Mechanisms of Adsorption with Respect to Sulfate Mobility in Multispecies Systems of Soils

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SUMMARY

The mobility of sulfate in soils depends on several factors including redox potential, soil mineralogy, pH, and the presence of other anions that compete for sorption sites with sulfate. The proposed model of adsorption mechanism for sulfate postulated that reaction is between anions in solution and charged surfaces of soil particles. With appropriate choice of parameters obtained from the adsorption-desorption experiments, the equation of transport model adapt an empirical approach, capable of handling most general equilibrium adsorption isotherms, suitable for multispecies systems.

INTRODUCTION

Anion and molecular retention in soils has been the subject of increasing research. Many anions and all molecular species are retained by more complex mechanisms than the simple electrostatic attractions involved in most cation adsorption reactions. Major soil anion species include Cl\(^-\), HCO\(_3\)^-, CO\(_3\)^-, SO\(_4\)^-, PO\(_4\)^-, OH\(^-\), and F\(^-\). Some micro nutrients exist as anions such as H\(_3\)BO\(_3\)^- and MoO\(_4\)^-, as do some heavy metals such as CrO\(_4\)^2- and HAsO\(_4\)^2-. Pesticides also exist as anions such as 2,4,5-T and 2,4-D. Molecular species include NH\(_3\), undissociated weak acids such as H\(_3\)BO\(_3\) and H\(_4\)SiO\(_4\), and the undissociated forms of many pesticides.

The ability of soil to adsorb anions depends on its inherent adsorption properties, the degree of anions previously adsorbed, and the concentration of anions in solution phase and pH in reacting solution relative to concentrations in which the soil has previously equilibrated. Surface area, surface aluminum and iron, pH, and exchangeable cations are the major factors influencing anion adsorption on clay minerals.

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Extensive studies have been carried out on the adsorption of $\text{SO}_4^{2-}$-S by clay minerals and following is an attempt to summarize the desorption of $\text{SO}_4^{2-}$-S by the anions competing for the limited same sorption sites. $\text{SO}_4^{2-}$ is of particular interest, as it can accumulate in soils because it is strongly adsorbed to Fe or Al oxide surfaces. Therefore, the influence of anions other than hydroxyl($\text{OH}^-$) and phosphate ($\text{PO}_4^{3-}$-$\text{P}$) on $\text{SO}_4^{2-}$-S adsorption–desorption has to elucidate relationships between soil properties, chemical reactions, and other phenomena involving $\text{SO}_4^{2-}$-S ions.

In this paper the generalized adsorption mechanism and transport model of sulfate in multispecies systems in soils were proposed to elucidate the actual fate of sulfate in a given conditions.

**Theoretical and Mathematical Backgrounds of Adsorption and Transport of Anion in Soils**

1. Adsorption Phenomena

Anion adsorption in soils is often categorized into two mechanisms: nonspecific adsorption and specific or chemisorption. With nonspecific adsorption the anions are adsorbed by positively charged sites on the soil surface by electrostatic forces in the outer Helmholtz plane, separated from the surface by at least one water molecule. The positive charge which retains an anion on the mineral surface is the result of protonation of the surface. With specific or chemisorption, specific adsorption of anions can occur by ligand exchange with aquo, hydroxo, or ol groups. For acid pH values the reactivity of these groups to ligand exchange is in the order of aquo $>$ hydroxo $>$ ol (16, 17, 18).

Hydrous metal oxide has a structure in which metal atoms are linked by groups as shown in Fig. 1.

![Fig. 1. Proposed structure of ol and oxo groups on the soil particle surface](image)

where M represents the metal ions on the mineral surfaces. At the surface of the polymeric structure the co-ordinate positions of the terminal atoms are occupied by aquo (M-$\text{H}_2\text{O}$) and hydroxo group (M-$\text{OH}$). The relative proportion of the aquo and hydroxo groups is determined by suspension pH which in turn determines the surface charge, resulting in equal numbers of aquo and hydroxo groups on the surface at the point of zero charge. When adsorption of protons occurs in excess of hydroxyl ions on the soil surface, surfaces become more positively charged resulting in an electrostatic attraction of such anions as chloride and nitrate.

Ligand exchange can occur on surfaces initially carrying net negative, net positive, or neutral charges. The anions are bonded by covalent or van der Waals forces in the inner Helmholtz plane by ligand exchange with surface OH or $-\text{OH}_2^-$ groups (8, 9). Ligand exchange of sulfate with aquo groups would add negative charge to the surface but would not increase the concentration of the hydroxyl ions in the solution, whereas ligand exchange with hydroxo group can affect the pH by release of $\text{OH}^-$ into the solution.
For sulfate, Parfitt et al. (10) showed that two surface hydroxyl groups (or $-\text{OH}_2^-$ ions) are replaced by one sulfate ion, and two oxygen ions of the sulfate ion are each co-ordinated to a different Fe$^{3+}$ ion, resulting in the binuclear bridging surface complex, as shown below (3, 6, 7, 10, 11).

Or $\text{SO}_4^{2-}$ ions may displace either OH or $\text{OH}_2^-$ from the Fe on the clay mineral surfaces. But both of these reactions leave the surface with a net negative charge instead of a neutral charge. The neutralization of the negative charge is proceeded by the adsorbed sulfate displacing another ligand (OH from a neutral site or water from a positive site) from the adjoining Fe resulting in a ring formation as shown in Fig 3. (5, 11).

Hingston (6) grouped adsorption of sulfate on metal hydrous oxides under nonspecific adsorption or ligand exchange. He suggested that at pH values near the $pK_a$ of the acid $\text{SO}_4^{2-}$-S accepts a proton from the soil surface, from a net positive site, resulting in $\text{HSO}_4^-$ adsorption as follows:

According to this, one mole of $\text{SO}_4^{2-}$-S

$\text{Al}-\text{OH}_2^+ + \text{SO}_4^{2-} \rightarrow \text{Al}-\text{OH} + \text{HSO}_4^- \rightarrow \text{Al}-\text{HSO}_4 + \text{OH}^- \text{removed from solution (or adsorbed as } \text{HSO}_4^- \text{)} \text{ neutralize one equivalent of surface charge, that is the adsorption of } \text{SO}_4^{2-}$-S \text{ is equivalent to the net positive charge of the surface, i.e., the charge measured by chloride adsorption in the absence of } \text{SO}_4^{2-}$-S.

For a miscible displacement technique, if the rate of adsorption of an ion onto a colloidal surface follows first-order kinetics, then

$$d\left(\frac{C_t}{C_0}\right) = -K_a(C_0-C_t)dt \quad [\text{Eq. 1}]$$

where

- $C_t$ = concentration of anion species at time $t$
- $C_0$ = initial concentration of anion species ($t = 0$)
- $K_a$ = anion adsorption coefficient

Using miscible displacement, adsorption will vary only slightly with flow rate, and since by definition the adsorption rate coefficient
$K_a$ is constant, a new term, the apparent rate coefficient $k_a$ is defined for each flow rate in the system (13, 14, 15).

Desorption depends upon a number of other factors, such as nature of adsorption, type of desorbing ion, soil:solution ratio, pH of suspension, vigor of shaking, and the time of contact between $SO_4^{2-}$-S and the adsorbent. Therefore, varying results are reported on $SO_4^{2-}$-S desorption. Sulfate adsorbed by Oregon soils appeared to be readily displaced by water (14), but Haque and Walmsley (4) found that only 33 and 76 % of the initially adsorbed $SO_4^{2-}$-S was recovered on four KH$_2$PO$_4$ extractions from Montserrat clay and Montreal sand loam of the West Indies, respectively. Aylmore et al. (1, 2) reported that $SO_4^{2-}$-S adsorbed by kaolinite clays was readily desorbed by water, but that adsorbed on freshly ground Fe and Al oxides was almost irreversible. Sanders and Tinkler (12) concluded that $SO_4^{2-}$-S adsorption on soils was reversible over short periods, but not over periods of days.

The desorption mechanisms can be categorized as two distinctive types such as non-specifically adsorbing anion, and anion exchange specifically adsorbed anions. To fully comprehend these reactions, a knowledge of the rate equations or rate law explaining the reaction system is required. A number of reactions have been employed to describe the kinetics of reactions in clay minerals and soils (13, 14, 15).

If the rate of desorption of an ion from a colloidal surface follows first-order kinetics, then for a miscible displacement technique (for the solid surface phase)

$$d\left(\frac{C_t}{C_0}\right) = -K_d \cdot C_t dt$$  \[ Eq. 2 \]

where $K_d$ = anion desorption coefficient

The apparent desorption rate coefficient $K'd$, the first-order kinetics for a miscible displacement technique is:

$$d\left(\frac{C_t}{C_0}\right) = -K' _d \cdot C_t dt$$  \[ Eq. 3 \]

However, these equations describing the adsorption and desorption only focused on single-species system even though the soil system have multospecies. Therefore, these equations should be modified to fit the real soil system. These adsorption-desorption equations can be incorporated into solute transport equation to describe the distribution and concentration of anion investigated.

2. Solute Transport

The commonly used one dimensional solute transport equation is given by Eq. 4.

$$\frac{\partial C}{\partial t} + \frac{\beta}{\theta} \frac{\partial S}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - \frac{V}{\theta} \frac{\partial C}{\partial z}$$  \[ Eq. 4 \]

where

- $C$ is desorbed(solution) phase concentration
- $D$ is adsorbed(solid) phase concentration
- $\beta$ is soil bulk density
- $\theta$ is volumetric water content
- $V$ is flow velocity
- $D$ is diffusion/dispersion coefficient
- $z$ and $t$ are vertical distance and time variables

The transport equation is coupled with the proper adsorption model and solve for $C$ and $S$ as the case may be. In most solute transport studies related to vertical movement of chemicals, adsorption processes are characterized by equilibrium isotherms that describe the relationship between solution phase and solid phases distribution of the species, at equilibrium, for different solution concentration.

Most adsorption studies in single-species systems are performed at high solution-to-solid ratios with continuous shaking or stirring. And these single species solute transport models can be readily extended to multi-component systems by using a few simplifying
assumptions. The generalized solute transport model in a system of \( n \) species can be described in one dimensional Cartesian coordinate as

\[
\frac{\beta}{\theta} \frac{\partial S_i}{\partial t} = D \frac{\partial^2 C_i}{\partial z^2} - \frac{V}{\theta} \frac{\partial C_i}{\partial z} \quad [\text{Eq. 5}]
\]

\[
\frac{\partial S_i}{\partial t} = f_i[ C_i, S_i, \frac{\partial C_i}{\partial t}, \ldots, (i=1,n)] \quad [\text{Eq. 6}]
\]

An important application of adsorption equations is to estimate adsorption parameters from experimental results. These parameters can be used to verify and improve the prediction of solute distribution and transport. To obtain the parameters an empirical approaches have to be used in conjunction with any general equilibrium isotherm, to account for competition for the sorption sites although this empirical setup of computations may slightly or significantly overestimates the effect of competition for sorption site.

The empirical Eq. 4 can be used to estimate adsorption in multi-species systems in soils below. However, this equation is to be characterized by preferential adsorption coefficients\((P_j)\) defined in Eq 7.

\[
\sum_j P_j = 1 \quad [\text{Eq 7}]
\]

A useful choice of defining \( P_i \) is \( K_i / \sum_j K_j \), where \( K_j \) are the equilibrium adsorption isotherms. And an empirical Eq. 8 of adsorption is as follow.

\[
S_i = S_{io} P_i C_i / \sum_j P_j C_i \quad [\text{Eq 8}]
\]

However, Eq. 8 should be incorporated into Eq. 2 and 3 to consider \( C_{io} \) while sulfate ions moves along the soil with continuous reaction with solid surfaces. Otherwise It may lead to misinformation of distribution and transport of sulfate. And resultant solution(desorbed) concentrations can be obtained from the mass conservation Eq. 9 for \( I = 1 \) to \( n \).

\[
\beta \cdot S_i + \theta C_i = \beta \cdot S_{io} + \theta C_{io} \quad [\text{Eq 9}]
\]

Complete derivation of the model and details of the simulation programs will be followed in subsequent paper by considering initial and boundary conditions which can happen in soil systems.

**Conclusions**

Adsorption of anionic species by soils has a profound effect on solute behavior and transport. Especially the adsorption phenomena in multispecies systems may be significantly different from single-species adsorption. The adsorption-desorption phenomena may influence the fate of anionic species depending on the type of exchange because the solution pH can be changes. For proper management of nutrition sources such as sulfate in soils under realistic multispecies systems, we need mathematical models capable of describing the behavior and transport including soil-solute interaction. In this paper, some of mathematical equations based on adsorption-desorption processes in multispecies systems in soils were introduced. However, some equations will be assessed their validity by the experimental observations in prediction. It is also important that the parameters obtained from adsorption isotherms can be changed from one set of experiment to another under the given circumstances such as pH, number of competing species and their concentration. Therefore accounting for competition should allow the correct parameters to be estimated independently of the experimental conditions.
References


토양의 다중이온체계내에서의 황산이온의 이동을 고려한 흡착기작

정덕영

요 약: 토양내에서 황산이온의 이동성이 산화환원전 위, 토양물질 특성, pH, 그리고 황산이온과 토양입자 표면에 흡착에 관여하는 타 음이온들에 의해 영향을 받는다고 알려져 있다. 제시된 황산이온의 흡착 기작은 토양입자 표면과 수용성상태의 음이온간의 상관 관계를 나타낸 것이다. 그러므로 흡착기작연구로 부터 얻어진 적정한 계수를 적용함으로서 다중 이온이 존재하는 토양내에서의 일반적 동온흡착 극선을 적용할 수 있는 이동모형은 실험적 접근 방법을 수용하게 된다.