

**Change in Surface Charge Properties of Nano-Ball Allophane with Different Si/Al Ratios During Competitive Oxalate and Phosphate Adsorption**

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**Abstract:** Change in surface charge of nano-ball allophane samples with different Si/Al ratios were studied under varying amounts of phosphate and oxalate adsorption. Cation exchange capacity increased with increase in solution pH and after competitive adsorption of phosphate and oxalate. On the other hand, anion exchange capacity decreased with increase in solution pH, and after competitive adsorption of phosphate and oxalate. Allophane samples after competitive adsorption of phosphate and oxalate with high Si/Al ratio were found to have higher cation exchange capacity than those of lower Si/Al ratio. The findings of this work suggested that increasing pH and competitive adsorption of phosphate and oxalate compounds result in changing the surface charge characteristics of nano-ball allophane.

**Key words:** Surface charge, competitive adsorption, nano-ball allophane, oxalate, phosphate.

## INTRODUCTION

Surface charge characteristics of colloids are critical for the retention and mobility of nutrients and pollutants in soil. Minerals that constitute the

colloidal fraction of soil are classified based on the differences in their surface charge properties into (i) permanent and (ii) variable charge minerals (Chorover *et al.* 2004; Moghimi *et al.* 2013). Allophane, is a mineral found in soils formed from volcanic ash, has unique properties of variable charge, with the positive and negative charges separated from each other in the nano-ball allophane structure. Whereas the positive charge results from the aluminol group ( $\text{Al-OH}_2^+$ ) located at the pores of the wall of hollow spherules, the negative charges come from the silanol group ( $\text{Si-O}^-$ ) at the inner surface of the hollow sphere of nano-ball structure (Parfitt 1980). Ion adsorption on allophane has been shown to affect its surface charge properties (Harsh *et al.* 1992; Elhadi *et al.* 2001). Cation exchange capacity (CEC) and anion exchange capacity (AEC) values either decrease or increase depending upon material adsorbed. Decreases in CEC and increases in AEC have been reported after adsorption of the cations copper and zinc on nano-ball allophane (Ghoneim 2006; 2007). Conversely, adsorption of phosphate (P), oxalate (Ox), and molybdate have been shown to result in an increase in CEC and decline in AEC values (Johan *et al.* 1999; Hanudin *et al.* 2000; Elhadi *et al.* 2001). Oxalate is a carboxylate ligand that occurs in significant concentrations in soils, surface waters, sedimentary basins and in chemical processing solutions, among other sources (Xu *et al.* 2003; Qafoku and Felmy 2007). The Ox anion has been shown to be easily adsorbed on natural nano-ball allophane (Hanudin *et al.* 1999; Elsheikh *et al.* 2008; 2009). The presence of other anions in the soil could affect its adsorption on allophane and other variable charge minerals and affect their charge characteristics.

Phosphorus is an essential nutrient element for plant growth and has great importance from agronomic and environmental aspects. Under acidic conditions phosphate is easily adsorbed on soils with high composition of minerals of variable charge, including allophane (Beck *et al.* 1999). Strong adsorption of P has been reported on the natural nano-ball allophane by Johan *et al.* (1997) and Elsheikh *et al.* (2008; 2009). The strong adsorption, on nano-ball allophane, of both Ox and P suggests that the presence of the two anions in solutions could result in competitive adsorption with effects on surface charge characteristics of the mineral and mobility of the anions.

Studies of the competitive adsorption of P and Ox on soil constituents like allophane are of great importance because they may be useful in predicting and explaining the behavior of P and Ox in the soil environment. While studies on surface charge properties after single anion adsorption of Ox (Hanudin *et al.* 2000; Xu *et al.* 2003) and P (Johan *et al.* 1999) have received attention from many researchers, binary adsorbate systems are closer to the natural environment. There is a paucity of studies on the change of surface charge properties of nano-ball allophane due to competitive adsorption of P and Ox. Therefore, the objective of this study is to determine the effects of competitive adsorption of Ox and P on charge characteristics of nano-allophane with different Si/Al ratios.

## MATERIALS AND METHODS

### Allophane Characteristics

Two nano-allophane samples, separated from volcanic pumice were collected from different field locations in Japan, were utilized in this study. One of the samples, obtained from Kurayoshi, Tottori prefecture (KyP), had Si/Al ratio of 0.67, while the other from Kakino, Kumamoto prefecture (KnP), had Si/Al of 0.99. The KyP and KnP samples were prepared as described by Henmi and Wada (1976). In order to obtain a pure nano-ball allophane sample, 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 ultrasonication at 28 kHz and dispersion at pH 4 for KyP and pH 10 for KnP. The KyP sample, contained more Al than Si and was hence easier to disperse under acidic conditions, whereas the KnP with a higher ratio of Si to Al that was better dispersed under alkaline conditions. The samples were flocculated by saturated NaCl solution, washed with water, and stored as suspension. The prepared allophane samples were characterized by X-ray diffractometry, infrared spectroscopy and differential thermal analysis (DTA). Concentrations of Al, Si and Fe were determined using the Polarized Zeeman Atomic Absorption Spectrophotometer (AAS). The chemical structure of nano-ball allophane samples is shown in Fig. 1.

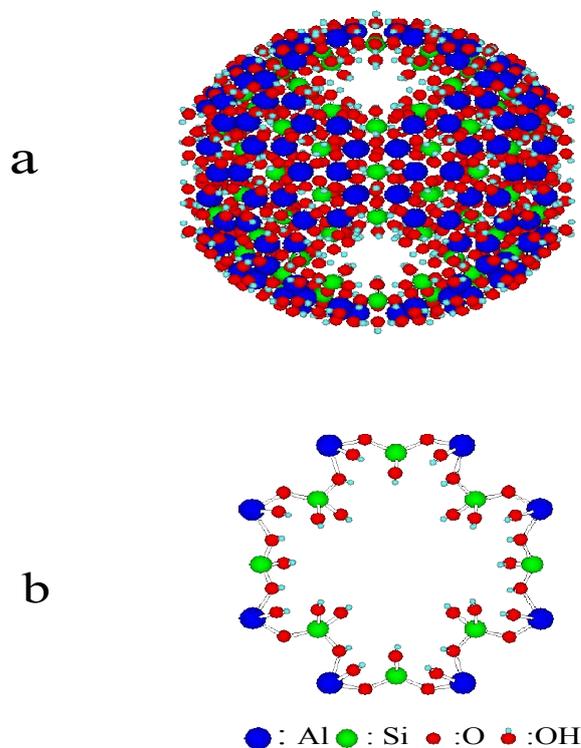


Fig. 1. (a) Whole structure of allophane unit particle and (b) schematic presentation of atomic arrangements at pore region of the particle. Pore opening is 0.3 to 0.5 nm

### Competitive Adsorption Experiments

Experimental procedures of competitive adsorption between P and Ox on nano-ball allophane samples were done as described by Elsheikh *et al.* (2009). The concentration of added P or Ox were adjusted to desired P or Ox adsorption value at equilibrium, after various preliminary experiments. Concentrations representing P/Ox molar ratios of 0/0, 4/0, 3/1, 2/2, 1/3 and 0/4 were chosen. The competitive adsorption experiment was carried out by equilibrating 25 ml suspensions containing 100 mg allophane (105 °C oven dry basis), with the P and/or Ox solutions in 250 ml tubes of known weight. Total Na concentration

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of the mixture was adjusted at 10 mM by adding NaCl and water to give total volume of 100 ml. Each suspension or solution (allophane sample and NaCl, P or/and Ox) was adjusted to pH 4 with HCl or NaOH solution before mixing. The mixtures were shaken for 24 hours, and then centrifuged at 7500 rpm for 15 min. The pH, and concentrations of P, Ox, Na and Cl, of the supernatants were measured. The concentration of P was analyzed colorimetrically (Murphy and Riley 1962), Ox by titration with 1 mM  $\text{KMnO}_4$ , Na by AAS, and Cl by the colorimetric mercuric thiocyanate method (Huang and Johns 1966). Each centrifuge tube plus residue was weighed to determine the volume of retained solution and the adsorbed and retained Na and Cl were extracted with 100 mL of 1M  $\text{NH}_4\text{NO}_3$ , and the amounts of Na and Cl on the allophane samples representing CEC and AEC, respectively, were calculated.

## RESULTS AND DISCUSSION

### Allophane Characteristics

Allophane gave an amorphous feature in X-ray diffraction pattern, with the maximum band varying from 1.23 to 1.45 nm, depending on its Si/Al ratio (Fig 2).

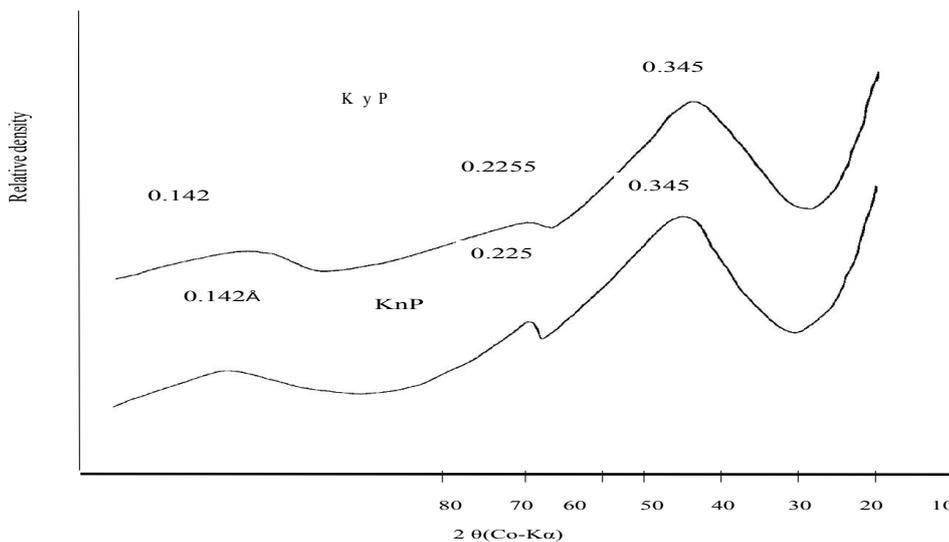


Fig. 2. X-ray diffraction patterns (nm) of the allophane samples

The two nano-ball allophane samples showed the common feature as reported elsewhere for the allophane samples (Fig 3). The major absorption bands appear in five regions with the frequencies of maximum absorption near 3470, 1440, 1000, 567 and 435  $\text{cm}^{-1}$ , which is in agreement to those reported by (Henmi *et al.*, 1981).

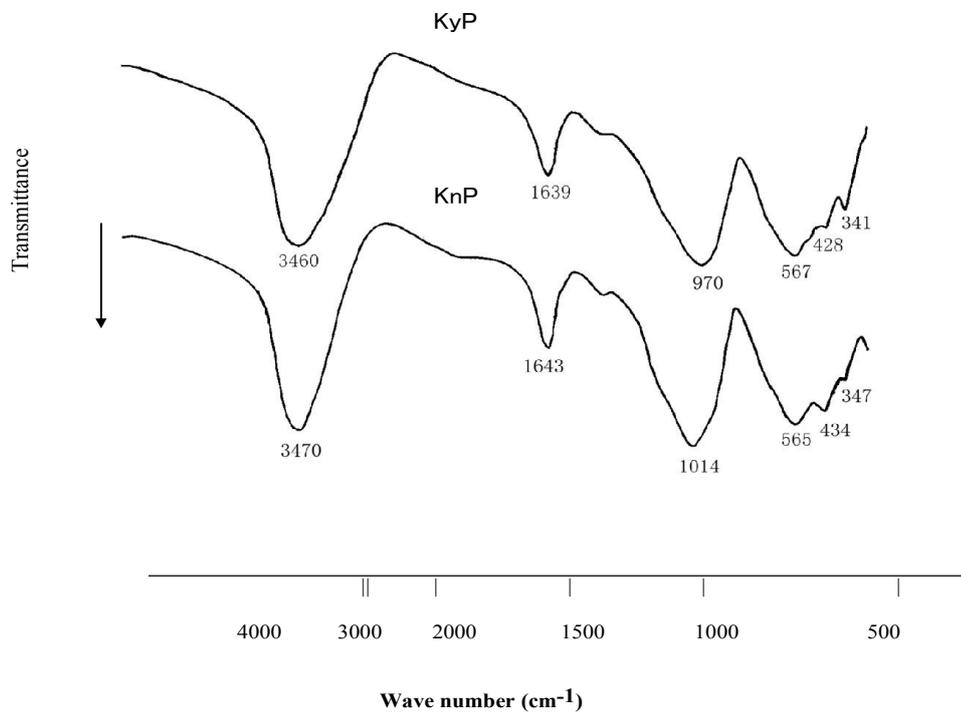


Fig.3. Infrared spectra of the allophane samples

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Analysis by DTA showed large endothermic peaks between 50 and 300°C (Fig 4),

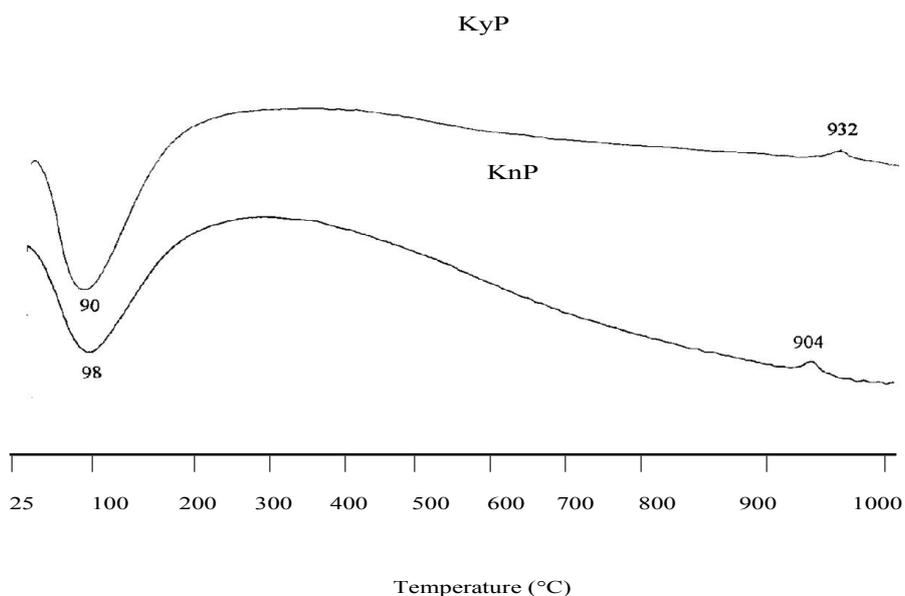


Fig.4. DTA curves of the allophane samples

arising from removal of large amount of adsorbed water. These results clearly showed that the nano-ball allophane samples were free from contaminants such as volcanic glasses, opaline silica and imogolite (Wada 1989). Concentrations of total Si, Al and Fe of the two nano-ball allophane samples were different with KnP having greater Si, Fe and Si/Al and slightly lower Al than the KyP sample (Table1).

Table 1. Chemical analysis of Si, Al, Fe and the Si/Al molar ratio of the allophane samples.

Sample	%			Si/Al (molar ratio)
	Si	Al	Fe	
KyP	13.7	19.6	2.3	1.34:2
KnP	18.8	18.2	5.8	1.98:2

### Charge Characteristics of Original Samples

The relation between pH and charge characteristics of original allophane for both KnP and KyP samples are depicted in Figs 5 and 6.

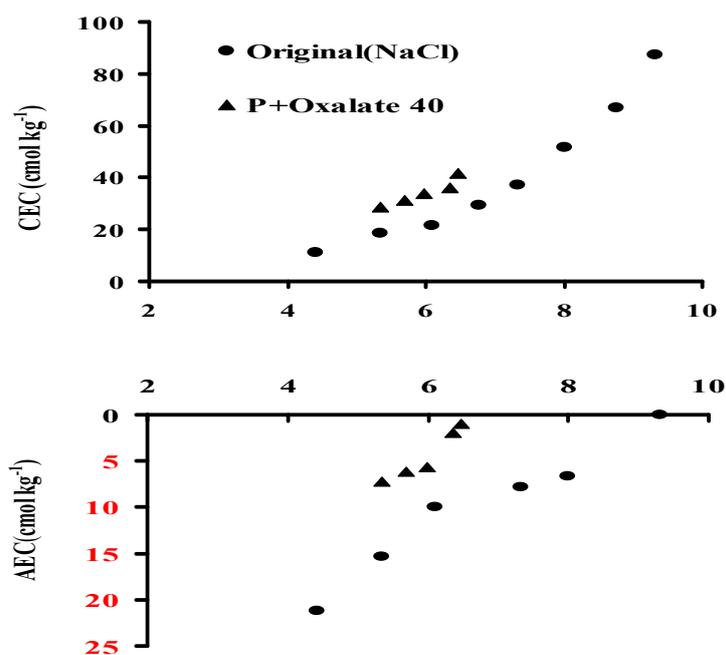


Fig.5. Charge characteristics of KyP sample in 10mM NaCl before and after Competitive Oxalate and Phosphate Adsorption

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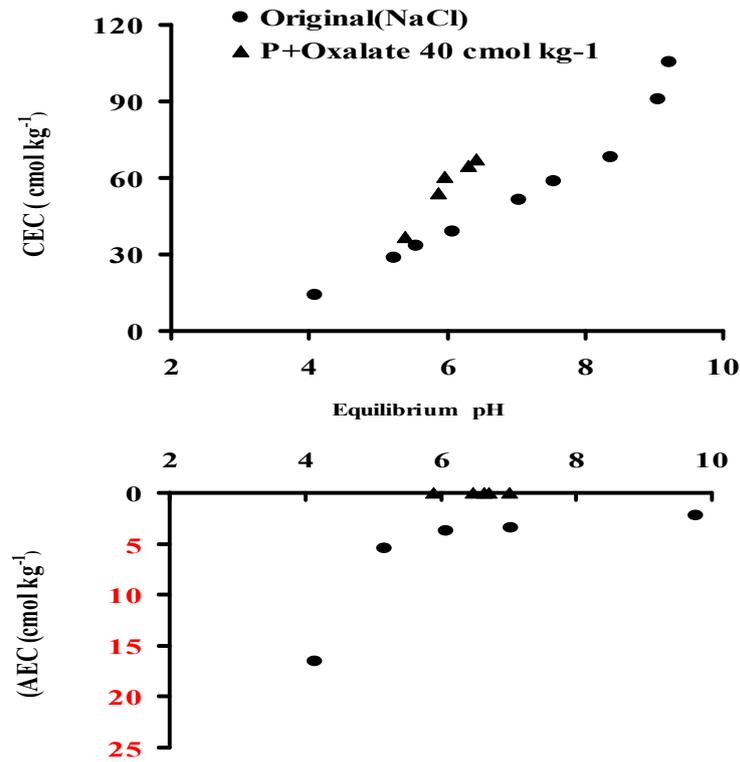


Fig.6.Charge characteristics of KnP sample in 10mM NaCl before and after Competitive Oxalate and Phosphate Adsorption

Generally, there were curvilinear increases in the CEC and decreases in the AEC of the allophane samples with increasing pH. Allophane as a variable charge mineral has CEC strongly dependent on electrolyte concentration, type of ion, solution pH and method of determination (Perrott 1977; Okamura and Wada 1983). At the same equilibrium pH, the KnP sample (Fig. 6) had greater negative charge than KyP (Fig. 5).

The greater negative charge of the KnP could be attributed to the existence of accessory, polymeric  $\text{SiO}_4$  tetrahedra, which could have caused an increase in the pKa value of Si-OH group in the allophane structure (Matsue and Henmi 1993; Henmi *et al.* 1997). The fundamental structure of allophane as proposed by Matsue and Henmi (1993) and Henmi *et al.* (1997) has Si/Al ratio of 0.5 imogolite structure, and additional accessory  $\text{SiO}_4$  tetrahedra increased the ratio. Hence, it can be assumed that allophane with higher Si/Al ratio, such as KnP sample, is an adsorption product of allophane with low Si/Al ratio, such as the KyP sample, and that the adsorbed tetrahedra caused an increase in the amount of negative charge. Lower positive charge of KnP than KyP at the same equilibrium pH is mainly due to its lower content of aluminol groups per unit mass. The amount of aluminol groups per unit mass decreases with increasing Si/Al ratio of allophane (Son *et al.* 1998). Steric hindrance effect by the polymeric  $\text{SiO}_4$  tetrahedra on the aluminol groups at the pore region may partly account for the lower positive charge of the KnP sample.

#### **Effect of Competitive Adsorption of P and Ox on CEC and AEC**

Effects of competitive adsorption of P and Ox on changes in surfaces charge were presented in Fig 5 (KyP) and Fig 6 (KnP). The total adsorption amount was  $40 \text{ cmol kg}^{-1}$  at the several of P/Ox ratio of 4/0, 3/1, 2/2, 1/4 and 0/4. The negative charges of both KnP and KyP increased after competitive adsorption of Ox and P (Figs. 5 and 6). The negative charge was enhanced by increasing the proportion of Ox in adsorption ratio. This finding suggested that allophane-rich soils that have a lower proportion Ox would have lower CEC than those with higher proportion. The increase in CEC of allophane, as affected by competition of Ox and P adsorption, may be through two ways; (i) the negative charge carried by the Ox and/ or P ( $\text{H}_2\text{PO}_4^-$  or  $\text{HPO}_4^{2-}$ ) and (ii) new negative charge created on silanol group as a result of reaction between aluminol group and Ox or P anions (Johan *et al.* 1999; Hanudin *et al.* 2000). After competitive adsorption of P and Ox there was an increase in solution pH, because the surface charge of allophane is variable in nature. The increase in solution pH was enhanced by increase in Ox added. For this reason, the sample with higher Ox added had higher CEC. Oxalate, a strong organic anion which has two  $\text{COO}^-$ , could

react easily with aluminol groups to form the allophane-oxalate complex. The oxalate adsorbed on allophane could have resulted in a lot of  $\text{OH}^-$  released to the solution phase and the hydroxyl group took proton from silanol group charge. As a result, Ox adsorbed in binuclear form, released two  $\text{OH}^-$  ions with adsorption of each Ox anion. In case of P, one  $\text{OH}^-$  is released with adsorption of one  $\text{H}_2\text{PO}_4^-$  anion, resulting in less increases in pH and CEC and decrease in AEC. The greater Si/Al in KnP than KyP resulted in greater silanol groups, which could have released more  $\text{OH}^-$ , resulting in greater CEC and lower AEC. The decreased AEC values with increase in equilibrium solution pH (Figs. 5 and 6) reflected the deprotonation of the surface hydroxyl groups. These results were supported by previous findings (Elsheikh *et al.* 2009) on adsorption behavior competition between P and Ox onto allophane which clearly showed that the competitive adsorption was largely dependent on Si/Al ratio of allophane, and the enhancement of the competition was caused by increasing pH.

Fig. 6 shows that there is a leak in AEC charge values in KnP. The leak may be due to modified new surface charge of nano-ball allophane after adsorption of some chemical species on allophane sample like P and OX especially via ligand exchange reaction. The nano-allophane with such adsorbate can be assumed as a new compound derived from the adsorption reaction, allophane-OX-P complex, and it is logical that the complex has different surface charge characteristic from the original nano-allophane. Moreover, as we mentioned above, the fundamental structure of allophane as proposed by Matsue and Henmi (1993) and Henmi *et al.* (1997) has Si/Al ratio of 0.5 imogolite structure and additional accessory  $\text{SiO}_4$  tetrahedra increased the ratio. Hence, it can be assumed that allophane with higher Si/Al ratio, such as KnP sample, is an adsorption product of allophane with low Si/Al ratio, such as the KyP sample, and that the adsorbed tetrahedra caused an increase in the amount of negative charge. The greater negative charge of the KnP could be attributed to the existence of accessory, polymeric  $\text{SiO}_4$  tetrahedra, which could have caused an increase in the pKa value of Si-OH group in the allophane structure (Matsue and Henmi 1993; Henmi *et al.* 1997).

## CONCLUSIONS

- Competitive adsorption of phosphate and oxalate causes increase in cation exchange capacity and pH and a decrease in anion exchange capacity on nano-ball allophane.
- The allophane samples with high Si/Al ratio had higher increase in cation exchange capacity and pH and decrease in anion exchange capacity as compared to allophane sample with lower Si/Al ratios. So, when research is carried out on competitive adsorption of phosphate and oxalate on allophane, the Si/Al ratio of allophane should be examined and be taken into account in the study.
- Findings of this study are of great significance in agriculture, especially at the soil-root interface where oxalate may compete with phosphate for sorption sites onto soil particles (including allophane), which may result in increasing the retention capacity of cations and decreasing that of anions. In addition, the increase in cation exchange capacity could reduce mobility of metal cations in polluted soils.

## REFERENCES

- Beck, M.A.; Robarge, W.P. and Buol, W. (1999). Phosphorus retention and release of anions and organic carbon by two Andisols. *European journal of soil science* 50,157-164.
- Chorover, J.; Amistadi, M. K. and Chadwick, O. A. (2004). Surface charge evolution of mineral-organic complexes during pedogenesis in Hawaiian basalt. *Geochimica et Cosmochimica Acta* 68(23),4859–4876.
- Elhadi, E. A.; Matsue, N. and Henmi, T. (2001). Effect of Molybdate adsorption on some surface properties of Nano-ball allophane. *Clay Science* 11,405-416.
- Elsheikh, M.A.; Abidin, Z.; Matsue, N. and Henmi, T. (2008). Competitive adsorption of oxalate and phosphate on allophane at low concentration. *Clay Science* 13 (6), 81-188.

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- Elsheikh, M.A.; Matsue, N. and Henmi, T. (2009). Effect of Si/Al ratio of allophane on competitive adsorption of phosphate and oxalate. *International Journal of Soil Science* 4 (1), 1-13.
- Ghoneim, A.; Matsue, N. and Henmi, T.(2006).Effect of copper adsorption on some charge characteristics of Nano-ball allophane. *International Journal of Soil Science* 1,243-250.
- Ghoneim, A.; Matsue, N. and Henmi, T (2007). charge characteristics of Nano-ball allophane as affected by zinc adsorption. *Journal of Applied Science* 7,103-108.
- Henmi, T. and Wada, K.(1976). Morphology and composition of allophane. *American Mineralogist* 61, 379-390.
- Henmi, T. ; Tange, K., Minagawa, T., and Yoshinga, N. (1981) Effect of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio on thermal reactions on allophane: II. Infrared and x-ray powder diffraction data. *Clays and Clay Minerals* 29(2),124-128.
- Henmi, T.; Matsue, N. and Johan, E.(1997). Change in the surface acidity of allophane with a low Si/Al ratio by reaction with ortho-silicic acid. *Japanese journal of soil science and plant nutrition* 68, 514-520 (in Japanese with English abstract).
- Hanudin, E.; Matsue, N. and Henmi, T.(1999). Adsorption of some low molecular weight organic acids on nano-ball allophane. *Clay science* 11, 57-72.
- Hanudin, E.; Matsue, N. and Henmi, T. (2000). Change in charge characteristics of allophane with adsorption of low molecular weight organic acids. *Clay science* 11, 243-255.
- Harsh, J.B.; Traina, S.J.; Boyle, J. and Yang, Y.(1992). Adsorption of cations on imogolite and their effect on surface charge characteristics. *Clays and clay minerals* 40,700-706.
- Huang, W. D.; and Johns, W. D. (1966). Simultaneous determination of fluorine and chlorine in silicate rocks by rapid

spectrophotometric method. *Analytica Chimica Acta* 37, 508-515.

Johan, E.; Matsue, N. and Henmi, T.(1997). Phosphorus adsorption on nano-ball allophane and its molecular orbital analysis. *Clay science* 10,259-270.

Johan, E.; Matsue, N. and Henmi, T.(1999). New concepts for change in charge characteristics of allophane with P adsorption. *Clay science* 10, 457-468.

Matsue, N. and Henmi, T.(1993). Molecular orbital study on the relationship between Si/Al ratio and surface acid strength of allophane. *Japanese journal of soil science and plant nutrition* 33,102-106. (In Japanese with English abstract).

Moghim, A. H; Hamdan, J.;Shamshuddin , J.;Samsuri, A .W and Abtahi , A.( 2013). Physicochemical Properties and Surface Charge Characteristics of Arid Soils in Southeastern Iran. *Applied and Environmental Soil Science*: 2013, 11. doi: 10.1155/2013/252861

Murphy, J. and Riley, J .P. (1961). A modified single solution method for determination of P in natural waters. *Analytica Chimica Acta* 27, 31-36.

Okamura, Y. and Wada, K. (1983). Electric charge characteristics of horizons of Ando(B) and Red-Yellow B soils and weathered pumices. *Journal of Soil Science*. 34, 287–295.

Qafoku, O. and Felmy, A.R. (2007). Development of accurate chemical equilibrium models for OX species to high ionic strength in the system: Na-Ba-Ca-Mn-Sr-Cl-NO<sub>3</sub>-PO<sub>4</sub>-SO<sub>4</sub>-H<sub>2</sub>O at 25°C. *Journal of Solution Chemistry*36, 81-95.

Perrott, K.W.(1977). Surface charge characteristics of amorphous Aluminosilicates. *Clays and clay minerals*. 25, 417–421.

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- Parfitt, R. L. (1980). Chemical properties of variable charge soils. In : *Soils with Variable Charge*, pp167-194. Theng, B .K. G.(Ed.) Soil Bureau, DSIR, Lower Hutt, New Zealand: NZSSS
- Son, L. T.; Matsue, N. and Henmi, T.( 1998). Boron adsorption on allophane with nano-ball morphology. *Clay Science* 10,315-325.
- Wada, K.1.(1989). Allophane and imogolite. In: *Minerals in Soil Environments*, pp1051-1087. Dixon, J.B. and Weed, S.B. (Eds),. Madison, Wisconsin: SSSA.
- Xu, R.; Zhao, A. and Ji, G. (2003). Effect of low-molecular weight organic anions on surface charge of variable charge soils. *Journal of Colloid and Interface Science* 264, 322-32.



## تغير خصائص الشحنة السطحية لكريات معدن الالوفان النانوية مختلفة المحتوى من نسب السليكون للألمونيوم بسبب عملية الادمصاص التنافسي لايونات الفوسفات والأوكسالات

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**المستخلص:** تمت دراسة التغير في خصائص الشحنة السطحية لكريات معدن الالوفان النانوية ذات النسب مختلفة المحتوى من السليكون للألمونيوم بعد عمليات ادمصاص مختلفة لكل من الفوسفات والأوكسالات. وقد وجد أن السعة التبادلية الكاتيونية تزداد مع زيادة الرقم الهيدروجيني، وبعد الادمصاص التنافسي لكل الفوسفات والأوكسالات. من ناحية أخرى وجد أن السعة التبادلية الأيونية تقل مع زيادة الرقم الهيدروجيني، وبعد الادمصاص التنافسي لكل من الفوسفات والأوكسالات. وجد أن عينات الالوفان ذات النسب العالية من تركيزات السليكون للألمونيوم لها سعة تبادلية كاتيونية عالية مقارنة مع عينات الالوفان ذات نسب التركيز المنخفض من تركيزات السليكون للألمونيوم. وتشير نتائج هذه الدراسة إلى أن زيادة الرقم الهيدروجيني والادمصاص التنافسي لكل من الفوسفات والأوكسالات يؤديان إلى تغيير في خصائص الشحنة السطحية لكريات الالوفان النانوية.

**الكلمات المفتاحية:** الشحنة السطحية، الادمصاص التنافسي، كرة الالوفان النانوية، الأوكسالات، الفوسفات