Sulfate Adsorption on a Volcanic Ash Soil (Allophanic Andisol) under Low pH Conditions

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ABSTRACT

The mechanisms of SO$_4$ adsorption on clays have been investigated by many researchers. However, few researches have focused on the fraction of SO$_4$ that is adsorbed in the diffuse layer to the total adsorbed SO$_4$. We investigated SO$_4$ adsorption in detail on an allophanic Andisol (volcanic ash soil), especially the fraction of SO$_4$ adsorbed in the diffuse layer to the total adsorbed SO$_4$, conducting experiments under conditions of low pH (pH 3.3 and 4.3) and low ion concentrations (1.0 and 0.1 mol c m$^{-3}$) to avoid a strong negative surface charge of the soil particles. SO$_4$ and NO$_3$ adsorption under their competitive conditions were measured by a batch method using mixtures of HNO$_3$ and H$_2$SO$_4$. Exchangeable SO$_4$ and NO$_3$ were extracted with 1000 mol c m$^{-3}$ KCl. Strongly adsorbed SO$_4$ was extracted with 10 mol c m$^{-3}$ NaOH after the extraction with 1000 mol c m$^{-3}$ KCl. The exchangeable SO$_4$ made up 72 to 77 % of the total adsorbed SO$_4$. These results suggested that both inner-sphere and outer-sphere complexes co-exist in the allophanic Andisol at low pH. SO$_4$ was strongly selective over NO$_3$ under these conditions. We compared adsorbed amounts calculated by the Gouy-Chapman model with the measured values at solution conditions of pH 3.3 and 1.0 mol c m$^{-3}$. The model overestimated NO$_3$ adsorption and underestimated SO$_4$ adsorption. The difference is due to the fact that SO$_4$ adsorption in the Stern layer is neglected. Next, we calculated SO$_4$ adsorbed in the diffuse layer using the Stern-Gouy-Chapman model under the assumption that all the measured NO$_3$ adsorbed was in the diffuse layer. Our results indicated that the SO$_4$ in the diffuse layer made up only less than 6 % of the total adsorbed SO$_4$. Most of the adsorbed SO$_4$ is likely to be found in direct contact with the soil surface.

Key Words: allophanic Andisol, volcanic ash soil, nitrate adsorption,
Stern-Gouy-Chapman model, sulfate adsorption, surface complexation
1. Introduction

The position of the adsorbed counterions on clays affects the soil structure. When the counterions are adsorbed only directly on the clay surface, the clay surface potential becomes small and the clay flocculates. On the other hand, when the counterions are adsorbed in the diffuse layers and thick diffuse layers develop, the clay swells or disperses due to the repulsive force of overlapping diffuse layers.

Allophanic Andisol (volcanic ash soil) contains a substantial amount of pH-dependent charges. The positive charge becomes predominant at low pH and the negative charge becomes predominant at high pH [1-4]. Thus, the soil disperses at low and high pH [3]. However, the soil suspension flocculates in dilute H₂SO₄ solution, while it disperses in dilute HNO₃ solution [5,6]. Ishiguro and Nakajima [6] suggested that weaker repulsive forces compared to attractive forces among soil particles cause flocculation in dilute H₂SO₄ solution because SO₄ is divalent and is strongly adsorbed on soils with pH-dependent charges. Ishiguro et al. [7] showed that repulsive potential energy between the soil clays decreased when SO₄ was adsorbed.

SO₄ is strongly adsorbed on allophanic clays and soils [8,9]. It induces NO₃ leaching due to its strong adsorption [10]. However, the mechanism of SO₄ adsorption at the clay-water interface has been a source of debate. Many researchers have indicated that SO₄ forms an inner-sphere surface complex on hydrous alumina [11], allophanic clays [9], kaolinitic Alfisols [12], hematite [13], and amorphous iron hydroxide [14]. On the other hand, other researchers showed that SO₄ does not form chemical coordination on the surface, or the sorption can largely be explained by electrostatic considerations [15-20]. Spectroscopic results [21-23] suggest that SO₄ forms both outer-sphere and inner-sphere surface complexes on goethite, and the ratio of the latter complex increases
with decreasing pH. SO₄ adsorption on goethite was evaluated with the Charge Distribution Multisite Complexation model and compared with the spectroscopic analysis [24]. Ishiguro et al. [25] indicated SO₄ surface precipitation, stronger and weaker SO₄ adsorption sites on allophanic soil by using theoretical adsorption isotherms. Prietzel et al. [26] showed that adsorbed SO₄ can be distinguished from SO₄ precipitated in soils by X-ray Absorption Near Edge Structure (XANES).

However, the SO₄ proportion of that adsorbed in direct contact with the soil surface to that in the diffuse layer has not been discussed in the studies. Therefore, in the present study, we evaluated the amount of SO₄ in the diffuse layer and the Stern layer for an allophanic Andisol under low pH and low concentration conditions. Low pH and low concentration conditions were selected because the positive charge was predominant and the negative charge could be neglected. SO₄ and NO₃ adsorption under their respective competitive conditions were measured by a batch method. Results were compared to predictions based on the Gouy-Chapman model. SO₄ adsorbed in the diffuse layer and the Stern layer were evaluated with the Stern-Gouy-Chapman model.

2. Materials and Methods

2.1. Soil

Allophanic Andisol was obtained from a field at the National Institute for Agro-Environmental Sciences in Tsukuba, Japan, from the 4Bw1 horizon of Typic Dystrandept [27]. Its physical and chemical properties measured by the National Institute of Agricultural Sciences [28] are listed in Table 1. The specific surface of
the soil obtained from N\textsubscript{2} adsorption was 211 m\textsuperscript{2} g\textsuperscript{-1} (QUANTACHROME AUTOSORB-1). Fresh raw soil sample, which had been passed through 2-mm-mesh sieves, was used in the experiment.

2.2. Anion Adsorption Experiments

NO\textsubscript{3} and SO\textsubscript{4} adsorptions, as well as the anion exchange capacity (AEC), were measured using the batch method of Wada and Okamura [29] with minor modification. AEC is defined herein as the sum of exchangeable anions extracted with 1000 mol\textsubscript{c} m\textsuperscript{-3} KCl solution. A NaOH solution at 10 mol\textsubscript{c} m\textsuperscript{-3} was used as an extraction solution for strongly adsorbed SO\textsubscript{4}, which was not extracted with a 1000 mol\textsubscript{c} m\textsuperscript{-3} KCl solution.

Solutions used for the equilibration according to step 1, mentioned below, were six different mixtures of NaNO\textsubscript{3} and Na\textsubscript{2}SO\textsubscript{4} at a total electrolyte concentration of 1000 mol\textsubscript{c} m\textsuperscript{-3}. Solutions used for the final equilibration according to step 2 were six different mixtures of HNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4} at pH 3 or pH 4. The mixed solutions at pH 3 and pH 4 were equivalent to total electrolyte concentrations of 1.0 and 0.1 mol\textsubscript{c} m\textsuperscript{-3}, respectively. Mixed ratios of SO\textsubscript{4} concentration (mol\textsubscript{c} m\textsuperscript{-3}) to NO\textsubscript{3}+SO\textsubscript{4} concentration (mol\textsubscript{c} m\textsuperscript{-3}) in those solutions (SO\textsubscript{4} ratio) were 0, 13, 30, 50, 75, and 100 \%. The procedure was as follows:

Step 1 (equilibration with electrolytes at 1000 mol\textsubscript{c} m\textsuperscript{-3}). Approximately 2 g of soil sample was equilibrated overnight with 200 cm\textsuperscript{3} of the mixture of NaNO\textsubscript{3} and Na\textsubscript{2}SO\textsubscript{4} at 1000 mol\textsubscript{c} m\textsuperscript{-3} and a specified SO\textsubscript{4} ratio. The soil solution pH was roughly adjusted to pH 3 or 4 with HNO\textsubscript{3} or H\textsubscript{2}SO\textsubscript{4}. The soil sample was centrifuged for 10 min at 3 000 rpm (1 900 g), and the supernatant was discarded.

Step 2 (final equilibration with electrolytes at 0.1 or 1.0 mol\textsubscript{c} m\textsuperscript{-3}). The soil sample
roughly adjusted to pH 3 was shaken for 1 h with 200 cm$^3$ of the mixture of HNO$_3$ and H$_2$SO$_4$ at 1.0 mol$_e$ m$^{-3}$ and a specified SO$_4$ ratio. The soil sample roughly adjusted to pH 4 was shaken with the mixture of HNO$_3$ and H$_2$SO$_4$ at 0.1 mol$_e$ m$^{-3}$ and a specified SO$_4$ ratio. The soil sample was then centrifuged for 30 min at 12000 rpm (15 000 g), and the supernatant was discarded. This procedure was repeated six times. The final supernatant was filtrated through a disposable membrane filter, pore size 0.2 μm, with a 10-mL disposable plastic syringe and kept to analyze the concentrations of SO$_4$, NO$_3$, H and Al. The final pH of the supernatant became pH 3.3±0.1 for 1.0 mol$_e$ m$^{-3}$ solution and pH 4.3±0.1 for 0.1 mol$_e$ m$^{-3}$ solution.

Step 3 (extraction with KCl). The centrifuged and decantated soil sample was shaken with 60 cm$^3$ of 1000 mol$_e$ m$^{-3}$ KCl for 15 min. The soil sample was then centrifuged for 10 min at 3000 rpm (1900 g), and the supernatant was collected. This procedure was repeated three times. The collected supernatant was filtrated as mentioned at step 2 and kept to analyze the concentrations of SO$_4$, NO$_3$ and H.

Step 4 (extraction with NaOH). The soil sample obtained after extraction with KCl was shaken with 200 cm$^3$ of 10 mol$_e$ m$^{-3}$ NaOH for 15 min. The mixture was then centrifuged, and the supernatant was collected. This procedure was repeated twice. The collected supernatant was filtrated as mentioned at step 2 and kept to analyze the SO$_4$ concentration.

The NO$_3$ concentrations of the supernatants were measured by the steam distillation method [30], and the SO$_4$ concentrations were measured by ion chromatography (IC-500S, Yokogawa Electric Corporation). The NO$_3$ and SO$_4$ adsorbed amounts were then calculated from the difference with the amounts in the original solutions remained in the soils after decantation at step 2. A reliable NO$_3$ adsorbed amount could not be
derived under pH 4.3 condition except for 100 % NO$_3$ ratio (=0 % SO$_4$ ratio), because concentrations in the collected solution with the KCl extraction were too low. The H concentrations of the supernatant were measured with a pH meter. The Al concentrations of the supernatant were measured by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) (MaximIII, Applied Research Laboratories).

2.3. Application of the Gouy-Chapman Model

To simplify the model calculation, the soil clay surface is assumed to be a flat plane. The charge density of the clay was calculated from the measured AEC, the clay content, and specific surface of the soil. If all exchangeable ions are present in the diffuse layer, the Gouy-Chapman model (GC model) can be applied. In this case, the relationship between the surface potential of the clay, $\Psi_s$, and its surface charge density, $\sigma$, is derived from the Poisson-Boltzmann equation [31]:

$$\sigma^2 = 2\varepsilon RT[NO_3] \left\{ \exp \left( \frac{F\Psi_s}{RT} \right) - 1 \right\} + 2\varepsilon RT[SO_4] \left\{ \exp \left( \frac{2F\Psi_s}{RT} \right) - 1 \right\} + 2\varepsilon RT[H] \left\{ \exp \left( -\frac{F\Psi_s}{RT} \right) - 1 \right\} + 2\varepsilon RT[Al] \left\{ \exp \left( -\frac{3F\Psi_s}{RT} \right) - 1 \right\}$$

(1)

where, [ ] is ion concentration in the bulk solution, $\varepsilon$ is the permittivity of the water, $R$ is the gas constant, $T$ is the absolute temperature, and $F$ is the Faraday constant. $\Psi_s$ is calculated from Eq. (1) when the charge density is given.

The potential distribution in the diffuse layer is given by the following approximation derived from the Poisson-Boltzmann equation:
\[
\left( \frac{d\Psi}{dx} \right)^2 = \frac{2RT}{\epsilon} [NO_3] \left\{ \exp \left( \frac{F\Psi}{RT} \right) - 1 \right\} + \frac{2RT}{\epsilon} [SO_4] \left\{ \exp \left( \frac{2F\Psi}{RT} \right) - 1 \right\} \\
+ \frac{2RT}{\epsilon} [H] \left\{ \exp \left( - \frac{F\Psi}{RT} \right) - 1 \right\} + \frac{2RT}{\epsilon} [Al] \left\{ \exp \left( - \frac{3F\Psi}{RT} \right) - 1 \right\}
\]

(2)

where \( x \) is the distance from the clay surface and \( \Psi \) is the potential at \( x \) [30]. The potential at \( x+\Delta x \), \( \Psi(x+\Delta x) \), is calculated by the explicit finite difference method as follows;

\[
\Psi(x + \Delta x) = \left[ \frac{2RT}{\epsilon} [NO_3] \left\{ \exp \left( \frac{F\Psi(x)}{RT} \right) - 1 \right\} + \frac{2RT}{\epsilon} [SO_4] \left\{ \exp \left( \frac{2F\Psi(x)}{RT} \right) - 1 \right\} \\
+ \frac{2RT}{\epsilon} [H] \left\{ \exp \left( - \frac{F\Psi(x)}{RT} \right) - 1 \right\} + \frac{2RT}{\epsilon} [Al] \left\{ \exp \left( - \frac{3F\Psi(x)}{RT} \right) - 1 \right\} \right]^{\frac{1}{2}} \Delta x + \Psi(x)
\]

(3)

where \( \Delta x \) is the increment of distance and \( \Psi(x) \) is the potential at \( x \), which is derived by iteration with Eq.(3) from \( \Psi_s \) at the clay surface.

Next, we obtain the anion concentration distribution in the diffuse layer as follows:

\[
C_i(x) = C_{0,i} \exp \left( - \frac{z_i F\Psi}{RT} \right)
\]

(4)

where \( C_i(x) \) is the concentration of anion \( i \) at \( x \), \( C_{0,i} \) is the bulk concentration of anion \( i \), and \( z_i \) is the valence of anion \( i \). We then obtain the approximated adsorbed amount of the anion \( i \) for the GC model, \( q_{Gi} \).

\[
q_{G,i} = \int_0^d \left( C_i(x) - C_{0,i} \right) dx
\]

(5)

where \( d \) is the distance over which the potential in the diffuse layer vanishes; we put \( d=20\kappa^{-1} \), where \( \kappa^{-1} \) is the Debye length which is often called the “thickness” of the diffuse layer.

In this model, the amounts of NO\(_3\) and SO\(_4\) adsorbed in the diffuse layer are
calculated using the measured values; the AEC, the clay content, the specific surface of
the soil, and the equilibrium bulk concentrations of NO$_3$, SO$_4$, H and Al. No fitting
parameters are required.

2.4. Application of the Stern-Gouy-Chapman model

If some of the exchangeable SO$_4$ is adsorbed in the Stern layer, the
Stern-Gouy-Chapman model (SGC model) must be used instead of the GC model.
Because NO$_3$ is an indifferent ion and the NO$_3$ concentrations in the experiment were
dilute (< 1.0 mol$_c$ m$^{-3}$), we assumed that all the adsorbed NO$_3$ exists in the diffuse layer.
Having measured the total adsorbed amounts of NO$_3$ and SO$_4$, we can estimate the
amounts of SO$_4$ adsorbed in the Stern layer and those in the diffuse layer by using the
SGC model. Because the potential distribution in the diffuse layer is determined by the
bulk solution conditions as shown in Eq. (2), the concentration distributions derived in
the GC model can also be used in this case.

The measured amount of adsorbed NO$_3$ per unit surface area, $Q$(NO$_3$), is equal to
the diffuse NO$_3$ adsorption:

$$Q(\text{NO}_3) = \int_{a}^{d} (C_{\text{NO}_3}(x) - C_{0,\text{NO}_3}) \, dx$$  \hfill (6)

where $a$ is the location of the Stern plane in the SGC model, that is, the distance of the
diffuse layer in this model is $d - a$, as the value of $d$ and the potential distribution
calculated from the GC model are used. The $a$ value is derived with Eq.(6); $Q$(NO$_3$) is
the measured value, $C_{\text{NO}_3}(x)$ is already obtained as the result of the GC model with
Eq.(4) and $C_{0,\text{NO}_3}$ is the known equilibrium concentration, then, the a value can be
obtained. We can then calculate the amount of adsorbed SO$_4$ in the diffuse layer,
The amount of SO$_4$ adsorbed in the Stern layer, $q_s$(SO$_4$), is

$$q_s(SO_4) = Q(SO_4) - q_d(SO_4)$$  (8)

where $Q(SO_4)$ is the measured amount of adsorbed SO$_4$ per unit surface area.

In this model, SO$_4$ adsorbed amount in the diffuse layer is calculated using the measured values, listed earlier in the GC model section, plus the NO$_3$ adsorbed amount. The equilibrium bulk concentrations of NO$_3$, SO$_4$, H and Al are also used for the calculation of $\Psi$ in Eq. (3). No fitting parameters are required.

3. Results

The experimental results of the anion adsorptions are shown in Figs. 1 and 2. The results at pH 3.3 and 1.0 mol$_c$ m$^{-3}$ are given in Fig. 1. The NO$_3$ adsorption was measured by extraction with 1000 mol$_c$ m$^{-3}$ KCl. The AEC is the sum of the NO$_3$ adsorption and the exchangeable SO$_4$ adsorption measured by extraction with 1000 mol$_c$ m$^{-3}$ KCl. The total anion adsorption is the sum of the AEC and the strong SO$_4$ adsorption measured by extraction with 10 mol$_c$ m$^{-3}$ NaOH. The amount of exchangeable SO$_4$ measured by extraction with 1000 mol$_c$ m$^{-3}$ KCl, is the difference between the AEC and the NO$_3$ adsorption in Fig. 1. These values ranged from 72 % to 74 % of the total anion adsorption at SO$_4$ ratios between 13 % and 100 %. The amount of strongly adsorbed SO$_4$, which was measured by extraction with 10 mol$_c$ m$^{-3}$ NaOH, is the difference between the total anion adsorption and the AEC. Strongly adsorbed SO$_4$ ranged from...
26 % to 28 % of the total anion adsorption at SO₄ ratios between 13 % and 100 %. Adsorbed NO₃ was completely exchanged with 1000 mol c m⁻³ KCl. The NO₃ adsorption at 0 % SO₄ was 103 mmol c kg⁻¹, while the exchangeable SO₄ adsorption at 100 % SO₄ was 294 mmol c kg⁻¹. NO₃ adsorption at SO₄ ratios between 13 % and 75 % ranged from 0.6 to 7.6 mmol c kg⁻¹, which was only 0.2 % to 3.2 % of the AEC. SO₄ is strongly selective over NO₃ under our experimental conditions.

The adsorbed amounts at pH 4.3 and 0.1 mol c m⁻³ are shown in Fig. 2. Although these results are similar to the results at pH 3.3, the total SO₄ adsorbed amounts were 64 % to 73 % of those at pH 3.3. The amount of strongly adsorbed SO₄, which is the difference between the total SO₄ adsorbed and the exchangeable SO₄, ranged from 23 % to 27 % of the total SO₄ adsorption at SO₄ ratios between 13 % and 100 % similar to the results adsorbed at pH 3.3. The NO₃ adsorbed amount for 100 % NO₃ ratio (0 % SO₄ ratio) at pH 4.3 was 33.9 mmol c kg⁻¹, which was 32.9 % of that at pH 3.3.

We could not adapt the GC model or the SGC model to the condition at pH 4.3 due to our inability to determine the NO₃ adsorbed amount. Therefore, only the results for the pH 3.3 were calculated. Adsorbed amounts calculated by the GC model are compared with the measured values in Fig. 3. The GC model overestimated NO₃ adsorption and underestimated SO₄ adsorption.

The SGC model was applied to the results at the pH 3.3, calculating the SO₄ in the diffuse layer with the assumption that all the measured NO₃ adsorbed was in the diffuse layer. The calculated SO₄ in the diffuse layer, measured strongly adsorbed SO₄, and measured exchangeable SO₄ are shown in Fig. 4. The SO₄ in the diffuse layer made up only 1.7 % to 6.1 % of the total adsorbed SO₄. The amount of exchangeable SO₄ in the Stern layer is the difference between the exchangeable SO₄ and the SO₄ in the diffuse layer shown in Fig. 4. These values ranged from 68 % to 72 % of the total adsorbed
SO\textsubscript{4} at SO\textsubscript{4} ratios between 13 % and 75 %. The strongly adsorbed SO\textsubscript{4} ranged from 26 % to 28 % of the total adsorbed SO\textsubscript{4} at SO\textsubscript{4} ratios between 13 % and 100 %.

4. Discussion

The GC model neglected the exchangeable SO\textsubscript{4} adsorbed in the Stern layer. However, when the SGC model was adopted, about 92 % to 98 % of the exchangeable SO\textsubscript{4} was adsorbed in the Stern layer. This amount could not be negligible, and it clearly accounts for the disagreement between the measured and the calculated values in Fig. 3.

Under the SGC model, the sum of SO\textsubscript{4} adsorbed in the Stern layer and the strongly adsorbed SO\textsubscript{4} became 94 % to 98 % of the total adsorbed SO\textsubscript{4}, assuming that all adsorbed NO\textsubscript{3} was in the diffuse layer. Gibb and Koopal [32] showed that amounts of surface complexation of NO\textsubscript{3} on rutile and hematite were considerable at lower pH with Koopal’s one-pK SGC model [33]. If we assume that some adsorbed NO\textsubscript{3} forms surface complexation, the SO\textsubscript{4} adsorbed in direct contact with the soil surface must be more than 94 % to 98 % of the total adsorbed SO\textsubscript{4}. We conclude that most of the adsorbed SO\textsubscript{4} (more than 94 %) was in direct contact with the soil surface and the amount of SO\textsubscript{4} in the diffuse layer was very small (less than 6 %) in our experimental condition at pH 3.3.

We consider that the exchangeable SO\textsubscript{4} is adsorbed by electrostatic forces, and that strongly adsorbed SO\textsubscript{4} extracted with NaOH reflects chemical adsorption. Another reaction that must be considered is a precipitation of basic aluminum sulfates [8]. However, when the solubility product (Al\textsuperscript{3+})(OH\textsuperscript{4+})\textsubscript{10}SO\textsubscript{4}=10^{-117.3} proposed by Singh and Brydon [34] is applied, basaluminite should not precipitate under our experimental conditions.

Both strongly adsorbed SO\textsubscript{4} and exchangeable SO\textsubscript{4} were found in our experiment,
consistent with the results of Gebhardt and Coleman [8]. Wijnja and Schulthess [23] determined that SO₄ forms both outer-sphere and inner-sphere surface complexes on alumin oxide at pH less than 6. Ishiguro et al. [25] showed both stronger and weaker adsorption sites on allophanic Andisol by using the Langmuir isotherm. In their research, most of the SO₄ was adsorbed on the stronger site and only about 2 % was adsorbed on the weaker site at pH 4 and 0.1 mol cm⁻³ SO₄. It is questionable whether the exchangeable and strongly adsorbed SO₄ correspond respectively to the outer-sphere and inner-sphere complex. The adsorption of the exchangeable SO₄ extracted with 1000 mol cm⁻³ KCl may not be entirely to electrostatic adsorption. Agbenin [12] has noted that 1000 mol cm⁻³ is a very high ionic strength and that under these conditions some inner-sphere complexes might be extracted. Further investigation is needed at this point.

From the results of the SGC model, nearly all of the adsorbed SO₄ (more than 94 %) was in direct contact with the soil surface and the amount of SO₄ in the diffuse layer was very small (less than 6 %) in our experimental condition at pH 3.3 for the allophanic Andisol. Therefore, the soil should flocculate under low pH, when SO₄ is the main counterion, because the effective surface charge is very low. Ishiguro and Nakajima [6] determined that the soil flocculated in H₂SO₄ at pH 3 and 4, but dispersed in HNO₃ at pH 3 and 4. Ishiguro et al. [7] showed that the repulsive potential energy between the soil clays became small when SO₄ was adsorbed. Their results are consistent with our experimental results.

REFERENCES


[23] H. Wijnja, C.P. Schulthess, Vibrational spectroscopy study of selenate and sulfate


[33] L.K. Koopal, Adsorption of ions and surfactants. In Coagulation and flocculation,
Figure legends

Fig. 1. Anion adsorption on the allophanic Andisol at pH 3.3 and 1.0 mol c m\(^{-3}\).

Fig. 2. SO\(_4\) adsorption on the allophanic Andisol at pH 4.3 and 0.1 mol c m\(^{-3}\).

Fig. 3. The Gouy-Chapman model estimations of NO\(_3\) and SO\(_4\) adsorption compared to the experimental data at pH 3.3.

Fig. 4. SO\(_4\) adsorption at pH 3.3. SO\(_4\) in the diffuse layer was calculated by the Stern-Gouy-Chapman model.
Fig. 1. Anion adsorption on the allophanic Andisol at pH 3.3 and 1.0 mol\textsubscript{c} m\textsuperscript{-3}.
Fig. 2. SO$_4$ adsorption on the allophane Andisol at pH 4.3 and 0.1 mol$_c$ m$^{-3}$. 
Fig. 3. The Gouy-Chapman model estimations of NO₃ and SO₄ adsorption compared to the experimental data at pH 3.3.
Fig. 4  SO₄ adsorption at pH 3.3. SO₄ in the diffuse layer was calculated by the Stern-Gouy-Chapman model.
Table 1. Physical and chemical characteristics of the soil.

(National Institute of Agricultural Sciences, 1984[28])

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<th>Soil characteristics</th>
<th>Value</th>
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