

Elution Patterns of Native Sulfate and Breakthrough Curve's of Anions from Bt Soils of Chungwon Series

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청원통 Bt 토양에 내재된 황산이온의 용출특성과 음이온의 파쇄특성

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ABSTRACT

Anions such as Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , and organic anions, that do not become a part of the clay mineral crystal lattice, are of considerable interest in soils which are a potential sink caused by acid rain. In this paper, elution of native sulfate and breakthrough curves (BTC) were obtained from miscible displacement of non-specifically or specifically adsorbed anions through non-saturated or saturated Bt soil of Chungwon series. The shape and position of the BTC's could be affected by adsorption and ion exchange onto the soil particle surfaces. Measured BTC's for oxalic acid under unsaturated and saturated conditions showed that less pore volumes were required to displace the native SO_4^{2-} -S from the soil column, and that maximum detection limit of oxalic acid reached earlier than under unsaturated. The retarded BTC's to the righthand side could be attributed by different adsorption behavior of each anion, although BTC's may be influenced by the smaller order of velocity change. The alternate breakthrough and elution curves show the rapid approach to the maximum detection limit of $C/\text{Co} = 1$, compared to progressive tailing of elution curve to reach to $C/\text{Co} = 0$. The probable explanation for asymmetric elution patterns for both anion is that the anion was selectively adsorbed on the positively charged soil surface from the solution passing in the soil column. On the other hand, the variations of pH in effluent showed that pH was increased to 7 in the first 6 pore volume and then gradually decreased to pH 4.

Key words : elution, sulfate, BTC, anions, BT soils, chungwon series

INTRODUCTION

The importance of transport processes in the unsaturated and saturated zones and the need for better theoretical and experimental understanding of them have been stressed in recent review papers, because of the mobility and the distribution of solutes is such particular interest in many agriculture problems (Nielson et al., 1986; van Genuchten and Jury, 1987).

When a solution containing an anion is introduced into a porous medium, the distribution and leaching

may be described in a physical manner. The flow of water through soil is often considered as bulk movement that can be described by Darcy's law. This description becomes inadequate for the purpose of defining movement of transient dissolved solutes and their chemical process. Because the transport of reacting solutes depends upon the adsorption-desorption behavior, the charges on the soil surfaces, pH of soil system, and presence of other anions. When solute reacts with porous material during flow, distribution of solute between the solution phase and

adsorbed phase is further modified by the continuous interaction between the solute and medium, e.g., exchange or adsorption.

The sorption of anions by soils and soil constituents is an important interphase mass-transfer process for many common conditions, including ion exchange, specific adsorption of cations or anions, and negative adsorption (anion exclusion). As with all interphase mass-transfer processes, description of sorption-desorption process requires information about the equilibrium achieved between phases and the rate equilibrium is approached. Both of these components (equilibrium and rate) may be affected by compound structure, solid-phase properties, aqueous properties such as pH and presence of competing solutes in solution-phase. Concentration of a one chemical in each phase in turn influences the other's transport and transformation processes. Adsorption reaction is instantaneous or time-dependent (Sparks, 1987). These relationships are sometimes linear, at least over narrow concentration ranges, but are more commonly nonlinear. Miscible displacement experiments have shown how the intricate nature of the structure and texture of medium influence the manner in which solutes move in the soil-water system. With these conditions, the mixing of solutes during miscible displacement would occur in a different manner. Biggar and Nielson (1962) showed that solute mixing by ion diffusion manifests itself more clearly the wider the distribution of microscopic pore water velocities. One of the earliest solutions for equilibrium adsorption between the solution and adsorbed phases was presented by Lapidus and Amundson (1952). Also, Hingston (1981) obtained a similar solution that included the longitudinal mixing process as well as equilibrium and linear adsorption during transport. Bond and Phillips (1990) speculated that the main approximations for solute transport that are assumed in deriving solutions of transport are: (1) the local chemical and physical equilibrium attained rapidly relative to the time scale for transport; (2) the reaction occurs in a region of constant total charge concentration in both the solution and solid phases; (3) the effects of dispersion and the shape of the adsorption isotherms may be treated separately and then combined; and (4) the water content and pore water velocity in flow regime influence the fate of reactive or non reactive solutes.

The purpose of this investigation is to show that column chromatography may be used to study soil-anion interactions, thus revealing certain features in the leaching behavior of anions in Bt soil of Chungwon series studied here. In this paper, elution of native sulfate and BTC's were obtained from miscible displacement of non-specifically or specifically adsorbed anions through non-saturated or saturated Chungwon Bt soil column.

MATERIALS AND METHODS

Paddy soil samples of Chungwon Bt soil (clayey, kaolinitic, mesic, Fluvaquentic Epiaquepts), collected at a paddy field near Shintanjin, Chungnamdo, were used. Soils were air-dried and ground to pass 2 mm-sieve. Columns were made of acrylic tubes (11.5 cm long and 1.9 cm in internal diameter). One end of column was sealed with No. 3 rubber stoppers covered with 4-fly nylon mesh to protect soil falling from the column. The columns were uniformly packed to a bulk density of 1.3 cm^{-3} to a depth of 11 cm soil from the bottom of column, and the other end was then sealed. The pore volume was calculated on the basis of porosity. The column was leached with deionized water before addition of the anion to be studied. The actual volume of pore were obtained by weighing the soil-packed column before and after application of water. The difference between the calculate and the actual was less than 1% pore volume.

Before introducing solution containing the anion to be studied, the column was saturated with double ionized water (hereafter DI) until the flux reached the steady state. The anions were then added to the inlet of the column at the constant flow rate using the cassette pump throughout the experiment. The leachate was collected in the conical tubes on an automatic fraction collector every hour for the measurement of effluent and analysis of anions recovered in the effluent.

1. BTC's were obtained for 5 different anions such as Cl^- (as KCl), NO_3^- -N (as KNO_3), SO_4^{2-} -S (as K_2SO_4), PO_4^{3-} -P (as KH_2PO_4), and oxalic acid (as $\text{HO}_2\text{CCOH}_2 \cdot 2\text{H}_2\text{O}$). The solution containing the anion was added to the inlet of the column. The effluent was collected in the conical tubes on the automatic fraction collector every hour, weighed, and analyzed for the added anion and SO_4^{2-} -S dis-

solved. For oxalic acid the pH and the changes of the specific discharge (q) were measured until the maximum detection limit of oxalic acid and no sulfate were detected in the effluent.

2. Alternate miscible displacement of Cl^- by NO_3^- -N or vice versa was observed in the order of $8 \mu\text{eq mL}^{-1}$ of Cl^- , $8 \mu\text{eq mL}^{-1}$ of NO_3^- -N, $8 \mu\text{eq mL}^{-1}$ of Cl^- , $4 \mu\text{eq mL}^{-1}$ of NO_3^- -N, $6 \mu\text{eq mL}^{-1}$ of Cl^- , finally $18 \mu\text{eq mL}^{-1}$ of NO_3^- -N. One anion replaced the previous one after the maximum detection limit of an anion reached.

The analysis of anions in the effluent was determined by Dionex 200 (Dionex, CA) equipped with Dionex automated sampler and AS4A anion column.

RESULTS AND DISCUSSION

Concentrations of tracer measured in the effluent from columns is presented in the following figures as a ratio of the concentration of the effluent to the original tracer concentration. This ratio, plotted as the pore volume of effluent, yields a BTC. In this paper, pore volume of effluent i.e., referred as the ratio of total volume of collected effluent to the volume of pore obtained from the saturated column.

Fig. 1 shows similar BTC's of Cl^- and NO_3^- -N from Chungwon Bt soil initially saturated with double-ionized water at the time the Cl^- or NO_3^- -N solution added. Both anions are nonspecifically adsorbed

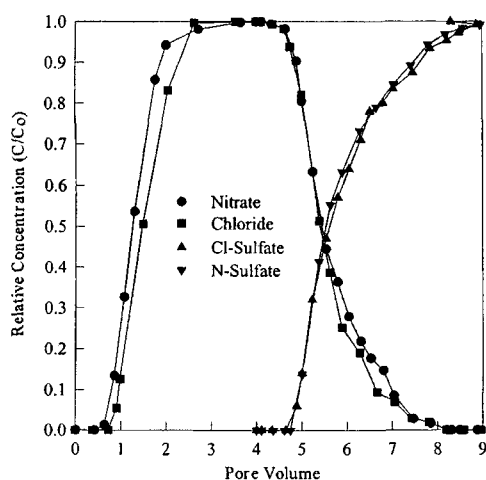


Fig. 1. Breakthrough curves of chloride and nitrate and sequential elution curves of chloride and nitrate by sulfate in Chungwon Bt soil.

on the positively charged sites of the soil surface. For Cl^- and NO_3^- -N, the volumetric water contents (θ_v) are 0.497 and 0.501, respectively, and the measured average fluxes ($q = Q/A$) are 1.96 and 2.01 cm h^{-1} . Both tracers rapidly approach to $C/C_0 = 1$ after approximately 2.7 pore volumes of effluent were collected. However the NO_3^- -N curve breaks are approximately 0.75 pore volumes earlier than that of Cl^- , due to molecular diffusion difference, but may well represent slightly different pore water velocities. When comparison is made between BTC's of Cl^- and NO_3^- -N, the BTC of Cl^- is slightly translated to the righthand side. This can be interpreted by the retarded appearance due to different adsorption behavior of each anion, although BTC's may be influenced by the smaller order of velocity change. These results are similar those of Nielson and Biggar (1961, 1962) who observed that the BTC may be translated to the right when solutes are retained within the column by any chemical or physical process. However, the shape of the curve is not determined by these retaining processes alone. Therefore, we assume that the BTC of Cl^- translated to the righthand than that of NO_3^- -N, due to the slightly higher affinity on the soil particles than NO_3^- -N.

In the same experiment, we studied the elution patterns of $\text{NO}_3^-/\text{Cl}^-$ displaced by the same equivalent of SO_4^{2-} -S following each peak of Cl^- and NO_3^- -N until no Cl^- or NO_3^- -N in the effluent was detected (Fig. 1). Solution containing SO_4^{2-} -S was added to the inlet of the column until 4 pore volumes of effluent collected. Elution curves of both anions started at 4 pore volumes as shown in Fig. 1.

The total pore volumes of SO_4^{2-} -S solution required to completely displace $\text{NO}_3^-/\text{Cl}^-$ in both solution and solid phases from the columns are approximately 4.2, whereas the total pore volumes for SO_4^{2-} -S to reach the relative concentration 1 was approximately 5.1 for both displacements. The relative concentration of $\text{NO}_3^-/\text{Cl}^-$ dropped sharply after 0.8 pore volumes of effluent collected and then leveled off as the leaching continued, whereas the relative concentration of SO_4^{2-} -S increases drastically to 1 after 0.9 pore volumes of effluent. The initial drop at 0.8 pore volumes indicates that mixing by diffusion takes place at approximately 0.7 pore volumes and followed by mixing and desorption of $\text{NO}_3^-/\text{Cl}^-$.

Comparison of the amounts of SO_4^{2-} -S and NO_3^- -

/Cl⁻ measured from effluent shows that the amount of adsorbed SO₄²⁻-S was greater than those of NO₃⁻/Cl⁻. From these results, we assume that NO₃⁻/Cl⁻ can be adsorbed only on the positively charged soil surface, SO₄²⁻-S is retained not only on the positively charged surfaces, but also by ligand exchange on the soil surface, as we observed in the adsorption isotherms of SO₄²⁻-S.

Using the soil column initially saturated with 8 μeq chloride, alternate displacement of one anion by the other having a similar adsorption characteristics was observed as shown in Fig. 2, that Cl⁻ and NO₃⁻ are believed to be retained on the positively charged soil surfaces and solution phase within a soil column. The experiment was run at 4 different concentrations of anions as follows: Section 1 and 2 (8 μeq equal equivalent basis); section 3 (8 μeq Cl⁻ by 4 μeq NO₃⁻); section 4 (4 μeq NO₃⁻ by 7 μeq Cl⁻); and finally section 5 (7 μeq NO₃⁻ by 7 μeq Cl⁻).

The alternate breakthrough and elution curves show similar shapes and pore volumes of effluent collected throughout the experiment. Each curve shows a rapid approach to the maximum detection limit of C/Co = 1, compared to progressive tailing of elution curve to reach to C/Co = 0. The probable explanation for asymmetric elution patterns for both anion is that the anion was selectively adsorbed on the positively charged soil surface from the solution passing in the soil column. Then as the solution containing displacing anion displaced the anion in solu-

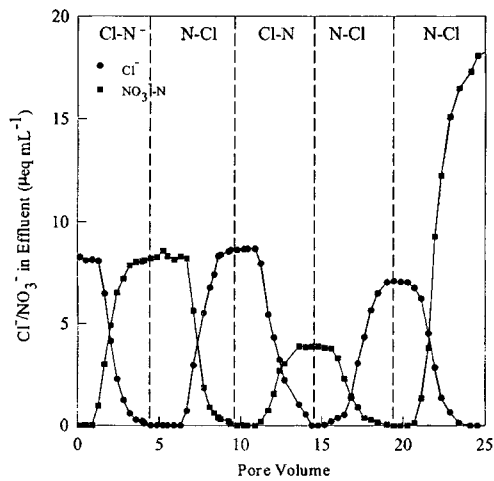


Fig. 2. Alternate elution patterns of chloride and nitrate in Chungwon Bt soil.

tion phase downward by piston flow and then decreasing order of displacing anion with moving water flow adsorbed on the positively charged soil surfaces. The volume of effluent which corresponds to the initial breakthrough of one anion by the other was approximately 0.8, indicating that mixing was occurred. Rao et al. (1980) reported that the degree of asymmetry or tailing in BTCs measured from miscible displacement of non-reactive solute (non-specific adsorption) through water-saturated columns of aggregated porous media is dependent upon the aggregate size, the pore-water velocity, and the column length. From the results of both Cl⁻ by NO₃⁻-N and NO₃⁻-N by Cl⁻ displacement obtained here, we may conclude that the strength of retention and adsorption capacity are similar for both anions when adsorption-desorption effects are considered. The progressive tailing of elution curve may also be explained by the rate-determining step at which solution containing a displacing ion pass through the soil column.

In Fig. 3A the BTC (left of C/Co = 1) and the elution pattern of SO₄²⁻-S by water (right of C/Co = 1)

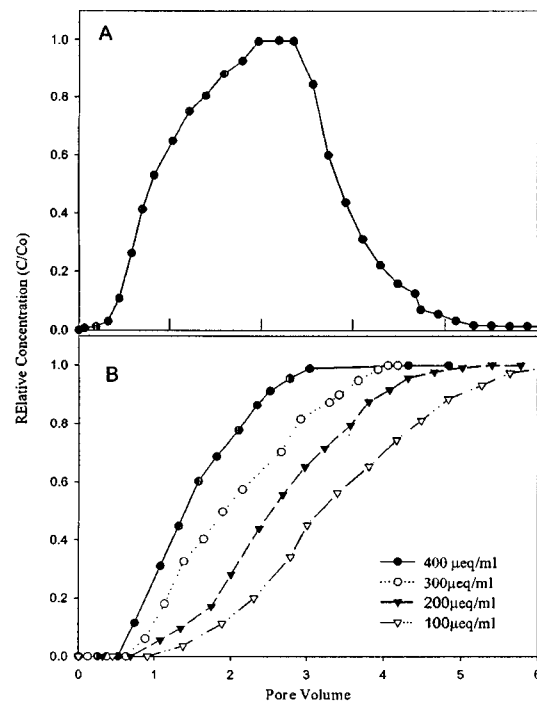


Fig. 3. Elution pattern of sulfate by water (A) and the breakthrough curves of sulfate in Chungwon Bt soil (B) under saturated flow regime.

are shown. The adsorption capacity of SO_4^{2-} -S is $11 \mu\text{eq g}^{-1}$. In this experiment, $C/\text{Co} = 1$ for SO_4^{2-} -S was obtained at 4.2 pore volume of effluent collected. And DI was then introduced into the column until the SO_4^{2-} -S in the effluent was stabilized, that is, C/Co is close to 0. At this time little amount of SO_4^{2-} -S from the column was found, due to at least the water-soluble SO_4^{2-} -S. The SO_4^{2-} -S elution pattern for Chungwon Bt soil is not symmetrical, but rather has a rapid approach to $C/\text{Co} = 1$ and a rather slowly falling tailing edge in elution curve. This behavior is compatible with the fact that the Chungwon Bt soil, with the clay fraction consisting largely of kaolin minerals and iron oxide, attracts SO_4^{2-} -S. Therefore, we may assume that the displacement of SO_4^{2-} -S from sorption sites includes either a diffusion-controlled process or a reversible kinetic process. The area under the elution curve is a rather smaller than that above the BTC. The difference of SO_4^{2-} -S calculated from the effluent of breakthrough and elution shows that approximately $2.33 \mu\text{eq SO}_4^{2-}$ -S are retained by the soil against the water displacement, as noted in the areas between two curves. This indicated that some fraction of SO_4^{2-} -S weakly held on the soil surface is not accessible for the displacing hydroxyl ions. Presumably SO_4^{2-} -S is strongly held against exchange through the specific adsorption on the soil surface that can not be displaced by hydroxyl ions. Nielson et al., (1986) reported that adsorption-exchange in soil is an important and overlooked phenomenon in reactive solute transport. Even with a small amount of stagnant water in the system or an uneven distribution of sorption sites can lead to significant transport and hence asymmetry and tailing when solutes are strongly adsorbed by soils. By comparison of elution curves of $\text{Cl}^-/\text{NO}_3^-$ and SO_4^{2-} -S, we conclude that SO_4^{2-} -S not only shows a higher affinity with Chungwon Bt soil, but also that a different adsorption mechanism may involve in the adsorption.

Fig. 3B shows the effects of SO_4^{2-} -S concentrations on the BTC's, indicated by the relationship between the ratio of SO_4^{2-} -S concentration in the effluent solution passing through the column and the influent solution entering the column (C/Co) and the volume of the effluent for Chungwon Bt soil. The initial breakthrough of SO_4^{2-} -S detected in the effluent was slightly delayed from 0.73 to 0.85 pore vol-

umes as the influent concentration of SO_4^{2-} -S, passing through the column, or increased from 100 to $400 \mu\text{g mL}^{-1}$, whereas fewer pore volumes were required to reach $C/\text{Co} = 1$ as the concentration of SO_4^{2-} -S increases from 100 to $400 \mu\text{g mL}^{-1}$. The BTC's are progressively shifted to the righthand side as the concentration of influent decreases, along with decreases in slopes. From this results, it may be concluded that the shape and transition of BTC depend on the concentration of SO_4^{2-} -S and the anion adsorption characteristics of soil. The initial breakthrough of SO_4^{2-} -S is controlled in part by diffusion and in part by adsorption, as is the gradual approach to the C/Co under the same flow conditions studied here. Biggar and Nielson (1962) reported that the approach to the maximum detection limit in the BTC would be more gradual for decreasing concentration and more abrupt for increasing concentration from inlet.

In Fig. 4, the BTC of 0.01 M oxalic acid shows a specific adsorption mechanism through ligand exchange with hydroxyl ions or anion exchange on the soil surface. The general trend of BTC shown in Figure 4A can be divided into 3 regions as follows: (1) a high and strong affinity for the adsorption sites; (2) convex to the y-axis; and (3) a retarded linear affinity for sorption sites. For the unsaturated run the

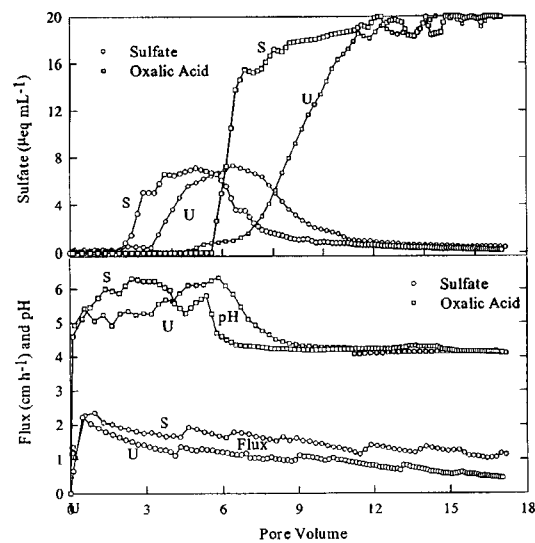


Fig. 4. Elution pattern of native sulfate displaced by 0.01 M oxalic acid subsequent changes of pH and fluxes in effluent, and BTC of oxalic acid in Chungwon Bt soil. (U:unsaturated condition, S:saturated condition).

observed BTC for oxalic acid exhibits three distinctive regions such as: (1) a retarded initial breakthrough of oxalic acid in the effluent (up to 5.6 pore volumes, $C/Co = 0$); (2) a rapid increases of oxalic acid in the effluent (5.6 to 6.7 pore volumes; $0 < C/Co < 0.85$); and (3) a linear affinity (6.7 to 12.2 pore volumes; $C/Co > 0.85$). From the total pore volumes of effluent we found that approximately 40% of the pore volumes were in the first region, another 10% for the second region, and the rest of pore volumes were required to reach the relative concentration 1. Calculated sum of adsorbed oxalic acid above the BTC in the first region was approximately 72% of the total oxalic acid adsorbed, and 15 and 13% of the total amount of oxalic acid adsorbed took for the second and third region, respectively.

Under saturated condition the shape of elution curve for oxalic acid is similar to that under unsaturated condition, as illustrated in Fig. 4A. However, the pore volumes required for each specific regions are slightly varied. The most noticeable difference between the two sets of curves for oxalic acid is the number of pore volumes required to complete the each distinctive elution region. Comparison of the pore volumes under saturated with respect to the unsaturated shows the initial breakthrough for saturated occurred earlier by approximately 1.2 pore volumes, i.e., 4.5 vs. 5.7 pore volumes; 6 times more pore volumes for the second region, i.e., 6.7 vs. 1.1 pore volumes; and 0.19 times (i.e., 1 vs. 5.3 pore volumes) for the linear affinity region. For the initial breakthrough the difference in pore volume may be explained that the column under the unsaturated condition was needed to pass the one pore volume of the solution through the column. The differences in shape and position of the curves may be explained by the interconnections of pore water contributing to degree of mixing by diffusion and the different rate of adsorption with moving water passing through the column. Self-diffusion coefficients decreased very rapidly as the water content decreased from saturation to near field capacity and enough pore space became available for the movement of water vapor, the diffusion coefficients of the soils increased very rapidly until a water content of about 5 to 10% on a volume basis was reached. Therefore, we assumed that the degrees of mixing by diffusion under saturated conditions were greater than under unsaturated conditions for the first region of the curves. And

flow velocities throughout experiment shown in Fig. 4B were greater under saturated condition than that under the unsaturated condition. Otherwise, it might be interpreted that under the saturated condition more oxalic acid traveled the entire length of the column in the solution phase without being involved in exchange on the soil surface even though oxalic acid has a strong affinity for the sorption sites.

Comparison of the areas above the BTC's between unsaturated and saturated shows that the oxalic acid sorbed by the soil under the saturated condition was approximately 1.35 times than that under the unsaturated condition. In addition to this, the oxalic acid sorbed in this experiment exceeds their sorption capacities determined from the adsorption isotherms. The general characteristics of the oxalic acid used in this experiment has the possibility of interacting with metal of hydrous oxide by ligand exchange through their carboxylic group, resulted in precipitation of oxalic acid forming chelated containing five and/or six membered rings with metal ions (Greenland, 1971; McColl and Pohlman, 1986; Martell and Calvin, 1952). In this study we observed the dissolution of metal ions in the effluent after approximately 8 pore volumes of effluent collected, but not throughout the unsaturated conditions. Therefore, it can be explained that the BTC for the saturated condition was affected by the chelation of oxalic acid with metal ions. However, a similar number of pore volumes were required to reach the maximum detection limit equal to the concentration of influent for both conditions. Biggar and Nielson (1961, 1963) demonstrated that unsaturating the soil results in a disproportionate shifting of the BTC for Cl^- to the left and drastic modification of the shape of curve.

The relative elution patterns of native SO_4^{2-} -S displaced by 0.01 M oxalic acid were shown in Fig. 4A. The elution curves of SO_4^{2-} -S are asymmetrical with significant tailing for both conditions, separated from each other. Bond (1986, 1987) demonstrated that asymmetry of the solute pulses may occur during unsteady flow in unsaturated soil due to differences in hydrodynamic dispersion coefficients. If the initial water content is relatively large, then the transition from asymmetry to symmetry occurs rapidly. This separation could be caused by the differences in initial water content between the unsaturated and saturated conditions, as well as pore

water velocity and the degrees of mixing by diffusion. Under the unsaturated condition the positions of initial breakthrough and peak concentration of SO_4^{2-} -S in the effluent was shifted to the right by approximately 1.4 pore volumes. This shift of BTC's was accompanied by the differences in an initial water content inside the soil columns. However, the peak concentrations of SO_4^{2-} -S in the effluent for both conditions were not influenced by the initial water content. It implies that the initial water condition does not influence the rate of desorption of native SO_4^{2-} -S. The difference in area between under the elution curve of SO_4^{2-} -S and above the BTC of oxalic acid represents that the total oxalic acid adsorbed was greater than the amount of SO_4^{2-} -S desorbed. This results agree with the adsorption isotherms observed in the batch experiment.

In Fig. 4B the changes of pH in effluent showed that pH increased as the concentration of SO_4^{2-} -S increased, and then pH was stabilized to pH 4.2 after maximum amounts of SO_4^{2-} -S in effluent was detected. This indicates that the adsorption of oxalic acid influenced not only the desorption of SO_4^{2-} -S but also increases in pH by 2.0 to 4.5 in the effluent compared to the initial pH of oxalic acid introduced to the column. The pH increase in the effluent can be interpreted as the release of hydroxyl ions into solution by ligand exchange from the soil surface and concomitant anion exchange with the native SO_4^{2-} -S. Also, the changes of pH followed the magnitude of adsorbed oxalic acid. And we observed, the flux was gradually retarded from 2.3 to 0.45 cm h^{-1} for 0 and 15 pore volume of effluent collected, indicating that dispersion within the process influenced the flux. A similar results for saturated condition was obtained in this study.

CONCLUSIONS

The shape and position of the BTC's would also be affected by adsorption and ion exchange. The BTC of Cl^- is slightly translated to the righthand side than that of NO_3^- -N. This can be interpreted by the retarded appearance due to different adsorption behavior of each anion, although BTC's may be influenced by the smaller order of velocity change. The alternate breakthrough and elution curves show similar shapes and pore volumes of effluent collected throughout the experiment. Each curve shows

a rapid approach to the maximum detection limit of $C/C_0 = 1$, compared to progressive tailing of elution curve to reach to $C/C_0 = 0$. The probable explanation for asymmetric elution patterns for both anion is that the anion was selectively adsorbed on the positively charged soil surface from the solution passing in the soil column. Measured BTC's for oxalic acid under unsaturated and saturated conditions showed that less pore volumes were required to displace the native SO_4^{2-} -S from the soil column, and that maximum detection limit of oxalic acid reached earlier than under unsaturated.

The variations of pH from the column experiment showed that pH was increased to 7 in the first 6 pore volume and then pH gradually decreased to pH 4 until BTC of oxalic acid reached to the detection limit. Variations of pH in the leachate showed that pH was increased until SO_4^{2-} -S in leachate reached the maximum and the dropped to below the soil pH.

요 약

산성비와 같은 요인에 의해 토양으로 유입되는 Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} 그리고 유기산 등의 음이온은 점토광물의 결정구조에 포함되지 않기에 관심 대상이다. 본 논문에서는 포화 또는 불포화 상태의 청원 통 Bt 층 토양에 특정 또는 비특정적으로 흡착된 음이온을 혼입치환시킴으로서 토양내 자연 황산이온의 용탈과 파쇄곡선을 조사하였다. 시험결과 파쇄곡선 모양과 형태는 토양입자 표면에서의 치환과 흡착에 따라 영향을 받은 것을 알 수 있었다. 포화와 불포화 토양수분 조건에서 조사된 옥살릭 이온의 파쇄곡선은 토양 자체의 황산이온을 치환시키는데 작은 공극수량이 필요하였으며 최대 감지한계에 도달은 불포화보다 포화조건에서 더 빨리 도달하였다. 그리고 오른쪽으로 치우친 파쇄곡선은 비록 토양내 유속변화순에 따라 영향을 받았지만 주로 각각의 음이온의 서로 다른 흡착 특성에 의해 영향을 받았다고 판단된다. 교호상태의 조건에서 얻어진 파쇄곡선과 용출특성은 C/C_0 가 0보다는 1에 빨리 도달하였다. 이와 같이 음이온의 비대칭형 형태의 용출 특성은 토양을 통과하는 토양수내의 음이온이 전화를 띠고 있는 토양 입자 표면과의 선택적 반응에 기인한다. 그리고 토양을 통과하는 용출수의 pH 변화를 조사한 결과 토양내의 치환과 흡착반응이 진행되는 6 공극수량까지는 pH가 7까지 증가되나 이 이후 점진적으로 4까지 감소됨을 알 수 있었다.

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