



# International Journal of **Soil Science**

ISSN 1816-4978



Academic  
Journals Inc.

[www.academicjournals.com](http://www.academicjournals.com)

### Effect of Si/Al Ratio of Allophane on Competitive Adsorption of Phosphate and Oxalate\*

<sup>1,2</sup>M. Abdalla Elsheikh, <sup>1</sup>N. Matsue and <sup>1</sup>T. Henmi

<sup>1,2</sup>Laboratory of Applied Chemistry for Environment Industry, Faculty of Agriculture,  
Ehime University, 3-5-7 Tarumi, Matsuyama 790-8566, Japan

<sup>2</sup>Department of Soil and Environment Sciences, Faculty of Agriculture,  
University of Khartoum, Shambat, Sudan

**Abstract:** Allophane is a soil clay constituent with high adsorption capacity for cationic and anionic solutes and the adsorption characteristics depend on its Si/Al molar ratio. Adsorption experiments of phosphate and oxalate on two natural allophane samples with low (0.67; KyP) and high (0.99; KnP) Si/Al ratios were conducted at initial adsorbate concentration of up to 0.6 mM and at pH of 5.0 to 7.0. In both single and binary (equimolar phosphate and oxalate) adsorbates systems, KnP had less capacity for adsorption of both phosphate and oxalate than KyP had, because in the structure of KnP, accessory Si is already adsorbed onto aluminol groups to which phosphate and oxalate will be adsorbed. For KyP with lower Si/Al ratio and higher adsorption capacity, the efficiency of phosphate to depress the adsorption of coexisting oxalate,  $E_{\text{OX}+\text{P}}$ , was always greater than the reverse efficiency,  $E_{\text{P}+\text{OX}}$ , at a same condition; the ratio of oxalate/phosphate adsorbed in the binary system was less than unity and the ratio decreased with increasing pH and initial adsorbate concentration. These indicated higher selectivity of KyP for phosphate than for oxalate and the selectivity increased with increasing the competition between phosphate and oxalate toward KyP. KnP with higher Si/Al ratio showed higher selectivity for phosphate than KyP did, but the ratio of oxalate/phosphate adsorbed was almost constant when pH and initial adsorbate concentration were raised. This means that even under the lowest pH and the lowest adsorbate concentration examined (pH 5.0, 80  $\mu\text{M}$ ), the competition between phosphate and oxalate toward KnP was already severe and further increase in the phosphate selectivity was not caused.

**Key words:** Selectivity, efficiency, Langmuir equation

### INTRODUCTION

Allophane is a main clay component of volcanic ash soils and podzols and a series name of naturally occurring amorphous hydrous aluminium silicate (Wada and Harward, 1974). The aluminium silicate had not been believed to have definite morphology and structure. However, Henmi and Wada (1976) found that allophane had definite hollow spherical morphology with some defects or pores and diameter of the hollow sphere was recently estimated as 4.2 nm (Abidin *et al.*, 2006). The Si/Al atomic molar ratio of natural and synthetic allophane samples ranges from 0.6 to 1.0 depending on the environment in which it is formed. For example, in Si-rich volcanic deposits, the Si/Al ratio of allophane contained is close to 1.0 (Wada and Wada, 1977). The wall structure of the nano-ball allophane has been proposed as aluminium-nesosilicate structure composed of curved gibbsite sheet with monomeric  $\text{SiO}_4$  tetrahedra attached to it (Abidin *et al.*, 2007). This structure is same as that of tubular imogolite, except for the defects or pores in the wall of allophane hollow sphere.

**Corresponding Author:** Mohammed Abdalla Elsheikh, Laboratory of Applied Chemistry for Environment Industry,  
Faculty of Agriculture, Ehime University, 3-5-7 Tarumi, Matsuyama 790-8566, Japan

\*Originally Published in International Journal of Soil Science, 2009

Adsorption of phosphate in soil constituents received much attention in soil chemical studies due to its important biogeochemical roles in environment (Parfitt, 1978; Guppy *et al.*, 2005; Arai and Sparks, 2007). This anion is easily adsorbed on allophonic soil (Pardo and Guadalix, 1990; Beck *et al.*, 1999) and very strongly adsorbed on natural nano-ball allophane samples (Johan *et al.*, 1997). Low-molecular-mass organic acids (LMMOAs) including oxalic, formic, citric, malic and acetic acids, can be of considerable ecological importance (Ryan *et al.*, 2001). They are secreted by plant root and released by microorganisms and play important roles in many processes at soil-root interface. Oxalate is a nearly ubiquitous dicarboxylate ligand that occurs in significant concentrations in soils, surface waters, sedimentary basins and chemical processing solutions (Fox and Comerford, 1990; Ryan *et al.*, 2001; Xu *et al.*, 2003; Qafoku and Felmy, 2007). Oxalate anion is easily adsorbed on natural nano-ball allophane (Hanudin *et al.*, 1999).

Interaction between phosphate and LMMOAs on clay minerals has a great importance for understanding their impacts on mineral dissolution and metal mobility in rhizosphere. The mobility and bioavailability of these ligands depends on characteristics of the mineral surface. Study on competitive adsorption between phosphate and LMMOAs 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 an acid soil (Hu *et al.*, 2001). The competitive adsorption of phosphate and oxalate on allophane was studied on a synthetic allophane and a natural allophanic soil (Jara *et al.*, 2006) and an allophane sample with low Si/Al ratio (0.67) separated from volcanic pumice grain (Elsheikh *et al.*, 2008). However, studies on competitive adsorption of phosphate and oxalate on allophane samples with different Si/Al ratios are still lacking. On the other hand, a literature on competitive adsorption between phosphate and LMMOAs in soils showed that previous studies were usually carried out at high adsorbate concentrations (1-100 mM) and resultant adsorption amounts of the adsorbates were much higher than those found in soils (Guppy *et al.*, 2005). Therefore, the aim of this research was to study competitive adsorption of phosphate and oxalate on two allophane samples with high (0.99) and low (0.67) Si/Al ratios at lower concentrations.

## MATERIALS AND METHODS

### Sample Preparations

Two species of pumice grains in Japan containing nano-ball allophane were used in this study: one with low Si/Al ratio designated as KyP, which was collected from Kurayoshi, Tottori prefecture and the other with high Si/Al ratio designated as KnP was taken from Kakino, Kumamoto prefecture. The KyP and KnP samples were prepared following the method of Henmi and Wada (1976). So as to obtain a pure nano-ball allophane sample that is free from contaminants such as volcanic glasses, opaline silica and imogolite, only the inner portion of the pumice grains were used. The separation was carried out by ultrasonification at 28 kHz and dispersion at pH 4 for KyP and at pH 10 for KnP. The collected samples were flocculated by adding saturated NaCl solution, then they were washed with water and stored as suspensions. The prepared allophane samples were subjected to X-ray diffractometry, infrared spectroscopy and thermal analysis and were proven to be free from contaminants mentioned above. The Si/Al ratio of the allophane samples was determined by acid oxalate method (Higashi and Ikeda, 1974) and Si/Al ratio was calculated as 0.67 for KyP and 0.99 for KnP.

### Adsorption Experiments

To the prepared allophane suspension, dilute HCl or NaOH solution was added to bring pH of the suspension to 5.0, 6.0 and 7.0. The obtained each allophane suspension contained about 100 mg of allophane at 105°C oven dry basis. In single adsorbate system, an adsorbate solution containing phosphate ( $\text{NaH}_2\text{PO}_4$ ) or oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ ) was prepared by mixing them with NaCl solution and

water. The pH of the solution was adjusted to 5.0, 6.0 or 7.0 by adding dilute HCl or NaOH solution. The obtained adsorbate solution (75 mL) was mixed with the allophane suspension of a same pH value (25 mL) in a 250 mL polypropylene centrifuge bottle and the mixture was shaken for 24 h. Initial concentration of phosphate or oxalate of the mixture was up to 600  $\mu\text{M}$  and NaCl concentration of the mixture was constant at 10 mM. The pH of the mixture was periodically kept as constant by adding dilute HCl or NaOH solution. After shaking, the mixture was centrifuged at 7500 rpm for 20 min. The supernatant was analyzed for phosphate by ascorbic molybdate method (Murphy and Riley, 1962) and for oxalate by  $\text{KMnO}_4$  titration method. The coexisting oxalate did not interfere phosphate determination at the concentrations used. The amount of phosphate or oxalate adsorbed was calculated from the difference between initial and final concentrations. In binary adsorbate system, adsorption experiments were carried out in a same way as in the single adsorbate system described above, but both phosphate and oxalate were contained in equimolar in the adsorbate solutions. Effect of pH on the adsorption of phosphate and oxalate on allophane was also examined similarly in the single adsorbate system, where phosphate or oxalate concentration was fixed at 400  $\mu\text{M}$  and pH of the allophane suspension and adsorbate solution was varied between 4.0 and 8.0.

The adsorption data were plotted according to the Langmuir adsorption equation below:

$$X = X_m KC / (1 + KC)$$

Where:

X = Amount of phosphate or oxalate adsorption ( $\mu\text{mol g}^{-1}$ )

K = A constant related to binding energy ( $\text{L } \mu\text{mol}^{-1}$ )

$X_m$  = Maximum phosphate or oxalate adsorption ( $\mu\text{mol g}^{-1}$ )

C = Equilibrium phosphate or oxalate concentration ( $\mu\text{mol L}^{-1}$ )

The equation can be rearranged and linearized as below:

$$C/X = 1/X_m K + C/X_m$$

## RESULTS AND DISCUSSION

### Single Adsorbate System

Figure 1 and 2 show adsorption isotherms of phosphate (Fig. 1) and oxalate (Fig. 2) on KyP and KnP samples at different constant pH values (5.0, 6.0 and 7.0). The isotherms indicated that the amount of phosphate and oxalate adsorbed on the allophane samples increased with increasing equilibrium solution concentration of the anions towards a maximum value and the amount of adsorption of phosphate was higher than that of oxalate on both allophane samples. These observations agree with previous studies (Violante and Gianfreda, 1993; Violante *et al.*, 1996; Jara *et al.*, 2006; Elsheikh *et al.*, 2008). All of the isotherms in Fig. 1 and 2 fitted well to the Langmuir equation,  $C/X = 1/X_m K + C/X_m$ , with  $R^2$  values of more than 0.99 (Table 1), indicating strong 1:1 type adsorption between aluminol groups on the two allophane samples and the two adsorbates.

In all combinations of adsorbate and adsorbent, the amount of adsorption decreased with increasing pH of the system (Fig. 1, 2, Table 1). This phenomenon is related to the charge characteristics of nano-ball allophane. Allophane possesses positive charge ( $\text{Al-OH}_2^+$ ) at lower pH at pore sites of the ball irrespective of the Si/Al ratio of allophane sample (Wada, 1987). At higher pH, allophane has no positive charge, but negative charges ( $\text{Si-O}^-$ ) generate at inner surface of the ball and the negative charges increase with increasing solution pH (Wada, 1987). Figure 3 shows the effect of pH on adsorption of phosphate and oxalate on KnP and KyP samples at a constant initial phosphate or oxalate concentration of 400  $\mu\text{M}$ . In case of phosphate adsorption, the amount of adsorption increased linearly with decreasing pH, due to increasing surface positive charge of allophane. In case

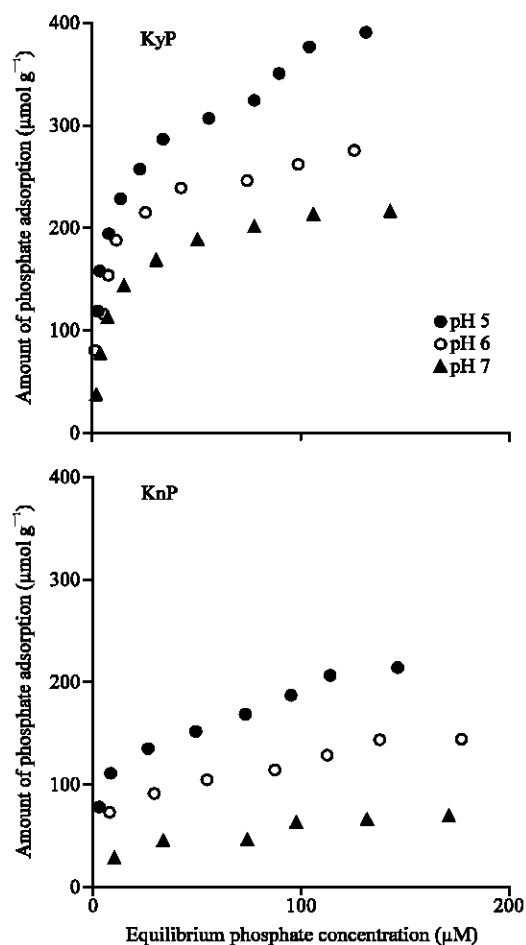


Fig. 1: Adsorption isotherms of phosphate in single adsorbate system

of oxalate, the amount of adsorption was greatest at around pH 5 and it decreased at both higher and lower pH values. The decrease in the amount of adsorption of oxalate at pH less than 5 may be attributed to an increase in soluble aluminium oxalate complex concentration when pH decreased (Bilinski *et al.*, 1986; Karlton, 1998). The complex becomes quantitatively important around pH 4 despite the increased positive surface charge on allophane due to the lower pH (Fig. 3) and this is consistent with previous adsorption studies onto goethite (Parfitt *et al.*, 1977), montmorillonite (Siffert and Espinasse, 1980), aluminum oxides (Violante *et al.*, 1991) and synthetic aluminium hydroxysulphate (Violante *et al.*, 1996). Change in chemical species of oxalate anion from divalent to monovalent with decreasing pH ( $pK_2 = 4.3$ ) may also be related to the decrease in the amount of adsorption of oxalate below pH 5.

Table 1 and Fig. 1, 2 also show that KyP with lower Si/Al ratio had higher adsorptivity for both phosphate and oxalate anions than KnP with higher Si/Al ratio had. This is ascribed to higher content of Al-OH and Al-OH<sub>2</sub> groups in the structure of KyP, because KyP has lower Si/Al ratio or higher Al content per unit mass than KnP has. Aluminol groups, Al-OH or Al-OH<sub>2</sub>, are responsible for phosphate and organic anions adsorptions in soils and clay minerals (Jara *et al.*, 2006). In the structure of allophane, the aluminol groups are only located at the pores of the wall of the hollow

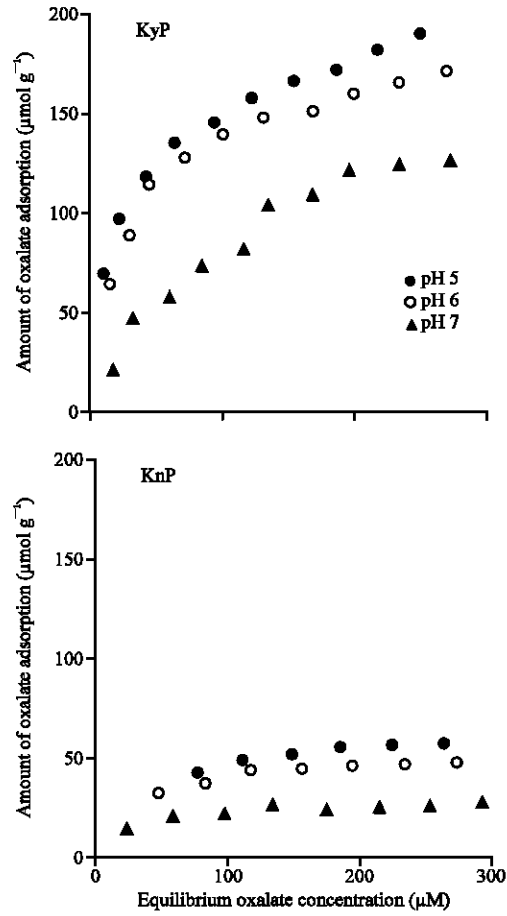


Fig. 2: Adsorption isotherms of oxalate in single adsorbate system

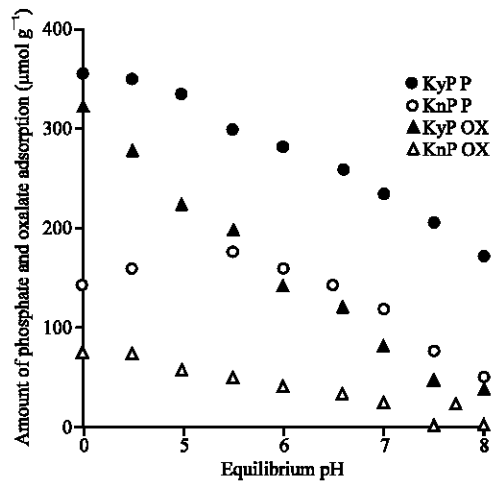


Fig. 3: Effect of pH on the adsorption of phosphate and oxalate in single system. Initial concentration of phosphate or oxalate was fixed as 400 µM

Table 1: Langmuir parameters for phosphate and oxalate adsorption on allophane

Adsorbate	Sample	Experiment	Parameter	pH		
				5.0	6.0	7.0
Phosphate	KyP	Single	$X_m$	400.00	285.70	277.30
			K	0.101	0.111	0.113
			$R^2$	0.992	0.998	0.999
		Binary	$X_m$	270.30	212.80	188.70
			K	0.147	0.113	0.108
			$R^2$	0.997	0.995	0.997
	KnP	Single	$X_m$	256.40	158.70	78.10
			K	0.031	0.044	0.050
			$R^2$	0.994	0.982	0.999
		Binary	$X_m$	114.90	97.10	113.60
			K	0.122	0.044	1.120
			$R^2$	0.998	0.949	0.128
Oxalate	KyP	Single	$X_m$	204.10	188.70	185.20
			K	0.035	0.031	0.009
			$R^2$	0.993	0.998	0.972
		Binary	$X_m$	129.90	95.20	52.10
			K	0.079	0.057	0.055
			$R^2$	0.999	0.983	0.979
	KnP	Single	$X_m$	68.50	52.10	28.70
			K	0.019	0.032	0.044
			$R^2$	0.997	0.999	0.996
		Binary	$X_m$	61.70	77.50	23.40
			K	0.013	0.006	0.015
			$R^2$	0.936	0.86	0.835

spherules (Henmi and Huang, 1985). Fundamental structure of allophane is considered to be that of KyP and allophane with higher Si/Al ratio like KnP has excess Si atoms accessorially attached to the fundamental structure (Henmi *et al.*, 1997). The excess Si atoms may also be adsorbed onto the aluminol groups, leading less aluminol groups or adsorption sites for phosphate and oxalate on KnP.

### Binary Adsorbate System

Competitive adsorption of phosphate and oxalate on allophane was examined by binary adsorption system, in which equimolar phosphate and oxalate anions were simultaneously added to allophane. Figure 4 and 5 show adsorption isotherms of phosphate (Fig. 4) and oxalate (Fig. 5) on two allophane samples in the binary adsorbate system. The shape of the isotherms and the effect of pH on the amount of adsorption were similar to the corresponding figures in the single adsorbate system for phosphate (Fig. 1) and oxalate (Fig. 2). KyP with lower Si/Al ratio showed higher adsorptivity for the two anions than KnP did and the amount of adsorption of phosphate was higher than that of oxalate: these trends were also same as the case of the single adsorbate system described in the previous section.

When the isotherms in Fig. 4 and 5 (binary adsorbates system) were compared with corresponding isotherms in Fig. 1 and 2 (single adsorbate system), decreases in the amount of adsorption of phosphate or oxalate in the binary system were observed in all cases. For example, in single adsorbate system, the amount of adsorption of phosphate on KnP at equilibrium phosphate concentration of  $100 \mu\text{mol L}^{-1}$  at pH 5 was nearly  $200 \mu\text{mol g}^{-1}$  (Fig. 1), but that in binary adsorbate system was about  $110 \mu\text{mol g}^{-1}$  (Fig. 4). The decrease in the amount of adsorption of phosphate is due to the effect of the coexisting equimolar amount of oxalate anion or the result of the competitive adsorption between phosphate and oxalate anions onto allophane.

In order to quantitatively estimate the ability of coexisting equimolar oxalate to depress adsorption of phosphate in the binary adsorbates system, the efficiency of oxalate on the depression of adsorption of phosphate was calculated according to the expression of Deb and Datta (1967).

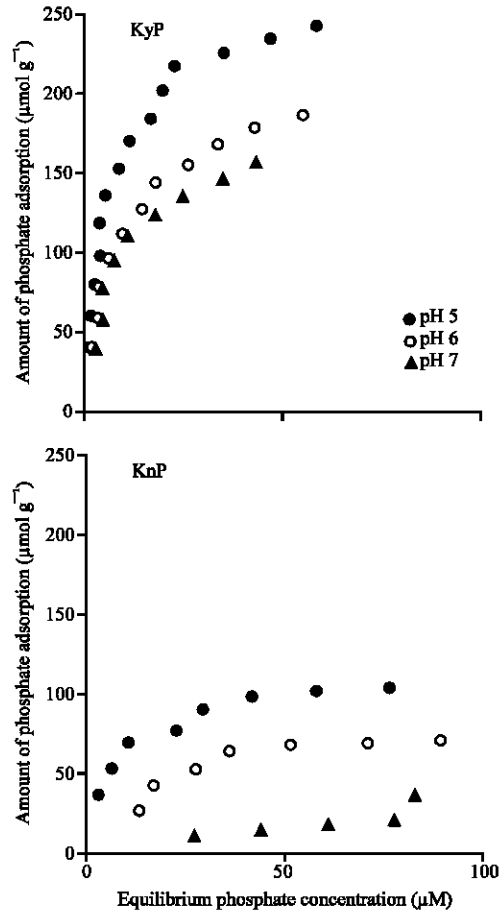


Fig. 4: Adsorption isotherms of phosphate in binary adsorbates system

$$E_{P-OX} = 100 (P_S - P_B) / P_S \quad (1)$$

where,  $E_{P-OX}$  is an efficiency of oxalate in reducing adsorption of phosphate in %,  $P_S$  is the amount of adsorption of phosphate in the single adsorbate system and  $P_B$  is the amount of adsorption of phosphate in the binary adsorbates system.

The ability of coexisting equimolar phosphate to depress adsorption of oxalate in the binary adsorbates system,  $E_{O-XP}$ , was also estimated similarly. This estimation method was frequently used in the studies on competitive adsorption on soils and soil constituents (Violante *et al.*, 1991; Violante and Giafreda, 1993; De Cristofaro *et al.*, 2000; Jara *et al.*, 2006; Guan *et al.*, 2006). The calculated  $E_{P-OX}$  and  $E_{O-XP}$  values for the two allophane samples at various pH and initial phosphate and oxalate concentrations are shown in Table 2.

When the  $E_{P-OX}$  values between two allophane samples were compared in Table 2, they were much higher for KnP than for KyP at all pHs and initial phosphate concentrations. This means the coexisting equimolar oxalate more effectively depressed adsorption of phosphate on KnP with higher Si/Al ratio than on KyP with lower Si/Al ratio. As has been discussed, the KnP sample had lower phosphate adsorptivity than KyP had (Fig. 1) and the lower adsorptivity of KnP had been ascribed to its lower available aluminol groups per unit mass, as compared to KyP. Therefore, at a same initial phosphate (and oxalate) concentration in the binary adsorbates system, the competition between



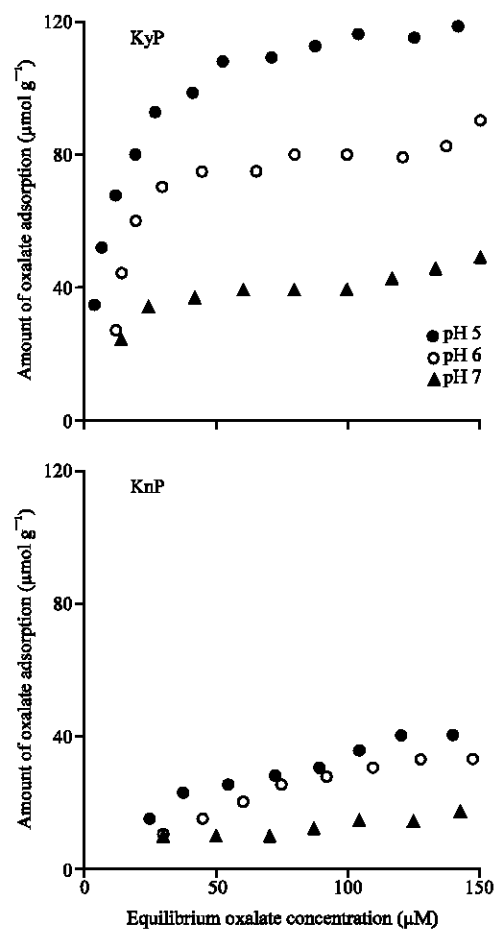


Fig. 5: Adsorption isotherms of oxalate in binary adsorbates system

Table 2:  $E_{P-OX}$  and  $E_{OX+P}$  values at various pHs

pH	Initial concentration of phosphate and oxalate (µM)	$E_{P-OX}$		$E_{OX+P}$	
		KyP	KnP	KyP	KnP
5.0	80	1.6	9.6	3.6	19.9
	120	1.2	18.3	5.7	28.5
	160	2.8	23.8	9.7	16.4
	200	4.5	27.0	17.5	12.2
	240	4.1	27.7	21.4	13.1
6.0	280	8.9	30.7	23.1	10.0
	80	0.0	25.2	7.7	35.9
	120	2.7	24.2	16.7	25.8
	160	6.2	32.8	30.5	24.3
	200	11.2	29.1	38.7	20.3
7.0	240	13.1	34.8	35.8	21.9
	80	1.9	59.1	22.2	53.4
	120	2.7	20.7	33.4	33.0
	160	6.4	30.2	42.2	32.4
	200	7.0	28.0	40.3	28.6

phosphate and oxalate toward aluminol groups on allophane was more severe for KnP than for KyP, because the numbers of aluminol groups for adsorption of phosphate and oxalate is less on KnP than on KyP. Due to such severer competition on KnP, the adsorption of phosphate was more depressed by coexisting oxalate and the  $E_{P-OX}$  values became greater, as compared to the case of KyP. The increasing trend in the  $E_{P-OX}$  value was also observed with increasing initial concentration of phosphate (and oxalate) in almost combinations of pH and sample and with increasing pH in each sample (Table 2). The increase in initial concentration of phosphate (and oxalate) caused increase in competition between phosphate and oxalate toward KyP. The increase in pH decreases the amount of adsorption sites on KyP for phosphate and oxalate and this also increase competition between phosphate and oxalate toward KyP.

Therefore, it is concluded that the increase in competition between phosphate and oxalate tends to increase  $E_{P-OX}$  value and the increase in competition is caused by three factors: increase in Si/Al ratio of allophane, increase in initial adsorbates concentrations and increase in solution pH. For  $E_{OX-P}$  values, similar trend was also observed (Table 2), indicating adsorption of oxalate was also more depressed by coexisting phosphate under stronger competition conditions. However this trend, increasing E value with increasing competition, did not observed for  $E_{P-OX}$  of KnP at pH 7 and  $E_{OX-P}$  of KnP at all pH values, where the E values did not increase with increasing the adsorbate concentration. In these cases, the isotherms in the binary adsorbates system did not fit well to the Langmuir equation (lower  $R^2$  values in Table 1) and the amounts of adsorption of phosphate and oxalate were very low (Fig. 4, 5). Therefore in these exceptional four cases, even at the lowest initial concentration in Table 2 (80  $\mu$ M), competition between phosphate and oxalate was already severe enough. Further increase in the initial concentration may caused sorption of phosphate and oxalate onto allophane with different mechanism from the other cases.

On the other hand, when corresponding  $E_{P-OX}$  and  $E_{OX-P}$  values were compared for the KyP sample,  $E_{OX-P}$  was greater than  $E_{P-OX}$  in all cases (Table 2). This means that, for KyP with lower Si/Al ratio, the depression in the adsorption of oxalate caused by coexisting phosphate is greater than the depression in the adsorption of phosphate caused by coexisting oxalate. In other word, for KyP, more oxalate anions to be adsorbed were superseded by the coexisting phosphate anions and less phosphate were superseded by oxalate. For KnP with higher Si/Al ratio, clear difference between  $E_{P-OX}$  and  $E_{OX-P}$  values was not noticed.

Figure 6 shows the amounts of adsorption of phosphate and oxalate in the single adsorbate system and sum of the amounts of adsorption of phosphate and oxalate in the binary adsorbates system, for KyP and KnP at pH 5, as a function of initial anions concentration. At pH 6 and 7, similar plots were obtained and therefore not presented here. In binary system in Fig. 6, the horizontal axis indicates initial concentrations of both phosphate and oxalate: for example, horizontal 200  $\mu$ M means a mixed solution containing 200  $\mu$ M of phosphate and 200  $\mu$ M of oxalate was added. For KyP, the sum of phosphate and oxalate adsorptions in the binary adsorbates system was smaller than the sum of phosphate and oxalate adsorptions in the single adsorbate system. This is due to the depression effect caused by the coexisting counterpart as has been shown in Table 2. However, the sum of phosphate and oxalate adsorptions in the binary system was higher than the amount of phosphate adsorption in the single system. This means that, for example, when 200  $\mu$ M of oxalate coexisted with 200  $\mu$ M of phosphate, the oxalate anions could adsorb on sites of KyP where 200  $\mu$ M of phosphate in the single adsorbate system could not adsorb. Our findings indicated that many sites on KyP with low Si/Al ratio are specific for phosphate, some others are common to both the anions with higher affinity for phosphate than for oxalate. However, some sites are specific for oxalate anions. Similar results were obtained by Hingston *et al.* (1971) for goethite and gibbsite, Violante *et al.* (1991) for aluminum oxides, Violante and Giafreda (1993) for aluminum hydroxide-montmorillonite complex, Bhatti *et al.* (1998) for Andisols and Wu *et al.* (2002) for  $\gamma$ - $Al_2O_3$ . On the other hand for KnP with

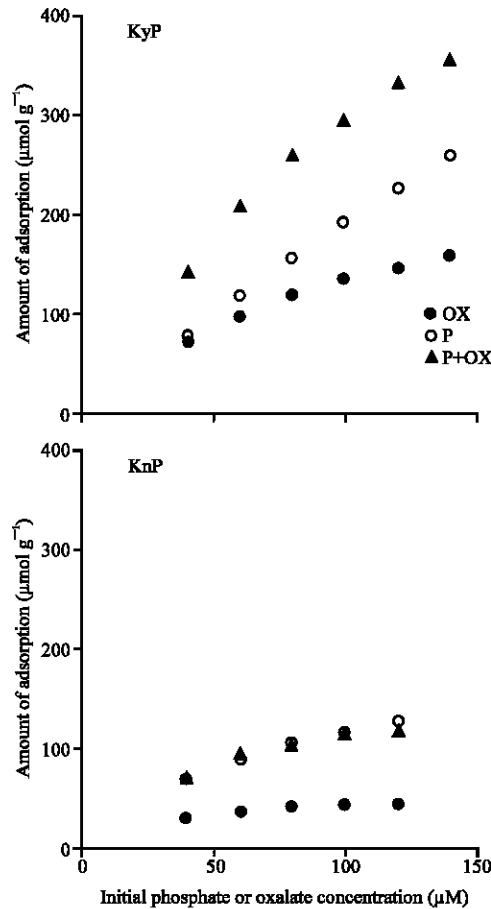


Fig. 6: Amount of adsorption of phosphate and oxalate in single adsorbate system and sum of amount of adsorption of phosphate and oxalate in binary adsorbates system

higher Si/Al ratio (Fig. 6), the sum of phosphate and oxalate adsorption in the binary system was nearly equal to the amount of phosphate adsorption in the single system. This means that, on KnP, adsorption site is common to both phosphate and oxalate and oxalate can not adsorb on sites where phosphate could not adsorb. Similar, phenomenon was found by Violante and Giafreda (1993) on ordered Al precipitation products.

Figure 7 shows oxalate adsorption/phosphate adsorption ratio as a function of initial phosphate (and oxalate) concentration in the binary adsorbates system, for KyP and KnP at pH 5, 6 and 7. In all cases, the ratio was less than unity, indicating higher adsorption selectivity of phosphate than oxalate on allophane in the binary adsorbates system. In KyP, the  $OX_B/P_B$  ratio decreased with increasing pH and with increasing initial phosphate and oxalate concentrations. As has been discussed, the increase in both pH and initial concentration cause increase in competition between phosphate and oxalate adsorption on allophane. Therefore the results in Fig. 7 indicated that the increase in the competition on KyP depressed more the adsorption of oxalate than the adsorption of phosphate. Similar trend was also observed by Violante and Giafred (1993, 1995), He *et al.* (1999) and DeCristofaro *et al.* (2000). Whereas in KnP with higher Si/Al ratio, the  $OX_B/P_B$  ratios are nearly constant at 0.4 except for those at lower concentration at pH 7 (Fig. 7). This feature is very different

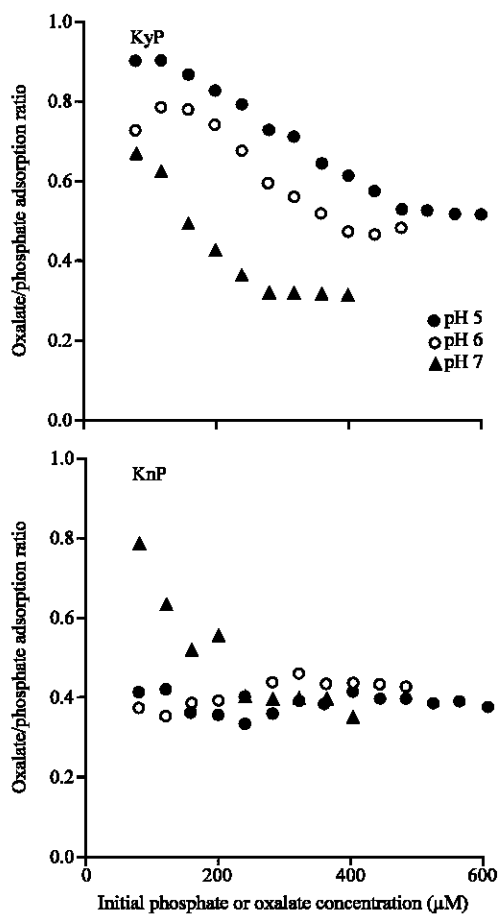


Fig. 7: Oxalate/phosphate adsorption ratio in binary adsorbates system

form that of KyP and the  $OX_B/P_B$  ratio of 0.4 for KnP is lower than almost  $OX_B/P_B$  ratios for KyP (Fig. 7). The independence of the  $OX_B/P_B$  ratio on pH and initial concentration and lower  $OX_B/P_B$  ratio in KnP indicate that even at lower pH and lower initial concentration in Fig. 7, the competition between phosphate and oxalate is already severe in KnP. Therefore in KnP, increases in pH and initial concentration did not cause further increase in the competition and the  $OX_B/P_B$  ratio did not decrease further.

### CONCLUSIONS

Competitive adsorption between phosphate and LMMOAS such as oxalate on soil constituents is important in views of agriculture and environmental conservation. Competitive adsorption behavior between phosphate and oxalate onto allophane were largely dependent on Si/Al ratio of allophane. The conclusions are as follow:

- Phosphate is more selectively adsorbed than oxalate onto allophane.
- The adsorption selectivity of phosphate against oxalate onto allophane increases with enhancement of the competition between phosphate and oxalate.

- The enhancement of the competition is caused by increasing pH and by increasing phosphate and oxalate concentrations.
- Allophane with higher Si/Al ratio has higher phosphate adsorption selectivity than allophane with lower Si/Al ratio has, because the competition is already severe due to restricted amount of adsorption sites in the former.
- When competitive adsorption of phosphate, oxalate and other LMMOAs on soils with much allophane content is studied, the Si/Al ratio of allophane in the soils should be measured and be taken into account in the analyses of observations.

## REFERENCES

- Abidin, Z., N. Matsue and T. Henmi, 2006. Validity of proposed model for the chemical structure of allophane with nano-ball morphology. *Clay Sci.*, 12: 267-269.
- Abidin, Z., N. Matsue and T. Henmi, 2007. Differential formation of allophane and imogolite: Experimental and molecular orbital study. *J. Comput. Aided Mater. Des.*, 14: 5-18.
- Arai, Y. and D.L. Sparks, 2007. Phosphate reaction dynamics in soils and soil minerals: A multiscale approach. *Adv. Agron.*, 94: 135-179.
- Beck, M.A., W.P. Robarge and W. Buol, 1999. Phosphorus retention and release of anions and organic carbon by two Andisols. *Eur. J. Soil. Sci.*, 50: 157-164.
- Bhatti, J.S., N.B. Comerford and C.T. Johnston, 1998. Influence of oxalate and soil organic matter on sorption and desorption of phosphate onto a spodic horizon. *Soil Sci. Soc. Am. J.*, 62: 1089-1095.
- Bilinski, H., L. Horvath, N. Ingriand and S. Sjöberg, 1986. Equilibrium aluminium hydroxo-oxalate phases during initial clay formation:  $H^+ - Al^{3+} - oxalic\ acid - Na^+$  system. *Geochim. Cosmochim. Acta*, 50: 1911-1922.
- De Cristofaro, A., J.Z. He, D.H. Zhou and A. Violante, 2000. Adsorption of phosphate and tartrate on hydroxy-aluminum-oxalate precipitates. *Soil Sci. Soc. Am. J.*, 64: 1347-1355.
- Deb, D.L. and N.P. Datta, 1967. Effects of associating anions on phosphorus retention in soil. I. Under variable phosphorus concentration. *Plant Soil*, 26: 303-316.
- Elsheikh, M.A., Z. Abidin, N. Matsue and T. Henmi, 2008. Competitive adsorption of oxalate and phosphate on allophane at low concentration. *Clay Sci.*, 13: 181-188.
- Fox, T.R. and N.B. Comerford, 1990. Low-molecular-weight organic acids in selected forest soils of the south eastern USA. *Soil Sci. Soc. Am. J.*, 54: 1139-1144.
- Guan, X.H., C. Shang and G.H. Chen, 2006. Competitive adsorption of organic matter with phosphate on aluminum hydroxide. *J. Colloid Interface Sci.*, 296: 51-58.
- Guppy, C.N., N.W. Menzies, P.W. Moody and F.P.C. Blamey, 2005. Competitive sorption reactions between phosphorus organic matter in soil: A review. *Aust. J. Soil Res.*, 43: 189-202.
- Hanudin, E., N. Matsue and T. Henmi, 1999. Adsorption of some low molecular weight organic acids on nano-ball allophane. *Clay Sci.*, 11: 57-72.
- He, J.Z., A. De Cristofaro and A. Violante, 1999. Comparison of adsorption of phosphate, tartrate and oxalate on hydroxy aluminum montmorillonite complexes. *Clays Clay Miner.*, 47: 226-233.
- Henmi, T. and K. Wada, 1976. Morphology and composition of allophane. *Am. Miner.*, 61: 379-390.
- Henmi, T. and P.M. Huang, 1985. Removal of phosphorus by poorly ordered clays as influence by heating and grinding. *Applied Clay Sci.*, 1: 133-144.
- Henmi, T., N. Matsue and E. Johan, 1997. Change in the surface acidity of allophane with low Si/Al ratio by the interaction with ortho-silicic acid. *Jap. J. Soil. Sci. Plant Nutr.*, 68: 514-520 (In Japanese with English abstract).

- Higashi, T. and H. Ikeda, 1974. Dissolution of allophane by acid oxalate solution. *Clay Sci.*, 4: 205-211.
- Hingston, F.J., A.M. Posner and J.P. Quirk, 1971. Competitive adsorption of negatively charged ligands on oxide surfaces. *Discuss. Faraday Soc.*, 52: 334-342.
- Hu, H.Q., J.Z. He, X.Y. Li and F. Liu, 2001. Effect of several organic acids on phosphate adsorption by variable charge soils of central China. *Environ. Int.*, 26: 353-358.
- Jara, A.A., A. Violante, M. Pigna and M.L. Mora, 2006. Mutual interactions of sulfate, oxalate, citrate and phosphate on synthetic and natural allophanes. *Soil Sci. Soc. Am. J.*, 70: 337-346.
- Johan, E., N. Matsue and T. Henmi, 1997. Phosphate adsorption on nano-ball allophane and its molecular orbital analysis. *Clay Sci.*, 10: 259-270.
- Karltun, E., 1998. Modelling  $\text{SO}_4^{2-}$  surface complexation on variable charge minerals. II. Competition between  $\text{SO}_4^{2-}$ , oxalate and fulvate. *Eur. J. Soil Sci.*, 49: 113-120.
- Lopez-Hernandez, D., G. Siegert and J.V. Rodriguez, 1986. Competitive adsorption of phosphate with malate and oxalate by tropical soils. *Soil Sci. Soc. Am. J.*, 50: 1460-1462.
- Murphy, J. and J.P. Riley, 1962. A modified single solution method for determination of phosphate in natural waters. *Anal. Chim. Acta*, 27: 31-36.
- Pardo, M.T. and M.E. Guadalix, 1990. Phosphate sorption in allophanic soils and release of sulphate, silicate and hydroxyl. *J. Soil Sci.*, 41: 607-612.
- Parfitt, R.L., A.R. Fraser and V.C. Farmer, 1977. Adsorption on hydrous oxides III. Fulvic acids and humic acid on goethite, gibbsite and imogolite. *Eur. J. Soil. Sci.*, 28: 289-296.
- Parfitt, R.L., 1978. Anion adsorption by soil and soil materials. *Adv. Agron.*, 30: 1-50.
- Qafoku, O. and A.R. Felmy, 2007. Development of accurate chemical equilibrium models for oxalate species to high ionic strength in the system: Na-Ba-Ca-Mn-Sr-Cl- $\text{NO}_3$ - $\text{PO}_4$ - $\text{SO}_4$ - $\text{H}_2\text{O}$  at 25°C. *J. Solution Chem.*, 36: 81-95.
- Ryan, P.R., E. Delhaize and D.L. Jones, 2001. Function and mechanism of organic anion exudation from plant roots. *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, 52: 527-560.
- Siffert, B. and P. Espinasse, 1980. Adsorption of organic diacids and sodium polyacrylate onto montmorillonite. *Clays Clay Miner.*, 28: 381-387.
- Violante, A., C. Colombo and A. Buondonno, 1991. Competitive adsorption of phosphate and oxalate by aluminum oxides. *Soil Sci. Soc. Am. J.*, 55: 65-70.
- Violante, A. and L. Gianfreda, 1993. Competition in adsorption between phosphate and oxalate on an aluminum hydroxide montmorillonite complex. *Soil Sci. Soc. Am. J.*, 57: 1235-1241.
- Violante, A. and L. Gianfreda, 1995. Adsorption of Phosphate on Variable Charge Mineral: Competition Effect of Organic Ligands. In: *Environmental Impact of Soil Component Interactions*, Huang, P.M., J. Berthelin, J.M. Bollag, W.B. McGill and A.L. Page (Eds.). Vol. 2. CRC Press Florida, Boca Roton, ISBN: 10: 0873719158, pp: 29-38.
- Violante, A., M.A. Rao, A. De chiara and L. Gianfreda, 1996. Sorption of phosphate and oxalate by a synthetic aluminium hydroxysulphate complex. *Eur. J. Soil Sci.*, 47: 241-247.
- Wada, K. and M.E. Harward, 1974. Amorphous clay constituents in soils. *Adv. Agron.*, 26: 211-260.
- Wada, S.I. and K. Wada, 1977. Density and structure of allophane. *Clay Miner.*, 12: 289-298.
- Wada, S.I., 1987. Adsorption of Al (III) on allophane, imogolite, goethite and noncrystalline silica and the extractability of the adsorbed Al (III) in 1M KCl solution. *Soil Sci. Plant Nutr.*, 33: 487-491.
- Wu, C.H., S.L. Lo, C.F. Lin and C.Y. Kuo, 2002. Modeling competitive adsorption of molybdate, sulfate, selenate and selenite using a Freundlich-type multi-component isotherm. *Chemosphere*, 47: 283-292.
- Xu, R., A. Zhao and G. Ji, 2003. Effect of low-molecular weight organic anions on surface charge of variable charge soils. *J. Colloid Interface Sci.*, 264: 322-326.