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MODELING COMPETITIVE ADSORPTION OF CHROMATE, SULFATE, AND SELENATE ON γ-Al_2O_3: COMPARISON BETWEEN THE TRIPLE-LAYER MODEL AND A FREUNDLICH-TYPE MULTI-COMPONENT ISOTHERM

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ABSTRACT

This work addressed the interactions of CrO_4^{2-} + SO_4^{2-} and CrO_4^{2-} + SeO_4^{2-} systems on γ-Al_2O_3, to better understand the competitive adsorption of these anions in the natural environment. The relative influence of binary and single anion systems of CrO_4^{2-} + SO_4^{2-} and CrO_4^{2-} + SeO_4^{2-} on competitive adsorption envelopes and isotherms on the oxide surface was evaluated. Anionic competitive adsorption efficiency depended on pH. A higher pH causes SO_4^{2-} and SeO_4^{2-} to prevent CrO_4^{2-} adsorption less efficiently. The experimental results concerning the competitive adsorption isotherm indicate that a higher concentration of competitive solute yields more efficient prevention by the competitive solute of CrO_4^{2-} adsorption. The suitability of the Sheindorf-Rebuhn-Sheintuch (SRS) equation in representing the competitive adsorption isotherm of CrO_4^{2-}, SO_4^{2-}, and SeO_4^{2-} on a γ-Al_2O_3 surface, was also examined. The proposed SRS equations are simple expressions that account for the competitive interactions of anions. More sites were found to be occupied in mixed anionic adsorbate systems than when either ion was present alone, suggesting that the γ-Al_2O_3 surface is composed of many groups of binding sites. Triple-layer model (TLM) predicted the competitive effects qualitatively, but not quantitatively, because of the heterogeneity of the adsorption sites.

INTRODUCTION

Adsorption of many elements onto particulate matter has been found to be important and may significantly affect the mobility of those elements in natural environments. The bioavailability of anions may also be affected by the interaction of anions in adsorption on oxides. The extent of this interaction normally depends on the affinity of the anions for the surface, the relative concentration of the anions, the change in the surface potential upon adsorption, and the pH. Chromium is commonly employed in acidic electroplating, tanning, printing, dye and drug manufacturing, and petroleum refining. The health and environmental effects of carcinogenic Cr (VI) are well known. The fate of sulfur and selenium in aquatic ecosystems is affected by a variety of physical, chemical, and biological factors. The presence of selenate and sulfate in wastewater and surface water is becoming a severe environmental and public health problem, since selenate is a major selenium species in drainage water [1] and sulfate is the most abundant anion in atmospheric deposition.

Anion adsorption at the oxide/water interfaces is commonly interpreted as a surface complexation mechanism in which anionic solute binds to the site of reaction on the surface to form either an inner-sphere or ion-pair complex. Adsorption of selenite, chromate, arsenate, and molybdate are regarded as specifically coordinated with surface hydroxyl groups [2-5], according to both the effect of the solution's ionic strength and the simulation by the TLM. Sorption of sulfate and selenate, however, is recognized to form an outer-sphere complex [5-8]. Krishna *et al.* [9] ex-

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plored that the amount of chromate adsorbed between pH 2 and 6 was one half of that at pH 1, and above pH 8 the adsorption was negligible. Weerasooriya and Tobschall [10] indicated chromate adsorption to goethite is ascribed to an inner-sphere surface complexation mechanism and the three-plane model (TPM) modeled calculations under-predicted chromate when surface loading is > 2×10^{-7} mol/m^2. In contrast, Ding *et al.* [11] showed that the potential molecular energy of FeOOH-Cr complex is small, resulting in a weaker chemical bond formation in this complex. Al and Fe oxides and organic matter played very important roles in the association with selenate and selenite in soil environment [12].

Complexation reactions at the surfaces of particles induce more complexity than corresponding reactions in homogeneous solution. The co-adsorption of several anions does not only imply a competition for available surface sites, but does affect the surface equilibrium by altering the charge on the surface. In practical situations, multi-component competition may increase the complexity of anion interactions at the water/oxide interface. Such complex systems frequently occur, and the magnitude of these competitive interactions must be clarified to better predict contaminant behavior and identify those anions more likely to be affected during transport in the presence of other anions. Hawke *et al.* [13] demonstrated that adsorption of strongly binding anions can only be depressed if the weakly binding anions are present in great excess at low pH. Mesuere and Fish [14] showed that the sorption of chromate onto α-FeOOH in acidic environments was diminished by the competitive adsorption of organic oxalate. Sulfate has been shown to decrease the adsorption of As(III) and As(V) in acidic systems [15, 16]. Goldberg *et al.* [17] showed that competitive anion effects on B adsorption increased in the order, sulfate < molybdate < phosphate. Geelhoed *et al.* [18] found that phosphate competed more strongly for adsorption on goethite than did sulfate, which result is consistent with the fact that phosphate has a higher affinity for the surface than does sulfate.

Wu *et al.* [19] demonstrated that the order of the relative retention of anions on the γ-Al_2O_3 surface was molybdate > selenite > selenate ≈ sulfate > chromate, following the magnitudes of the overall proton coefficients of the corresponding anions. Wu *et al.* [20] also showed that more alkaline conditions reduce the efficiency with which molybdate inhibits sulfate and selenate adsorption; these researchers obtained similar results for the depression of sulfate adsorption by selenate. Wu *et al.* [21] further modeled the competitive adsorption of molybdate, sulfate, and selenate using a Freundlich-type multi-component isotherm. The authors established that the proposed SRS and modified SRS equations are simple expressions that account for the competitive interactions of anions present in a mixture for the range of concentrations over which each individual component exhibits Freundlich behavior. Gao and Mucci [22] demonstrated that the adsorption of arsenate on goethite decreases in competitive experiments with phosphate, and the adsorption of phosphate also decreases in competitive experiments with arsenate. Lehmann *et al.* [23] displayed the presence of EDTA caused a certain decrease of removal efficiency for the cause of chromate, due to competition for the same sorption sites. Sharmasarkar and Vance [24] demonstrated the percent selenite sorption was always greater than selenate. The Freundlich model resulted in better statistical fitting of the data compared to the Langmuir model for both Se species. The researchers also showed that the equilibrium model, derived by combining the single oxyanion subsystems, predicts the shape of the competitive adsorption data but fails to reproduce quantitatively the degree of adsorption.

Accurately predicting the extent of anionic adsorption onto oxide surfaces involves (i) an understanding of the competitive effects among anions and (ii) a descriptive model to describe accurately adsorption characteristics in the presence or absence of competition. This research investigated the envelopes and isotherms of the adsorption of chromate, sulfate, and selenate in single and binary mixture solutions, to determine the competitive adsorption of these anions. The objectives were to (i) determine the extent of the competitive adsorption envelopes between chromate, sulfate, and selenate on γ-Al_2O_3, as a function of pH; (ii) to investigate the competitive adsorption isotherms of these anions over a range of concentration ratios; and (iii) to model the experimental results using the SRS equation and the TLM.

MATERIALS AND METHODS

1. Materials

All solutions were prepared with deionized water (Milli-Q) and reagent-grade chemicals. Stock anion solutions (10^{-2} M) were prepared with Na_2CrO_4, Na_2SO_4, or Na_2SeO_4. The adsorbent γ-Al_2O_3, obtained from Aerosil Co. (Japan), was purified by electrodialysis (1200 V, 3 mA) before being used in the sorption experiments. The specific surface area of γ-A_2O_3 was calculated to be 100 m^2/g based on the BET measurements.

2. Competitive Sorption Experiments

In the competitive adsorption envelope experiments, anions (5×10^{-3} M) were equilibrated with γ-Al_2O_3 suspension (30 g/L). A small amount of HNO_3 or NaOH was added to cover the pH range from 2 to 10 for the reactions, CrO_4^{2-} + SO_4^{2-} and CrO_4^{2-} + SeO_4^{2-}. In the competitive adsorption isotherm ex-

Table 1. TLM parameters and basic surface complexation constants.

Specific surface area (m^2/g)	100 (BET measurement)
Site density ($site/nm^2$)	8 [27]
C_1 (o-plane capacitance, $\mu F/cm^2$)	80 [28]
C_2 (β-plane capacitance, $\mu F/cm^2$)	20 [28]
$\log K_{a1}^{int}$, $\log K_{a2}^{int}$	-6.9, -9.7(acid/base titration)
$\log K_{Na+}^{int}$, $\log K_{NO3-}^{int}$	-8.3, 6.9(acid/base titration)

Table 2. Surface complexation reactions and equilibrium constants for anion/γ- Al_2O_3 systems.

Anions	Reactions in system[a]	$\log K_{eq}^{int}$
CrO_4^{2-}	$SOH + H^+ + CrO_4^{2-} = SOH_2^+\text{-}CrO_4^{2-}$	10.5[a]
	$SOH + 2H^+ + CrO_4^{2-} = SOH_2^+\text{-}HCrO_4^-$	14.5[a]
SO_4^{2-}	$SOH + H^+ + SO_4^{2-} = SOH_2^+\text{-}SO_4^{2-}$	10.4[a]
SeO_4^{2-}	$SOH + H^+ + SeO_4^{2-} = SOH_2^+\text{-}SeO_4^{2-}$	9.8[a]

Note. K_{eq}^{int} is the intrinsic equilibrium constant.

[a] Wu *et al.* [19].

periments, CrO_4^{2-} (2000, 1500, 1000, and 700 μM) was equilibrated with γ-Al_2O_3 suspension (10 g/L), and the concentrations of competitive solutes (SO_4^{2-} and SeO_4^{2-}) were between 300 and 7000 μM. A little HNO_3 or NaOH was added to maintain the pH of the competitive systems at 5.7 ± 0.2. When the desired pH was obtained, 10 ml of the suspension was removed to a 15-ml polypropylene tube. All experiments were conducted in a tightly capped 15-mL polypropylene tube in an atmosphere of N_2 at 25 ± 0.1 °C, over 24 hours. The pH of each suspension was determined at the end of the equilibrium period. The suspensions were centrifuged at 9500 rpm for 10 min, and the supernatant was then filtered through 0.2 μm filter paper (Gelman Sciences) for later determination of the anion concentration. All anion concentrations were obtained by ion chromatography (Dionex 2000i SP).

3. TLM and SRS Equation Simulation

The TLM developed by Davis and Leckie [25] and subsequently modified by Hayes and Leckie [26] was employed to simulate the equilibrium partitioning of anion species at the γ-Al_2O_3/water interface. Table 1 specifies the TLM parameters, intrinsic acidity surface hydrolysis constant (K_{a1}^{int} and K_{a2}^{int}) and binding constants (K_{Na+}^{int} and K_{NO3-}^{int}) of the background electrolyte ($NaNO_3$) with the surface [19]. The parameters and equations in Tables 1 and 2 were used in the model analysis to establish the partition of anions in the competitive adsorption envelope experiments.

The adsorption of anions onto soils or other adsorbents is specified by a Freundlich isotherm ($q = KC^n$), where K represents adsorption capacity and n is the intensity of adsorption. Sheindorf *et al.* [29] extended the single component Freundlich isotherm, using the concept of competition coefficients, to multi-component systems.

A general SRS equation can be given as

$$q_i = K_i C_i \left(\sum a_{ij} C_j\right)^{n_i - 1} \tag{1}$$

where q_i is the adsorption of component i per gram weight of sorbate in μmol/g; C_i and C_j are the concentrations of i and j in the equilibrium solution in μM; K_i and n_i are the Freundlich constants obtained for i in a single-component system; and a_{ij} is the competition coefficient for the adsorption of component i in the presence of component j. The bicomponent isotherm can be written,

$$\frac{C_1}{C_2} = \frac{\beta_1}{C_2} - a_{12} \tag{2}$$

$$\frac{C_2}{C_1} = \frac{\beta_2}{C_1} - a_{21} \tag{3}$$

with

$$\beta_1 = \left(\frac{K_1 C_1}{q_1}\right)^{\frac{1}{(1-n_1)}} \text{ and } \beta_2 = \left(\frac{K_2 C_2}{q_2}\right)^{\frac{1}{(1-n_2)}} \tag{4}$$

The consistency of the data with the proposed isotherm is demonstrated by a plot of C_1/C_2 against β_1/C_2 which should yield a straight line of unity gradient; the competition coefficient is determined from the intercept on the y-axis. This study simulated competitive adsorption isotherms by the SRS equation and compared the results with those of TLM simulations.

RESULTS AND DISCUSSION

1. TLM Simulation of Competitive Adsorption Envelope

The competitive adsorption envelopes of CrO_4^{2-} + SO_4^{2-} and CrO_4^{2-} + SeO_4^{2-} by γ-Al_2O_3 were simulated by a TLM model and are given in Figs. 1 and 2. In simulating the competitive adsorption of chromate, sulfate, and selenate at the surface of γ-Al_2O_3, the surface acidity constants, the complexation constants and other related parameters were maintained at the values derived from the single-component systems (Tables 1 and 2). The results of the simulations of SO_4^{2-} and SeO_4^{2-} in binary-adsorbate systems were almost the same as those in the single-adsorbate system. In contrast, the results for CrO_4^{2-} were markedly underestimated. The TLM may only qualitatively represent mixed chromate-sulfate and chromate-selenate anion systems, but it reproduces the shape of adsorption envelopes over the entire pH range of interest. Benjamin and Leckie [30] demonstrated that measured adsorption equilibrium constants were often mean values for adsorption reactions which involve many types of site. Consequently, the assumption that surface sites are in

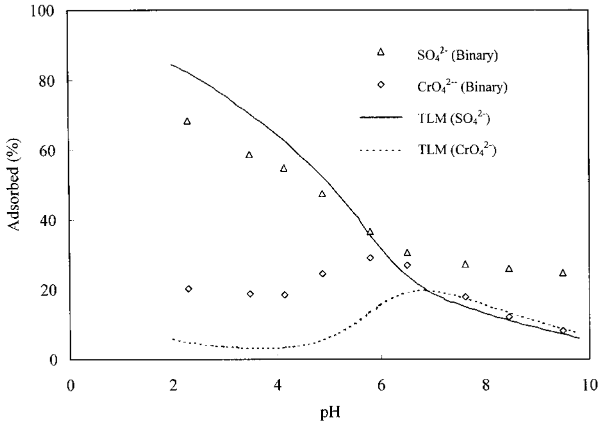

Fig. 1. Binary solute adsorption of CrO_4^{2-} and SO_4^{2-} on γ-Al_2O_3 as a function of pH. TLM simulations are shown with lines and symbols denote experimental data.

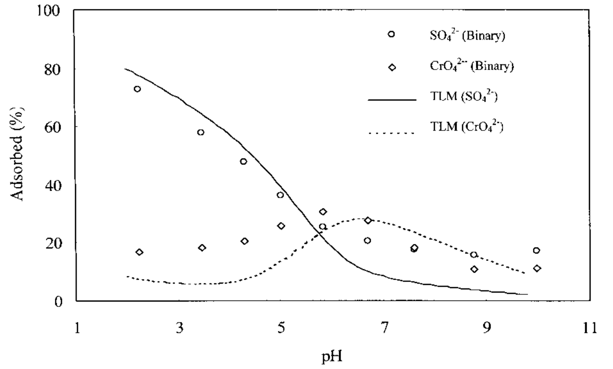

Fig. 2. Binary solute adsorption of CrO_4^{2-} and SeO_4^{2-} on γ-Al_2O_3 as a function of pH. TLM simulations are shown with lines and symbols denote experimental data.

excess may be false for some types of sites, even though the overall surface is far from saturated. The TLM works on the assumption that adsorption occurs on only one type of site. Although this assumption has sufficed for modeling single anion systems, this research shows that it is probably an oversimplification. TLM is very probably an appropriate representation of anionic competition since it can qualitatively determine the shape of anion adsorption envelopes from mixed solutions. However, quantitative verification of the model's ability to describe anionic competition using a single set of reactive sites is impossible without improvements in certain model parameters.

2. Competitive Adsorption Isotherm and the SRS Equation Simulation

Adsorption isotherms were determined by plotting equilibrium concentration against adsorption for single-component systems. Table 3 presents the Freundlich equations involving CrO_4^{2-}, SO_4^{2-}, and SeO_4^{2-} for single-component systems. Accurately determining K_i and n_i enables both the adsorption of single-component systems and competitive adsorption to be modeled, as both parameters are included in the SRS equations.

Table 3. Competitive SRS equations for mixtures of CrO_4^{2-}, SO_4^{2-}, and SeO_4^{2-} adsorbing on γ-Al_2O_3 at 25°C and pH 5.7, where q_i and C_i are given in μmol/g and μM, respectively

Single component

$$q_{CrO_4^{2-}} = 21.01 C_{CrO_4^{2-}}^{0.1808}$$

$$q_{SO_4^{2-}} = 28.87 C_{SO_4^{2-}}^{0.1225}$$

$$q_{SeO_4^{2-}} = 21.43 C_{SeO_4^{2-}}^{0.1788}$$

Binary mixtures

$$q_{CrO_4^{2-}} = 21.01 C_{CrO_4^{2-}} \left(C_{CrO_4^{2-}} + 0.723 C_{SO_4^{2-}} \right)^{-0.8192}$$

$$q_{CrO_4^{2-}} = 21.01 C_{CrO_4^{2-}} \left(C_{CrO_4^{2-}} + 0.512 C_{SeO_4^{2-}} \right)^{-0.8192}$$

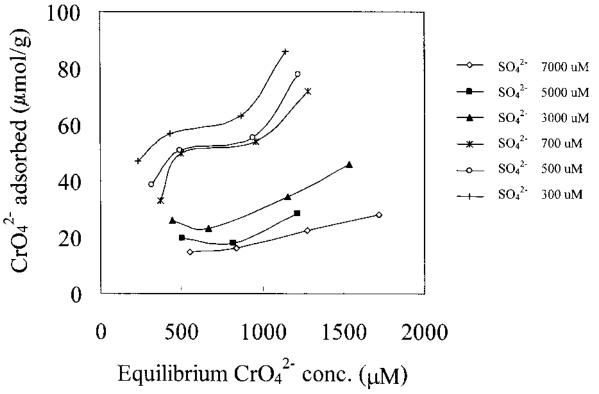

Fig. 3. Competitive adsorption isotherm for CrO_4^{2-} in the presence of SO_4^{2-} at different constant concentrations.

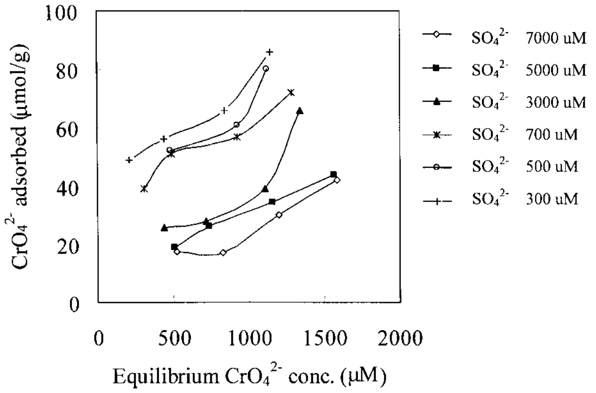

Fig. 4. Competitive adsorption isotherm for CrO_4^{2-} in the presence of SeO_4^{2-} at different constant concentrations.

Figures 3 and 4 present adsorption isotherms for

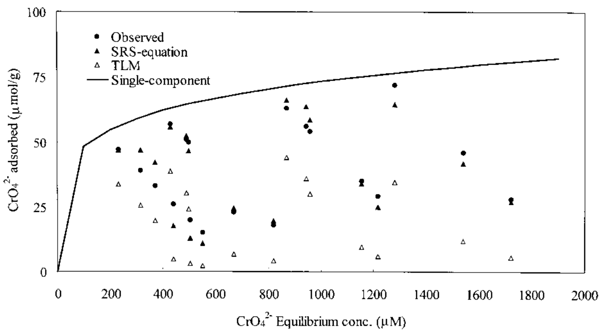

Fig. 5. Comparison between predicted (SRS equation and TLM) and observed values for the competitive adsorption isotherm of CrO_4^{2-} in the binary mixture $CrO_4^{2-} + SO_4^{2-}$.

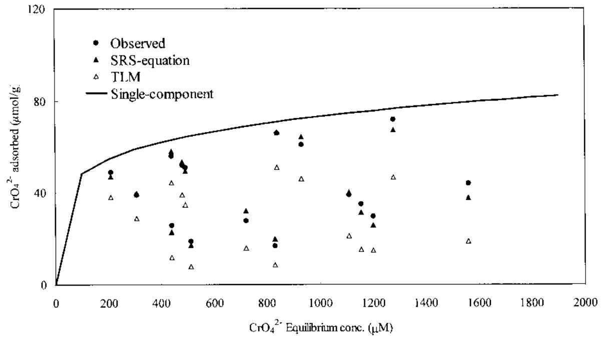

Fig. 6. Comparison between predicted (SRS equation and TLM) and observed values for the competitive adsorption isotherm of CrO_4^{2-} in the binary mixture $CrO_4^{2-} + SeO_4^{2-}$.

$CrO_4^{2-} + SO_4^{2-}$ and $CrO_4^{2-} + SeO_4^{2-}$ under competitive conditions. The experimental results demonstrate that a higher competitive solute concentration yields competitively affects CrO_4^{2-} more significantly, implying that increasing the competitive adsorbate concentration enhances the opportunity of competitive adsorbate to occupy the binding sites on the surface of the oxide. Correspondingly, the oxide surface tended to be more negatively charged than the original surface and resisted CrO_4^{2-} adsorption onto γ-Al_2O_3.

The summed concentrations of adsorbed solute in CrO_4^{2-} (700 μM), SO_4^{2-} (700 μM), SeO_4^{2-} (700 μM), CrO_4^{2-} (700 μM) + SO_4^{2-} (700 μM), and CrO_4^{2-} (700 μM) + SeO_4^{2-} (700 μM) systems were 51, 53, 44, 73, and 71 μmol/g, respectively. The competitive adsorption experiments established that the total amount of CrO_4^{2-}, SO_4^{2-}, or SeO_4^{2-} anions adsorbed in a binary-solute system was normally higher than that adsorbed when one species of anion was added alone. Evidently, some sites were specific to a single anion. Similar results were obtained by Wu *et al.* [21], who determined that, in mixed molybdate and sulfate, molybdate and selenate, or molybdate and selenite systems, more sites can be occupied by a mixture of anions than by either of the ions alone.

Conformation to the SRS equation was considered neither to justify nor verify to the competition coefficients that were defined by Sheindorf *et al.* [29]. Rather, these coefficients were considered to be convenient single-valued terms that could be used to specify the degree of competition in the specific system under experimental conditions. The competition coefficients were estimated by Eqs. (2) and (3) according to concentration. The competition coefficient is the negative value of the y-axis intercept of a line of gradient unity that passes through the points. The competition coefficients of $a_{CrO_4^{2-}-SO_4^{2-}}$ and $a_{CrO_4^{2-}-SeO_4^{2-}}$ were 0.723 and 0.512, respectively. The higher competition coefficient was obtained for the $CrO_4^{2-} + SO_4^{2-}$ system; the lower coefficient was for the $CrO_4^{2-} + SeO_4^{2-}$ system, implying that SO_4^{2-} exhibited a tendency than SeO_4^{2-} to inhibit CrO_4^{2-} adsorption onto γ-Al_2O_3.

A "calculated" adsorption value was obtained for each set of conditions by substituting the parameters, K_i and n_i in single-component systems, and the competition coefficients in binary-component systems, into the SRS equation. These numbers were compared to the experimentally measured adsorption values to assess the applicability of the SRS equation. Table 3 displays the Freundlich-type isotherms of single-component and binary mixtures.

Figures 5 and 6 present the "calculated" values of TLM and the SRS equation; the observed competitive adsorption results, and the function that described single-component adsorption to make enable a visual comparison of the performance of the SRS equation and TLM. The figures reveal that the data "calculated" by the SRS equation were closer to the observed results than were the values obtained by TLM simulation; all the observed data were lower than those of the single-component system. These findings also show that SO_4^{2-} and SeO_4^{2-} inhibited CrO_4^{2-} adsorption in binary mixtures systems. Clearly, the TLM predicts the pattern of the adsorption edge for chromate, sulfate, and selenate (Figs. 1 and 2) but fails to reproduce accurately the percentage of adsorption (Figs. 1, 2, 5, and 6). The SRS equation combined with the competition coefficients, determined from the experimental adsorption data for bicomponent systems, can be viewed as a means of quantifying competitive interactions. Therefore, the simulated results of the SRS equation are closer to the observed values than are the TLM simulation data for bicomponent systems.

The SRS equation successfully modeled competitive adsorption in a relatively simply mathematical representation, and can assist studying competitive adsorption at the solid/water interfaces. The model of surface competitive adsorption is not fully understood. Coupled inner-sphere and outer-sphere exchange reactions and the influence of site heterogeneity must be further examined, and present models must be improved.

CONCLUSIONS

Competitive adsorption of anions influenced the partitioning and transport of anionic solutes in subsurface and surface waters. For intermediately binding anions such as chromate, sulfate, and selenate, adsorption of chromate is markedly inhibited by the presence of sulfate or selenate. These findings indicate that adding a higher competitive solute concentration leads to a greater competitive effect on CrO_4^{2-}. The TLM adequately describes experimental anionic adsorption envelopes on γ-Al_2O_3 and is useful in providing a modeling framework within which to test assumptions regarding the mechanism of anion adsorption. For chromate, sulfate, and selenate, the shape of the competitive adsorption envelope predicted by the TLM is similar to that of the experimental adsorption envelope, suggesting that the TLM may be useful in predicting chromate, sulfate, and selenate adsorption on γ-Al_2O_3. The presented SRS equations are successfully applied to specify competitive adsorption isotherms and are relatively simple expressions that can be used to model experimental data.

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鉻酸根、硫酸根及硒酸根於 γ-氧化鋁表面之競爭吸附模擬：三層模式及 Freundlich 型式之多成分等溫吸附式比較

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關鍵詞：鉻酸根、硫酸根、硒酸根、γ-氧化鋁、三層模式、SRS 方程式

摘　要

本研究藉由鉻酸根+硫酸根及鉻酸根+硒酸根於 γ-氧化鋁表面之吸附了解陰離子於天然環境下之競爭吸附現象。鉻酸根、硫酸根及硒酸根於 γ-氧化鋁表面之單一吸附及競爭吸附皆被探討。本研究結果指出陰離子之競爭吸附受 pH 影響顯著，且高 pH 下，硫酸根及硒酸根抑制鉻酸根之吸附尤為明顯。另外，硫酸根及硒酸根之共存濃度愈高時，鉻酸根之吸附率則明顯下降。本研究利用 SRS 等溫吸附方程式模擬鉻酸根、硫酸根及硒酸根於 γ-氧化鋁表面之競爭吸附。結果顯示 SRS 等溫吸附式為一簡易之陰離子競爭吸附結果表示式。本研究競爭吸附結果亦指出 γ-氧化鋁之吸附位置具非均質性，故三層模式模擬僅能進行定性預測，而無法做定量分析。