Soil permeability as affected by repulsive potential energy

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Abstract

The repulsive potential of soil affects its pore structure and consequently water permeability. This is evident in Allophanic Andisols, which have a significant pH-dependent charge. Therefore, at low and high pH, soil dispersion and swelling occur easily due to electric repulsive force. The permeability of the soil then decreases because of structural changes that occur when dilute monovalent acid or alkaline solution is percolated in the soil. However, soil permeability does not decrease, rather increases, when dilute H_2SO_4 is percolated in the soil. This is because SO_4^{2-} strongly adsorbs on the soil surface at low pH and the soil remains flocculated. The difference of permeability is explained by the calculated repulsive potential energy based on zeta potential. Permeability of a high humic soil with only negative charge decreases when an anionic surfactant solution is percolated. The surfactant is adsorbed in the soil by hydrophobic interaction. The repulsive potential energy increases and the permeability decreases due to the increase of negative charge.

Key Words

Electric charge, permeability, repulsive potential energy, soil structure, soil dispersion

Introduction

Charge characteristics of soils strongly influence pore structure and permeability. Although permeability is supposed to decrease in response to an increase in electric repulsive force among soil particles, the relationship between permeability and repulsive potential energy has not been evaluated (Ishiguro *et al*., 2003). A numerical solution of the equation for swelling pressure in mixed systems with nonsymmetrical electrolytes was proposed (Bresler, 1970). However, research into repulsive potential energy in multivalent counterion systems has been rare (Ishiguro *et al*., 2003). In this research, soil structure and permeability changes of the allophanic Andisol, which is characterized by a number of variable charges, were investigated. Especially, the repulsive potential energies were evaluated in an NO_3–SO_4 systems in relation to permeability. The permeability change of high humic Andisol whose negative charge was increased by adding anionic surfactant was also investigated.

Materials and Methods

Soils

An allophanic Andisol (Hapludand) was obtained from a field at the National Institute of Agro-Environmental Sciences in Tsukuba, Japan, from a depth of approximately 90 cm (4Bw1 horizon). The predominant clay minerals were allophane and imogolite. The sand content was 130 g/kg, silt content was 375 g/kg, and clay content was 495 g/kg. The organic C content was 11.6 g/kg. The <2-mm sieved field moist soil was used in all experiments. As pH decreased, the cation exchange capacity (CEC), the negative charge of the soil, decreased, and the anion exchange capacity (AEC), the positive charge of the soil, increased. Both the CEC and the AEC increased with an increase in ion strength. A non-allophanic high humic Andisol at a pasture in Daisen Mountain in Tottori prefecture, Japan, from the A horizon was also used. The total carbon content was 138 g/kg, the sand content was 436 g/kg, the silt content was 318 g/kg, and the clay content was 246 g/kg. The CEC was 12.3 $mmol_c$/kg in 1 mmol/L potassium solution, and the AEC was 0 $mmol_c$/kg at pH 6.

Hydraulic conductivity study under different pH conditions

Saturated hydraulic conductivity (K) for the allophanic Andisol was determined at a constant hydraulic gradient of 3 m/m using a column 3-cm long and 3-cm ID. The initial soil solution pH was under natural condition at about pH 6. The electrolyte concentration of the influent solutions (Na-H-Cl-OH system) was 1 $mmol_c$/L under different pH conditions (pH 3 to 11).

Hydraulic conductivity study at pH 3 and 4

Values of K for the allophanic Andisol were determined at a constant hydraulic gradient of 5 m/m using a column 3-cm long and 3.2-cm ID. The initial soil solution pH was under natural condition at about pH 6. The

influent solutions were mixtures of HNO_3 and H_2SO_4 at pH 3 and pH 4 with different mixed proportions.

Hydraulic conductivity study during the percolation of anionic surfactant solutions
Values of *K* for the non-allophanic high humic Andisol were determined at a constant hydraulic gradient of 3 m/m using a column 13-cm long and 5-cm ID during the percolation of anionic surfactant (sodium dodecyl sulfate, SDS) solutions.

Results and Discussion
Hydraulic conductivity study under different pH conditions
The results of the hydraulic conductivity study with different pH solution percolation are shown in Figure 1(a). The values of *K* decreased drastically when HCl at pH 3 was percolated as shown in Figure 1(a). *K* also decreased when NaOH at pH 11 was percolated (Nakagawa and Ishiguro, 1994). Photo 1(a) shows the surface structure of the soil before HCl percolation when soil aggregates were observed. Photo1 (b) shows the surface structure with collapsed aggregates after HCl at pH 3 percolation. The collapse of the structure was caused by swelling of the soil aggregates and the clogging of larger pores resulted from soil dispersion. This structural change in the upper layer caused a decrease in permeability (Ishiguro, 2005). The influence of the solution pH on soil dispersion is shown in Figure 1(b) in which the vertical line indicates the dispersion ratio of the absorbance of the soil suspension after 12 hours of settling to that just after shaking. The soil was well dispersed in solutions with lower pH levels due to the predominant positive charge and in those with higher pH levels due to the predominant negative charge (Nakagawa and Ishiguro, 1994). This phenomenon corresponds to the decrease in the saturated hydraulic conductivity.
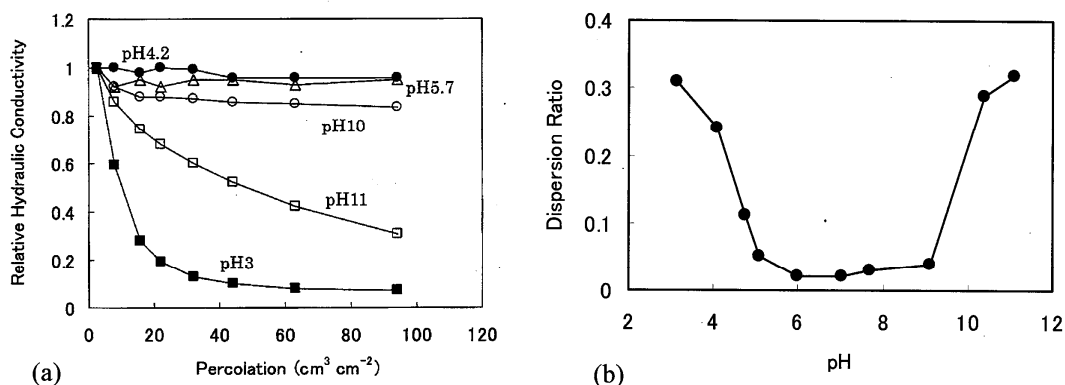
Figure 1. (a) Influence of influent pH on saturated hydraulic conductivity with Na-H-Cl-OH system. The pH values in the figure denote those for influent solutions. (b) Influence of pH on soil dispersion with the same system (Nakagawa and Ishiguro, 1994).
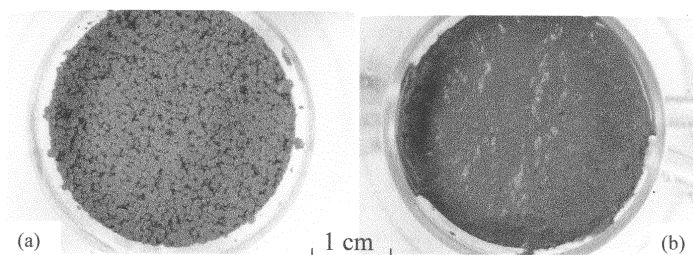
Photo 1. Surface soil structure (a) before and (b) after the percolation of a HCl solution. (Ishiguro, 2005).

Hydraulic conductivity study at pH 3 and 4
Values of *K* were found to decrease when dilute HNO_3 was percolated in the soil as shown in Figure 2. However, this decrease was restricted as the proportion of SO_4^{2-} to total anions in the solution increased. We also performed a dispersion study under the same solution conditions as those in the soil column for the hydraulic conductivity study. The soil was well dispersed at higher proportions of NO_3^- to the total anions in the solution, and well flocculated at higher proportions of SO_4^{2-}, corresponding to the change in *K* values (Ishiguro and Nakajima, 2000; Ishiguro *et al.*, 2003). The electric repulsive potential energies, $V\varsigma$, between soil clay particles in mixtures of HNO_3 and H_2SO_4 at pH 3 and 4 were calculated with the following equation using the Gouy-Chapman theory (Ishiguro *et al.*, 2003) and electrophoretic mobility data as shown in Figure 3.

$$V_\varsigma = -2 \int_b^0 \Pi \, \mathrm{d}D,$$

$\Pi = RT\Sigma(C_i - C_{0,i})$

where Π is the osmotic pressure difference between the midpoint of two soil clay particles and the bulk solution, D is the distance from the plane of the zeta potential to the midpoint, b is the distance from the zeta potential plane to the boundary of the bulk solution, R is the gas constant, T is the absolute temperature, C_i is the concentration of ion i at the midpoint, and $C_{0,i}$ is the concentration of ion i in the bulk solution. The horizontal axis in Figure 3 indicates the concentrations of NO_3^- and SO_4^{2-} (mmol$_c$/L) in the acid solution at pH 3 and 4. The repulsive potential energy increased with an increase in NO_3^- proportion, and the increase near 100% NO_3^- proportion was particularly steep. Repulsive potential energy caused dispersion and swelling of the soil at higher NO_3^- proportions under low pH conditions, and permeability decreased as a result of this dispersion and swelling. On the other hand, the repulsive potential energy decreased and the soil flocculated more with an increase in SO_4^{2-} proportion, because SO_4^{2-} forms complexes on the clay surface at low pH (Ishiguro et al., 2006).
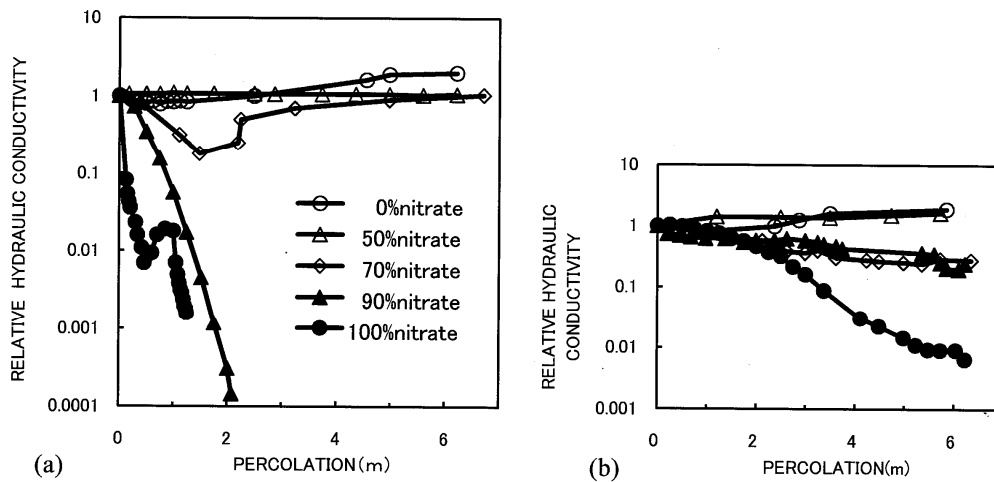
Figure 2. Relative hydraulic conductivity change during the leaching of dilute acid at (a) pH 3 and 1 mmol$_c$/L and (b) pH 4 and 0.1 mmol$_c$/L. The percentages denote the ratio of NO_3^- to $NO_3^- + SO_4^{2-}$ concentrations in the leaching acids (Ishiguro et al., 2003).
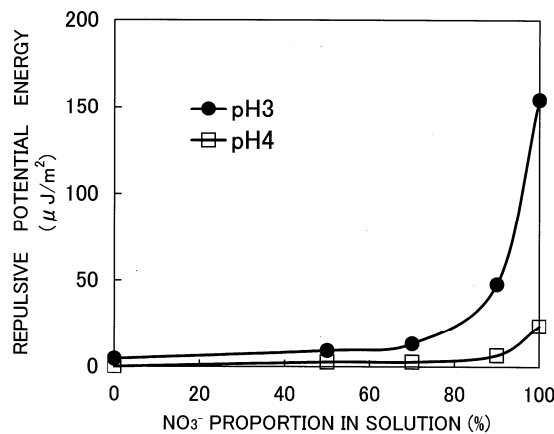
Figure 3. Calculated repulsive potential energies in dilute acids (Ishiguro et al., 2003).

Hydraulic conductivity study during the percolation of anionic surfactant solutions
Values of K decreased with the increase of SDS percolation amount and the decrease of SDS concentration in the discharged solution except for that of 10 mmol/L SDS solution as shown in Figure 4 (Ishiguro et al., 2008). The surface negative charge of the soil increased during the SDS percolation due to SDS adsorption. Then, the repulsive potential energy between soil particles increased and the soil swelled and dispersed. This caused the decrease of K. The K of the 10 mmol/L solution, which was higher than cmc, did not decrease well, because of highest electrolyte concentration.
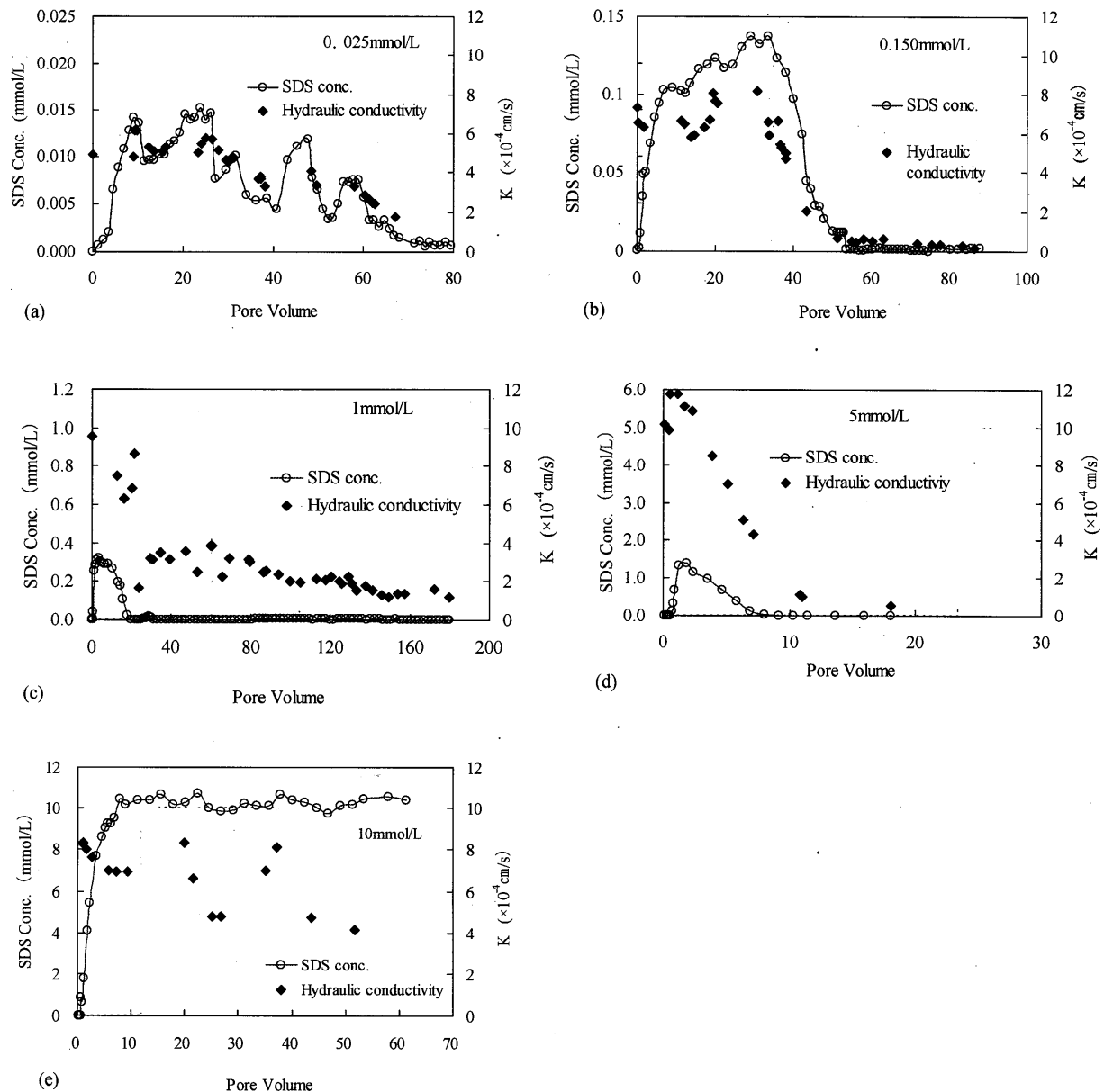
Figure 4. Anionic surfactant (SDS) breakthrough curves and hydraulic conductivities. Pore Volume is the effluent volume divided by water volume in the soil column (Ishiguro *et al.*, 2008).

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