3). The relationship between the Na concentration and the repulsive potential energy is —— shown in Fig. 3(c). Even at the similar Na concentration (····· 1 mmol L-1 or ——10 mmol L^{-1} in Fig.3) at their lower values, the repulsive potential energy increased where the phosphate sorption increased as shown in Fig. 3(b). The repulsive potential energy for the initial $NaNO_3$ concentration of 1 mmol L^{-1} and the equilibrium electrolyte concentration smaller than 10 mmol L^{-1} was larger than that for the initial NaNO3 concentration of 10 mmol L^{-1}, because the potential was shielded when the electrolyte concentration was larger (Fig. 3(b)).

NO3 adsorption

The measured values of the NO_3 adsorption at pH 4 for the initial $NaNO_3$ concentration of 1 mmol L^{-1} were 0.72 mmol NO_3 kg^{-1} at the phosphate sorption of 0 mmol P kg^{-1}, 1.0 mmol NO_3 kg^{-1} at the phosphate sorption of 0.15 mmol P kg^{-1}, 0.74 mmol NO3 kg^{-1} at the phosphate sorption of 1.6 mmol P kg^{-1} and 0.30 mmol NO3 kg^{-1} at the phosphate sorption of 13 mmol P kg^{-1}. Those at pH 5.5, pH 7 and pH 8.5 were negative values ranged from -0.1 to -0.45 $mmol_c$ NO_3 kg^{-1}.

DISCUSSION

Evaluation with repulsive potential energy

The influence of phosphate sorption on the dispersion of Ferralsol was clearly evaluated with the data of absorbance of the soil suspension (Fig. 1(a)). The results can be explained with the calculated repulsive potential energy between the soil particles because the absorbance and the repulsive potential energy corresponded well (Fig. 3(a)). When the repulsive potential energy becomes larger, the soil dispersion is stable because the soil particles cannot stick together due to the high repulsive potential energy. At lower pH, the soil was relatively flocculative because the repulsive potential energy was smaller. On the other hand, the soil was dispersive at higher pH because that potential energy was larger (Fig. 3). The difference between flocculative and dispersive conditions is quite relative because it changes with time. Out of convenience, we define that the soil is well flocculative when the absorbance is less than 0.05 and the soil is well dispersive when the absorbance is 4. When the repulsive potential energy was less than 0.064 μJ m^{-2}, the soil was well flocculative. When it was larger than 0.3 μJ m^{-2}, the soil was well dispersive (Fig. 3(a)). Even at pH 4, the soil became rather dispersive when phosphate was sorbed; the repulsive potential energy became larger than 0.064 μJ m^{-2} at 9 to 20 mmol P kg^{-1} (Fig. 3(b)). At pH 5.5 for the initial NaNO3 concentration of 1 mmol L^{-1}, the soil dispersed from smaller phosphate sorption of 0.15 mmol P kg^{-1}; the repulsive potential energy was 0.19 μJ m^{-2}. At pH 5.5 for the initial NaNO3 concentration of 10 mmol L^{-1}, the soil gradually dispersed with the increase of phosphate sorption and it dispersed at 15 mmol P kg^{-1} where the repulsive potential energy was 0.23 μJ m^{-2} (Fig. 3(b)). The influence of phosphate sorption on the soil dispersion was remarkable at pH 4 and pH 5.5 (Fig. 1(a)). The pH 5.5 is also close to pHwater in the field in Table 1. Therefore, the similar phenomena can occur in the real field soil. When we evaluated it from the phosphate concentration, the soil gradually became dispersive with increasing the concentration from about 1 mmol P L-1 at pH 4 and from 0.0015 mmol P L^{-1} at pH 5.5 for the initial NaNO3 concentration of 10 mmol L^{-1} (Fig. 1(b)). At pH 5.5 for the initial $NaNO_3$ concentration of 1 mmolc L^{-1}, the soil condition changed significantly after phosphate sorption of 0.15 mmol P kg^{-1} at 0.002 mmol P L^{-1} from flocculative to well dispersive; the absorbance increased from 0.44 to 4 and the repulsive potential energy increased from 0.07 to 0.19 μJ m^{-2} (Fig. 1(b), Fig. 3(a)). At those lower pHs the soil was more flocculative for the initial $NaNO_3$ concentration of 10 mmol L^{-1} than that for the initial $NaNO_3$ concentration of 1 mmol L^{-1} because of the shielding effect as mentioned before.

When the equilibrium electrolyte concentration was larger than 10 mmolc L^{-1}, the soil gradually became flocculative (Fig. 1(d)) because the electric field near the soil particle surface was shielded by the electrolyte at high concentration and the repulsive potential energy decreased (Fig. 3(c)). At pH 5.5 and pH 7, decrease of absorbance from 4 to 1.8 and 4 to 3 resulted from the decrease of repulsive potential energy from 0.41 to 0.20 μJ m^{-2} and from 0.81 to 0.25 μJ m^{-2} (Fig. 3(a)). The overall correlation between the absorbance and repulsive potential energy was well although a slight spread was observed among the data between 0.069 μJ m^{-2} and 0.3 μJ m^{-2} where the soil suspension turned to dispersion/flocculation. The precise evaluation can be conducted by using the DLVO theory which includes attractive Van der Waals potential energy. However, its evaluation is difficult because the repulsive potential energy is based on the measured zeta potential in this study; the distance from the soil surface to the zeta potential plane is difficult to estimate. Therefore, we evaluated with only the repulsive potential energy because the attractive Van der Waals potential energy is independent from pH and electrolyte concentration. This evaluation is similar to that which Ishiguro et al. (2003) has done in a sulfate and nitrate system. In this paper, we evaluated it concerning phosphate sorption. Kobayashi et al. (2005) evaluated aggregation for a silica successfully and Kobayashi et al. (2009) did deposition for simple latex spheres successfully by using the DLVO theory. Good estimation of the distance of the slipping plane of simple latex spheres was also shown (Kobayashi et al. 2008). The theoretical evaluation by using total potential energy for the complicated soil system remains as a future research.

Inspection with zeta potential and soil charge

The repulsive potential energy was smaller at lower pH and larger at higher pH (Fig. 3(b)) because the negative charge of the soil increased with the increase of pH. This was confirmed with the increase of the magnitude of the zeta potential with the increase of pH and Na adsorption (Fig. 2(b) and 2(c)); effect of pH can be detected when the data of the same equilibrium electrolyte concentration were compared among those different pHs. Na adsorption equals the negative charge of the soil. Haynes and Naidu (1999) pointed out that repulsive forces between particles dominate and lead to dispersion when the pH increases. We elucidated it using the repulsive potential energy. The repulsive potential energy was smaller at larger electrolyte concentration due to the shielding of electric field as mentioned before (Fig. 3(c)). The shielding effect can be verified by the decrease of the magnitude of the zeta potential with the increase of the equilibrium electrolyte concentration; the equilibrium electrolyte concentration equals to Na concentration in this system (Fig. 2(d)). The repulsive potential energy increased with the increase of phosphate sorption when the equilibrium electrolyte concentration was smaller than or equal to 10 mmolc L^{-1} (Fig. 3(b) and 3(c)). This resulted from the increase of the magnitude of the zeta potential with the increase of the phosphate sorption when the equilibrium electrolyte concentration was smaller than or equal to 10 mmolc L^{-1} (Fig. 2(b)). When phosphate is sorbed, the sorbed site is negatively charged in some cases. When phosphate is sorbed on initially positively charged site, the positive charge disappears (Stoop 1983; Nanzyo 1988; Celi et al. 2000). In both cases, the net negative charge increases after phosphate sorption. It is supposed that the increased net negative charge affected strongly to the electric field near the soil surface. Then the magnitude of the zeta potential increased and the repulsive potential energy increased.

The Na adsorption equals the negative charge of the soil. Although the magnitude of the zeta potential increased with increasing the phosphate sorption until reaching their peak (Fig. 2(b)), the Na adsorption did not increase in proportion to the increase of the magnitude of the zeta potential when the phosphate sorption was smaller than 3 mmol P kg^{-1} (the smallest 3 data of the Na adsorption for each pH and less than 10 mmol L^{-1} concentration condition in Fig. 2(c) and 2(d)). The absorbance increased while the negative charge of the soil = the Na adsorption did not increased in this region (Fig. 1(c)). In the case that an initial positive charge was deleted and no negative charge was generated after phosphate sorption, Na was not adsorbed. Even though Na was adsorbed on a new negative charge site after phosphate sorption, the amount was smaller compared with the total Na adsorption. Therefore, Na adsorption did not correlated with the zeta potential directly under those conditions.

The particles smaller than 0.002 mm were quartz (61 %), kaolinite (34.4 %), and goethite and hematite (<4.6 %) in the soil. The point of zero charge of quartz is about pHs 0.5 - 3.5 (Iler 1979), that of kaolinite is about pH 4.1 (Wei et al. 2014), and that of goethite is about pH 8.2 (Wei et al. 2014) according to the literatures. They and the organic materials have variable charges and the positive charge decreases

or the negative charge increases with the increase of pH. The zeta potentials were all negative values in this experiment and the magnitude increased with the increase of pH. This result coincides with the expected trend of the zeta potential from the composition of the particles; the negative charge dominates at pH > 4 when the quartz predominates. Because the goethite has the positive charge when pH is lower than the point of zero charge, it might affect the soil flocculation to some extent, especially at lower pH.

Because the soil has a positive charge at lower pH, it affected the soil flocculation strongly. The positive charge was equal to NO3 adsorption; that was about 1 mmol NO_3 kg^{-1} at pH 4 at 1 $mmol_c$ $NaNO_3$ L^{-1} and not detected when pH was >=5.5. The increase of the phosphate sorption canceled the positive charge and sometimes added the negative charge. That resulted in the increase of the magnitude of the zeta potential and the increase of repulsive potential energy as mentioned above.

The absorbance increased with the increase of the magnitude of the zeta potential (Fig. 2(a)). However, the data at pH 5.5 and the absorbance of 1.8, and that at pH 8.5 and the absorbance of 3.6 deviated from the other data. Although the zeta potential itself is not a direct physical parameter to soil dispersion, it is a good indicator. Lima et al. (2000) indicated a related result that electrophoretic mobility corresponded to the soil dispersion and they showed phosphate-induced clay dispersion. Ilg et al. (2008) indicated that the critical value of zeta potential for phosphorus-induced dispersion was about -20 mV. Sugimoto et al. (2014) showed that zeta potential is a good indicator and fast coagulation regime is attained by reducing its magnitude below 25 mV for a carboxyl latex. Our result also showed that the soil dispersion was observed under -20 mV to -25 mV as shown in Fig. 2(a). In this research, different from the other researchers, we evaluated the influence of phosphate sorption on the soil dispersion by calculating the repulsive potential energy based on the zeta potential.

CONCLUSIONS

We successfully evaluated the influence of phosphate sorption on the Ferralsol dispersion by calculating repulsive potential energy based on zeta potential. The influence was systematically inspected for the Ferralsol. The soil was flocculative at lower pH. However, it became dispersive after phosphate sorption. Because the soil dispersion sometimes causes soil erosion and a decrease of soil permeability and soil erosion, it is better to avoid the dispersive condition when applying phosphate fertilizers even if the soil is initially flocculative. Moreover, because phosphate is easily conveyed by soil particles with moving water to the water environment when the soil is dispersed after phosphate sorption, the soil must be maintained in flocculative condition in order to use phosphate effectively and prevent soil erosion and water contamination.

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