



International Journal of **Soil Science**

ISSN 1816-4978



Academic
Journals Inc.

www.academicjournals.com

Effect of Copper Adsorption on Some Charge Characteristics of Nano-Ball Allophane

Adel Ghoneim, Naoto Matsue and Teruo Henmi
Faculty of Agriculture, Environmental Soil Science,
Ehime University, 3-5-7 Tarumi, Matsuyama 790-8566, Japan

Abstract: Mechanisms of change in charge characteristics after copper adsorption on one low Si/Al (KyP) and one high Si/Al (KnP) nano-ball allophane samples were investigated. The CEC values of the two nano-ball allophane samples tended to decrease while AEC increased after copper species adsorption at the initial concentration of 1.60 mM. The change in charge characteristics of the allophane samples was governed by the pH, Cu^{2+} , CuOH^+ in the solution and amounts of adsorption. The decline in the CEC values after adsorption was due to the neutralization reactions between the monomeric Cu^{2+} with Si-O^- or Al-O^- functional groups. Molecular orbital calculations indicated that Cu^{2+} and CuOH^+ could adsorb not only on the dissociated Si-O^- but also with the undissociated Si-OH groups. When copper ion reacted with undissociated Si-OH groups, dissociation reaction of silanol groups accelerated. The Cu^{2+} ion has a possibility to accelerate the deprotonation of undissociated Si-OH groups near the adsorption sites. The decrease in change CEC values was found to be higher in case of a higher Si/Al ratio (KnP) than that for the lower Si/Al ratio (KyP) counterpart, due to its a higher adsorptive capacity for copper species. The slight increase in the AEC values after zinc adsorption was probably due to in part to the initial H^+ ions released into the bulk solution.

Key words: Nano-ball allophane, copper adsorption, CEC, AEC, molecular orbital analysis

Introduction

Protection of soil resources and environment as well as sustainable development of agriculture are important problems laid ahead of humankind with increasing the population and acceleration of industry development (He *et al.*, 1998). Some heavy metals are beneficial whereas some of them are toxicity for the plant growth. Copper is essential to plant, but is toxic when its concentration exceeds a certain critical level (Baker, 1990; Pires and Mattiasso, 2003). Copper enters agricultural ecosystems through applications of Cu-containing fungicides, stable manure and solid wastes from Cu-related mining and manufacturing. There are two types of minerals that involved in the adsorption-desorption of Cu^{2+} in soils: permanent charge and variable charge. Permanent charge minerals such as montmorillonite carry out a negative charge as a result of ion substitution during the formation of the minerals. Variable charge minerals such as nano-ball allophane carry charge varying from negative to positive depending on pH changes. Copper adsorption and desorption in soil are affected by the proportion of these 2 types of minerals (Atanassova and Okazaki, 1997). Organic matter and pH are the factors that directly or indirectly affect the Cu^{2+} bioavailability (Rodriguez-Rubio *et al.*, 2003). Organic radicals, as well as iron and aluminum oxides, have OH^- sites with high potential for specific copper adsorption (Yin *et al.*, 2002). Moreover, the Fe, Al and Mn oxides have a relatively strong affinity (pH dependent) for Cu^{2+} adsorption (Martins *et al.*, 2003).

Corresponding Author: Adel Ghoneim, Faculty of Agriculture, Environmental Soil Science,
Ehime University, 3-5-7 Tarumi, Matsuyama 790-8566, Japan

The surface charge of variable charge surfaces depends on the solution pH and the pK of the type of surface functional group. For the most agricultural soils, bioavailability of Cu^{2+} is controlled by adsorption-desorption process (Xie, 1996). The surface charge characteristics are an important factor to limit the behavior of the copper adsorption-desorption (Yin *et al.*, 2002). Remediation of Cu-contaminated soils requires an understanding of Cu^{2+} adsorption-desorption behavior and the major factors.

Allophane is poorly ordered aluminumsilicates, with silica to alumina ratio between 1.0 and 2.0 (Henmi and Wada, 1976). Allophane used to be describing as amorphous but recent investigations using the state of art technique has established the morphology and chemical structure as shown in Fig. 1. Allophane has CEC values which are strongly dependent on the electrolyte concentration, type of cation and solution pH. In addition, nano-ball allophane as a pH-dependent clay mineral has a unique characteristics; it can has both negative and positive charge simultaneously. The main positive and negative charge is separated each other in the nano-ball allophane structure as shown in Fig. 1. The negative charge come from the silanol groups (Si-O^-) on the inner side of the nano-ball allophane structure while the positive charge result from the aluminol groups (Al-OH_2^+), which placed at the pore region of the ball of allophane whereas the. These charge characteristics are different from those of the other pH-dependent clay minerals such as goethite and gibbsite (Parfitt, 1980). The CEC and AEC values of the nano-ball allophane samples might be, therefore, decrease or increase along with the type of the adsorbed materials. The declining in AEC values and increase in CEC values have been reported after molybdate (Elhadi *et al.*, 2001) and citrate (Hamudin *et al.*, 2000) adsorption on the nano-ball allophane samples. Recently investigations on Cu^{2+} adsorption by the nano-ball allophane samples at different pH levels indicated that the noticeable amounts of copper were adsorbed by the KyP and KnP samples (Ghoneim *et al.*, 2002). In addition, the equilibrium solution pH decreased after

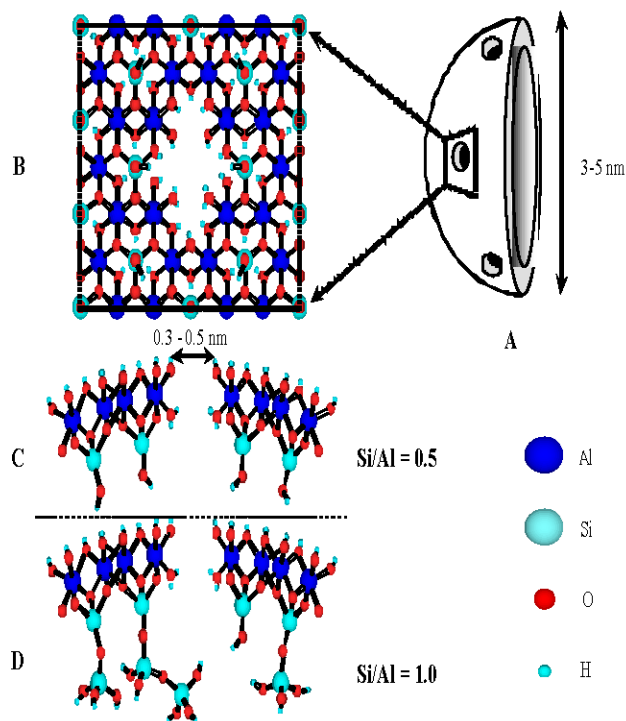


Fig. 1: Chemical structure of nano-ball allophane (A: Morphology in section; B: Atomic arrangements near the pore; C and D: Atomic arrangement in cross section at the pore)

adsorption, H^+ being replaced by Cu^{2+} ions (Ghoneim, 2002). Moreover, the adsorption was greatly controlled by the difference in the chemical structure between the allophone samples, copper species in the solution and pH (Ghoneim *et al.*, 2002). When significant amount of copper was adsorbed then, a new compound, called allophone-copper complex different from the original allophone samples may be produced. The purpose of this research was to investigate the mechanisms of change in CEC and AEC of two nano-ball allophone with various Si/Al ratios upon copper adsorption.

Materials and Methods

Allophone Samples Preparation

Two allophone samples used in this study were separated from weathered pumice grains taken from two different volcanic ash locations in Japan. The KyP sample was collected from Kurayoshi, Tottori prefecture and KnP sample from Kakino, Kumamoto prefecture. Fine clay fraction ($<0.2 \mu m$) was separated from the inner part of pumice according to the method of Henmi and Wada (1976). The KyP and KnP allophone samples have molar ratios of 1.34:2 and 1.98:2, respectively. The KyP is accordingly considered as a low Si/Al while KnP as higher Si/Al ratio (Henmi *et al.*, 1981). The chemical structure of nano-ball allophone samples is shown in Fig. 1.

CEC and AEC Measurements

To 50.0 mg of the freeze dried KyP and KnP samples in pre-weighted 100 mL centrifuge bottles, an appropriate volume of NaCl and $CuCl_2$ solution were added and topped with distilled water to attain final concentration of copper concentration of 1.60 and 10.0 mM for NaCl. Concurrently, the pH of the solution was adjusted to the levels between 3 and 10 by adding either HCl or NaOH solutions. After that, the suspensions were shaken for 24 h, centrifuged at 5000 rpm for 20 min after which the equilibrium pH of the supernatant was measured. In the next stage, the levels of Cu^{2+} and Na^+ concentrations of the supernatant were determined using the Polarized Zeeman Atomic Absorption Spectroscopy (Z-5000) and the Cl^- concentration determined calorimetrically according to the method of (Huang and Johns, 1967). Here, the amounts of zinc adsorbed were calculated in each case from the reduction in the concentrations initially and that remaining after the equilibration. Later, the CEC and AEC values of the samples were determined according to the modified equilibrium method of (Schofield, 1949). The centrifuge bottles with their contents were weighed after decanting the supernatant to calculate the volume of entrained solutions. Then, 50 mL of 1.0 M NH_4NO_3 solution was added to the contents of the centrifuge bottles, shaken for 5 h and then, centrifuged and the NH_4NO_3 supernatant decanted and kept. The last process was repeated and the levels of Na^+ and Cl^- concentrations in the bulked NH_4NO_3 determined. Finally, the CEC and AEC values of the samples were estimated as the difference in the concentration of NH_4NO_3 , which extracted Na^+ and Cl^- ions and that of the entrained solution. The MOPAC 2002 with AM1 basis set as a semi empirical computational method in Chem 3D program was employed to find out the more feasible of some of the reactions proposed. Cluster models for allophone were built up with Si tetrahedra and Al octahedra by using bond distances of Si-O = 0.1618 nm, Al-O = 0.1912 nm and O-H = 0.0944 nm.

Results and Discussion

Change in Charge Characteristics

The relationship between equilibrium pH, CEC and AEC values of original KyP and KnP samples at initial concentration of 1.60 mM in 10 mM NaCl background solution are shown in (Fig. 2 and 3). With increasing equilibrium pH, there are increases in the CEC values of the two allophone samples. Nartey *et al.* (2001); Elhadi *et al.* (2001) and Hanudin *et al.* (2000) made similar results and

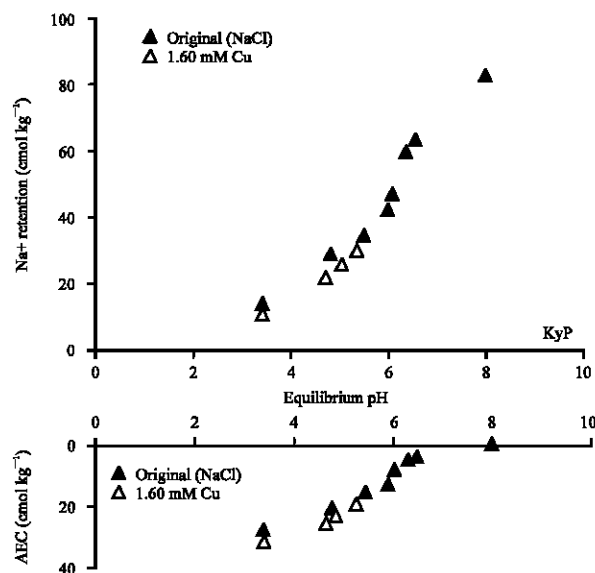


Fig. 2: Charge characteristics of the KyP sample with and without copper adsorption at initial Cu concentration of 1.60 mM

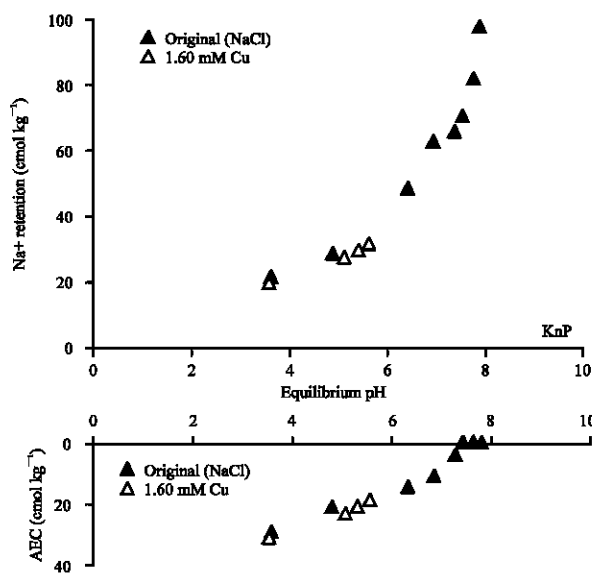


Fig. 3: Charge characteristics of the KnP sample with and without copper adsorption at initial Cu concentration of 1.60 mM

demonstrated that this concave shaped CEC-pH curve of original allophone sample in 10 mM NaCl background solution is representative of nano-ball allophone morphology. The CEC value for the original KnP allophone sample with a higher Si/Al ratio (1.98:2) was higher than for the KyP (1.34:2). These results are attributed to the difference in the chemical structure between the two nano-ball allophone samples as shown in Fig. 1. The higher amounts of the negative charges for the KnP sample confirm the existence of more accessory polymeric SiO₄ tetrahedra attached to the main frame of nano-

ball allophane structure; which causes an increase in the K_a value of the Si-OH group in the nano-ball allophane structure. The fundamental structure of the nano-ball allophane as proved (Henmi *et al.*, 1997; Matsue and Henmi, 1993) has shown that the Si/Al ratio of 0.5, the imogolite structure and the additional polymeric SiO₄ tetrahedra, which increase the ratio. Therefore, the KnP allophane sample with a higher Si/Al ratio is considered as the SiO₄ adsorption product of the lower Si/Al ratio (KyP) and the adsorbed SiO₄ tetrahedra let to increase in the amounts of negative charge. The AEC values decreased as the equilibrium pH increase, indicating that the deprotonation of the surface OH⁻ groups and the consequent, the decline in the positive charge. Furthermore, AEC was higher in KyP sample than in the higher Si/Al ratio (KnP). This higher AEC value is attributed to the higher aluminum content per unit mass of the KyP sample. A lower AEC of KnP is attributed in part due to the tendency for the attached polymeric SiO₄ tetrahedra, which cause a steric hindrance effect on the aluminol functional groups at the pore region of the nano-ball allophane (Johan *et al.*, 1999). Below equilibrium pH 8, it is seen that the two original allophane samples, in 10 mM NaCl have both negative (CEC) and positive AEC charges (Fig. 2 and 3). These strikingly unique properties feature of the nano-ball allophane unlike the other variable charged minerals such as gibbsite and goethite (Parfitt, 1980) is attributed to the difference in the location of the silanol and aluminol functional groups in the nano-ball allophane structure as shown in (Fig. 1). The silanol groups (Si-O⁻), which accounts for a large fraction of the CEC values in nano-ball allophane are located at the inner surface of the mineral, while the positively charge aluminol groups (Al-OH₂⁺) are located at the pore region of the nano-ball allophane. Generally, the CEC values of the two nano-ball allophane tend to decrease after Cu²⁺ adsorption at the initial concentration of 1.60 mM as shown in (Fig. 2 and 3) for the KyP and KnP, respectively. The figures also showed that the decrease in the CEC value from the original sample was found to be slightly higher in a higher Si/Al ratio (KnP) than for the lower Si/Al counterpart (KyP) allophane sample. The decline in the CEC values after copper adsorption was coupled with proton release into the bulk solution (Ghoneim *et al.*, 2001; Ghoneim, 2002). The release of H⁺, which was found to be higher in case of the KnP, with a higher Si/Al ratio than for the KyP could be an indication of its higher decreasing in the CEC values than for KyP. The decrease in the CEC value after copper adsorption has been attributed to the neutralization reactions between the dissociated Si-O⁻ functional groups with the positive species of copper such as Cu²⁺ and Cu(OH)⁺. Substantial decrease in the amounts of positive charge (AEC) values has been reported after molybdate (Elhadi *et al.*, 2001), citrate and oxalate (Hanudin *et al.*, 2000) and phosphate (Johan *et al.*, 1999) adsorption on the KyP and KnP nano-ball allophane samples. In these published studies, the decreases in the AEC values were thought to be due to the neutralization of the positive charges Al-OH₂⁺ by the anionic form of the compounds adsorbed. In the current research, a small increase in the AEC values was found for the KyP and KnP samples after copper adsorption at initial concentrations of 1.60 mM as shown in Fig. 2 and 3. The slight increase in the AEC values after adsorption was maybe due to in part to the initial H⁺ released into the bulk solution after copper adsorption, which may have reacted with Al-OH functional group to form the new positive charge, Al-OH₂⁺.

Figure 4 shows the relationship between the amounts of Cu²⁺ adsorbed and the net change in the CEC (Δ CEC) of the KyP and KnP samples at the initial copper concentration of 1.60 mM. From the figure it is seen that there was a linear decrease in the Δ CEC values with the increasing the amounts of copper adsorbed by the two allophane samples, indicated that the very high correlation between Δ CEC value and the amounts of copper adsorbed ($r = 0.99^{**}$). Also, at any set point within the pH range, the Δ CEC values of the nano-ball allophane samples were always smaller than the amounts of copper adsorbed by the two nano-ball allophane samples. For example, the amount of copper adsorbed by the KyP allophane sample with a lower Si/Al ratio at the initial solution pH 4, 5 and 6 were 20.0, 24.5 and 39.5 cmol kg⁻¹, respectively and the corresponding Δ CEC values were 3.8, 4.0 and 4.33 cmol kg⁻¹, respectively. The amounts of copper adsorbed by the KnP allophane sample with a

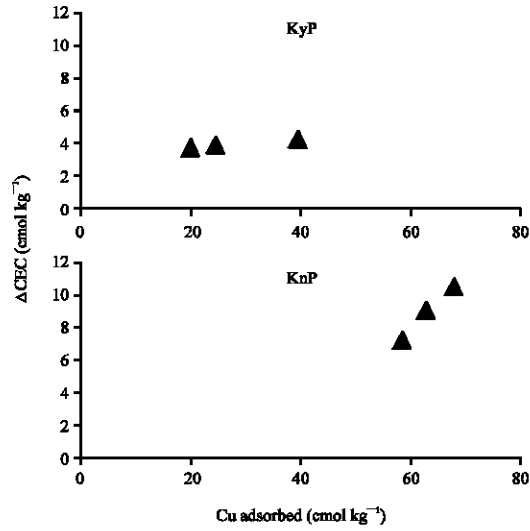
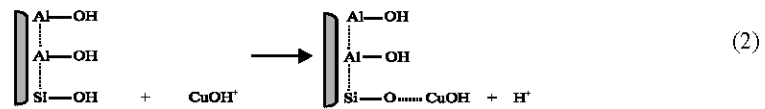
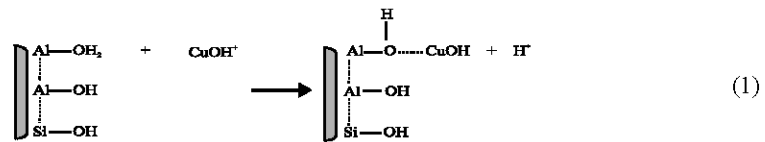


Fig. 4: Relationship between amounts of copper adsorbed and changes in CEC. Initial copper concentration was 1.60 mM

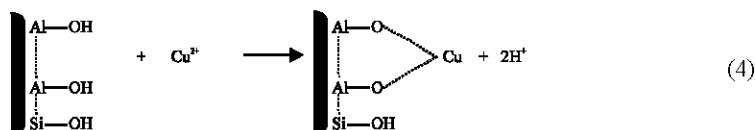
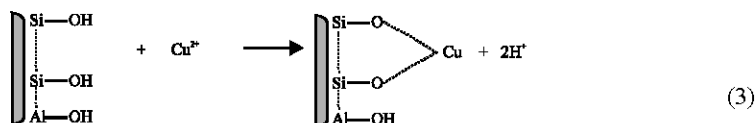
higher Si/Al ratio were greater than that for the KyP (59.2, 63.3 and 68.3 cmol kg⁻¹) at the initial pH levels of 4, 5 and 6 and the consequent ΔCEC values also were higher (7.0, 9.2 and 10.9 cmol kg⁻¹, respectively). The higher decrease in the CEC value of KnP sample was attributed to its higher adsorptive capacity for copper species than KyP sample with a lower Si/Al ratio even at the same solution conditions (Ghoneim, 2002).

Mechanism of Change in Charge Characteristics

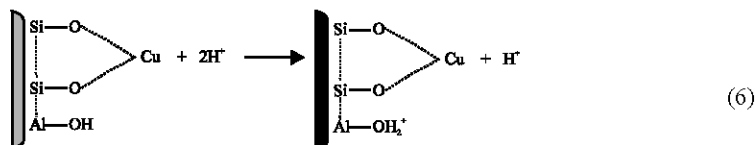
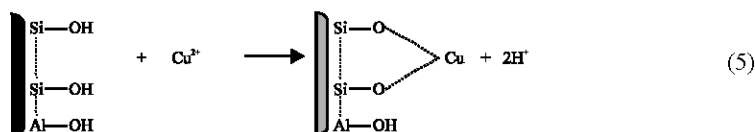
The reaction between Cu species and nano-ball allophone resulted in new compound which has different charge characteristics than the original allophone. By using the detailed chemical structure of allophone Fig. 1 and molecular orbital calculation, the mechanisms in development of surface charge on allophone sample upon copper adsorption could be known. The main adsorption sites of allophone for the copper adsorption are mainly Al-OH, Al-OH₂ and Si-OH functional groups. The reaction of CuOH⁺ with Al-OH₂ or Si-OH groups can describe as:



In these equations, copper adsorbed as CuOH⁺ (monodentate reaction) with Al-OH₂ or Si-OH and one proton released into solution caused decreases in pH. The decrease in CEC values upon copper adsorption at the initial concentration of 1.60 mM was attributed to neutralization reaction as follows:



Reactions 3 and 4 describe the specific adsorption of monomeric Zn^{2+} either with dissociated Si-O^- or Al-O^- as (bidentate reaction) and 2 protons were released for each mole of Cu^{2+} ion adsorbed. The molecular orbital calculations indicated that when allophone model has one dissociated Si-O^- , the monomeric Cu^{2+} adsorbed strongly to the Si-O^- group and weakly adsorbed with undissociated Si-OH groups. The O-H bond lengths of the two silanol groups bonded to copper ion was longer than those of the other silanol groups. These results indicated that, Cu^{2+} has a possibility to accelerate the deprotonation of undissociated Si-OH groups near the adsorption sites. In addition, Ghoneim (2002) reported that the bond length between Zn^{2+} , Cu^{2+} ions and the O atoms of the Si-OH groups were shorter for Cu^{2+} than Zn^{2+} . The little increase in AEC values after copper adsorption could be explained by the next reactions:



In reaction 5, part of 2H^+ was released after Cu^{2+} adsorption into the bulk solution may reacted with, Al-OH group to form Al-OH_2^+ with the positive charge as shown in reaction 6 and the excess of the proton decreasing the pH. The molecular orbital calculations indicated that when copper ions reacted with undissociated Si-OH , dissociation reaction of silanol groups accelerated due to the bonding formation between copper and the O atoms of silanol groups and coincide with the observed pH decrease (Ghoneim, 2002).

References

- Atanassova, I.D. and M. Okazaki, 1997. Adsorption-desorption characteristics of high levels of copper in soil clay fractions. *Water Air Soil Pollut.*, 98: 213-228.
- Baker, D.E, 1990. Copper. In: *Heavy Metals in Soils*. Alloway, B.J. (Eds.), Blackie and Sons Ltd., London, pp: 151-176.
- Elhadi, E.A., N. Matsue and T. Henmi, 2001. Effect of molybdate on some surface properties of nano-ball allophane. *Clay Sci.*, 11: 405-416.

- Ghoneim, A.M., N. Matsue and T. Henmi, 2001. Zinc adsorption on nano-ball allophanes with different Si/Al ratios. *Clay Sci.*, 11: 337-348.
- Ghoneim, A.M., 2002. Reaction of nano-ball allophane with zinc and copper and its mechanism by molecular orbital method. Ph.D Thesis, The United Graduate School of Agricultural Sciences, for Doctoral Course, Ehime University, Japan, pp: 148.
- Ghoneim, A.M., N. Matsue and T. Henmi, 2002. Adsorption mechanisms of copper and zinc on nano-ball allophanes. *Clay Sci.*, 11: 615-624.
- Hanudin, E., N. Matsue and T. Henmi, 2000. Change in charge characteristics of allophane with adsorption of low molecular weight organic acids. *Clay Sci.*, 11: 243-255.
- He, Z.L., Z.Q. Xing and X.Z. Miao, 1998. Soil chemical equilibrium of pollutant and beneficial elements. Chinese Environment Science, Publishing House, Beijing.
- Henmi, T. and K. Wada, 1976. Morphology and composition of allophone. *Am. Miner.*, 61: 379-390.
- Henmi, T., K. Tange, T. Minagawa and N. Yoshinaga, 1981. Effect of SiO₂/Al₂O₃ ratio on the thermal reactions of allophone. II. Infrared and X-ray powder diffraction data. *Clays Clay Miner.*, 29: 124-128.
- Henmi, T., N. Matsue and E. Johan, 1997. Change in the surface acidity of allophone with a low Si/Al ratio by reaction with orthosilicic acid. *Jpn. J. Soil Sci. Plant Nutr.*, 68: 514-520.
- Huang, W.D. and W.D. Johns, 1967. Simultaneous determination of fluorine and chlorine in silicate rocks by rapid spectrophotometric methods. *Anal. Chem. Acta*, 37: 508-515.
- Johan, E., N. Matsue and T. Henmi, 1999. New concepts for change in charge characteristics of allophone with phosphate adsorption. *Clay Sci.*, 10: 457-468.
- Martins, A.L.C., O.C. Bataglia and O.A. Camargo, 2003. Copper, nickel and zinc phytoavailability in an oxisol amended with sewage sludge and liming. *Scientia Agricola*, 60: 747-754.
- Matsue, N. and T. Henmi, 1993. Molecular orbital study on the relationship between Si/Al ratio and surface acid strength of allophone. *J. Clay Sci. Soc. Jpn.*, 33: 102-106 (in Japanese with English abstract).
- Nartey, E., N. Matsue and T. Henmi, 2001. Charge characteristics mechanisms of nano-ball allophone upon orthosilicic acid adsorption. *Clay Sci.*, 11: 465-477.
- Parfitt, R.L., 1980. Chemical Properties of Variable Charge Soils. In: *Soil with Variable Charge*. Theng, B.K.G. (Ed.). Offset publication, Palmerson North, New Zealand, pp: 167-188.
- Pires, A.M.M. and M.E. Mattiasso, 2003. Biosolids conditioning and the availability of Cu and Zn for rice. *Scientia Agricola*, 60: 161-166.
- Rodriguez-Rubio, P., E. Morillo and L. Madrid, 2003. Undabeytia T, Maqueda C. Retention of copper by calcareous soil and its textural fractions influence of amendment with two agroindustrial residues. *Eur. J. Soil Sci.*, 54: 401-409.
- Schofield, R.K., 1949. Effect of pH on electric charges carried by clay particles. *J. Soil Sci.*, 1: 1-8.
- Xie, Z., 1996. Chemical balance of soil copper. *Adv. Environ. Sci.*, 4: 1-23.
- Yin, Y., C.A. Impellitteri, S.J. You and H.E. Allen, 2002. The importance of organic matter distribution and extract soil: Solution ratio on the desorption of heavy metals from soils. *Sci. Total Environ.*, 287: 107-119.