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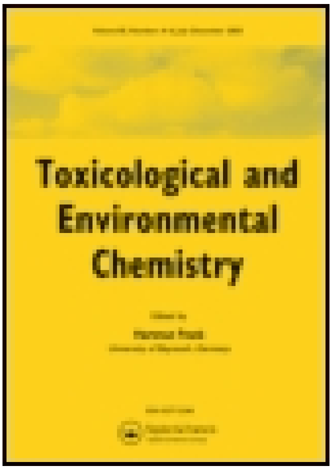

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FLUORIDE ADSORPTION BY GOETHITE IN IODIDE MEDIATED SIMULATED ENVIRONMENTAL SYSTEMS

(Dedicated to Birthday Celebrations of Professor Cyril Ponnamperuma)

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This work presents the data on fluoride adsorption by goethite at varying pH (4.00–10.00), ionic strengths (0.05M–0.1M) and concentrations of a competing ion (iodide). The triple layer surface complexation model(TLM) was shown to be able to describe fluoride adsorption on goethite in mono-adsorbing systems. However, the TLM approach was not very successful in predicting the experimental data of multi-adsorbing systems using the ion binding constants obtained for mono-adsorbing systems. Nevertheless, this information is important in determining the bioavailability of iodide and fluoride in real environmental systems.

KEY WORDS: Adsorption, iodide, fluoride, triple layer model

INTRODUCTION

The adsorption of fluoride by soil colloids may be expected to have a significant, if not a determining, influence on its bioavailability, toxicity, and mass transport in natural systems[1]. Mechanistic models for transport of fluoride must therefore incorporate mathematical formalisms of the chemical processes of adsorption as well as the physical processes of advection and dispersion. In such models adsorption can be described either by the kinetics or the equilibrium approach: the choice of either approach depends on what the relative rates of adsorption reactions and physical transport processes are, and also on the permissible level of error[2].

For better prediction of the fate of fluoride in natural soil systems, there is a need for reference data for the adsorption of fluoride on individual minerals such as goethite and gibbsite, (commonly referred to as natural soil "building blocks") that are ubiquitous in soil systems. Although a considerable amount of information is available on fluoride adsorption by whole soils[3] or their clay fractions[4], availability of systematic data concerning more simplified and well characterized systems is relatively low.

Such studies geared for the better understanding of the fate of fluoride in soil systems are particularly important for a country like Sri. Lanka, in view of its natural environmental problems associated with high fluoride concentrations in groundwater systems[5] (e.g. 12 mg/L in certain cases).

We have therefore attempted to investigated the behavior of fluoride in well-characterized goethite and fluoride experimental systems at varying conditions of pH and ionic strengths. The effect of a competing anion, iodide, on fluoride adsorption was also examined. The experimentally obtained mono-and multi-adsorbate system adsorption data was quantified, using triple layer surface complexation model (TLM)[6]. The information presented here will be helpful for engineers designing fluoride decontamination plants, epidemiologists engaged in dental health studies, and geochemists who use fluoride as a path finder element in mineral exploration[7].

MATERIALS AND METHODS

(A) Materials

Goethite was prepared by dissolving analytical grade $Fe(NO_3)_3.9H_2O$ in double distilled water and aging the solution for 24 h at a pH of ~ 12.0. The exact details of preparation are given in Djafer *et al.*[8]. The goethite samples prepared were purified several times with 0.001 M acid/ base and doubly distilled water until the supernate shows no significant variations in pH. Fluoride standards were prepared with analytical grade Sigma, USA NaF. All other reagents were of laboratory grade from BDH, UK.

(B) Methods

Fluoride adsorption experiments were carried out in temperature regulated batch reaction systems. Known amounts of Goethite were placed in a 300 ml reaction vessel and stirred for 24 h with various concentrations of $NaClO_4$. After adding a measured quantity of fluoride, the reaction mixture was stirred for 2 hrs at the same pH. The effect of iodide on fluoride adsorption was determined by introducing known amounts of standard iodide into the reaction mixture. In this case the other experimental procedures remain the same.

Thereafter, 25 ml sample portions were pipetted into centrifuge tubes after adjusting the pH of the reaction mixture to a value between 4.00 and 10.00 (The adjustment of pH was done either with 0.01M $HC10_4$ or 0.01M NaOH). The fluoride/goethite suspensions were equilibrated for 24 hrs and measured for pH. The colloid mixture was then centrifuged at 1000 rpm for 30 min and the supernate was decanted for fluoride determination. Duplicates were prepared for each experimental determination.

Fluoride and pH analyses: Fluoride in the supernatant solutions was determined using the specific ion analyzer(Orion EA 920), the fluoride ion selective electrode (Orion 94-09-00) and the single junction reference electrode (Orion 94–01). The total ionic strength adjustable buffer (TISAB) was prepared according to the chemical recipe tested in this laboratory. The detection limit for fluoride ion was 10^{-6}M. All pH determinations were carried out with ion analyzer and the Ross combination pH electrode (Orion 00-90-01).

Model calculations: The triple layer surface complexation model[6] (TLM) assumes that the interfacial region of mineral-water comprises (a) a surface or o-plane, (b) a beta-plane, and (c) a diffuse layer or d-plane. Although it was originally conceived as forming outer-sphere complexes by placing adsorbing ions in the beta-plane, Hayes *et al.*[9] and Hayes and Leckie[10] recently suggested a generalized version of this model by considering both inner and outer sphere complex formation mechanisms of the adsorbing ions. The mathematical formulae essential for surface species calculations are given in Table 1. All computations for determination of ion binding constants were carried out with FITEQL[11] and HYDRAQL[12] computer programs written in fortran 77. The following surface physico-chemical properties of goethite were obtained from the literature[13] (Table 2).

RESULT AND DISCUSSION

Investigating the factors that influence the adsorption of elements is an important scientific process to understand what physico-chemical conditions in the environment

Table 1 Mathematical formulae in triple layer model assumptions.

Parameter	*TLM*
Site density[13] (N_s)sites/m^2	2.5
Surface area[13] (S)m^2/g	31
Inner layer capacitance (C_1)F/m^2	1.2
Outer layer capacitance (C_2) F/m^2	0.2

Table 2 Some physico-chemical parameters of goethite.

Surface hydrolysis and electrolyte binding		*Log K*
$[>SOH_2^+]$	$= [> SOH][H^+] \exp(-F\Psi_0/RT)(K_{a1})^{-1}\gamma_1$	–8.10
$[>SO]^-$	$= [>SOH][H^+]^{-1} \exp(-F\Psi_0/RT)(K_{a2})^{-1}\gamma_1$	–12.4
$[>SOH_2^+–ClO_4^-]$	$= [>SOH][H^+]]ClO_4^-]^{-1} \exp(-F\Psi_0/RT)(K_{ClO4^-})^{-1}(\gamma_1)^2$	9.60
$[>SO]^-\_Na^+$	$= [> SOH][H^+][Na^+] \exp(F(\Psi_0–\Psi_\beta/RT)\ K_{Na}{}^+$	–9.12
Anion (F^- and I^-) adsorption		
$[>SOH_2^+–F]$	$= [> SOH][F^-]^0 [H^+]^0 \exp(F(2\Psi_\beta–\Psi_0/RT)K_1\gamma_1\gamma_2$	–11.6
$[>SOH–HF]$	$= [> SOH][H^+]^0 [F^-]^0 \exp(F(\Psi_\beta–\Psi_0/RT)K_2\gamma_1\gamma_2$	16.9
$[>SOH_2^+–I^-]^0$	$= [> SOH][H^+]^0 [I^-]^0 \exp(F(\Psi_\beta–\Psi_0/RT)K_3\gamma_1\gamma_2$	17.9
$[>SOH_2^0–I^-]^0$	$= [> SOH][I^-]^0 \exp(F(\Psi_\beta–\Psi_0/ RT)K_4y_1$	18.9

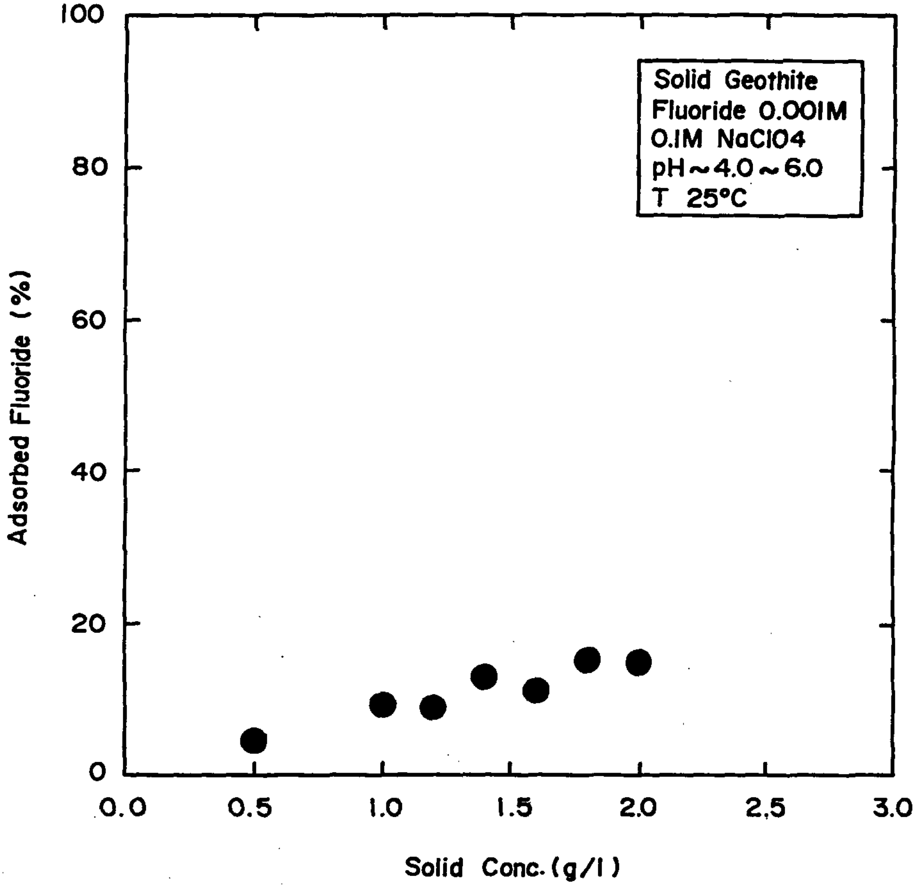

Figure 1 Adsorption of fluoride on goethite as a function of total sites concentraiton in 0.1M $NaClO_4$.

enhance adsorption and, thereby, limit mobility. In this report, we have presented chemical data on the effects of the solid concentration, pH, swamping ionic strength, and a competing anion on fluoride adsorption by goethite.

The adsorption of fluoride on goethite as a function the colloid content is compared in Figure 1 (however, the variation of fluoride adsorption on goethite with the solution pH is not given in the graph). It is apparent both from the data and in agreement with the results obtained by previous workers e.g.[14,15], that the pH and particle concentration influence the adsorption of anion on mineral oxide. Either an increase of pH or a decrease in particle concentration (which reduces surface sites) should cause a decrease in fluoride adsorption. (We selected a 1 g/L particle concentration for the rest of the experiments).

Hayes *et al.*[9] and Hayes and Leckie[10] showed that it is possible to distinguish between inner-sphere and outer-sphere surface complexes by examining whether or not the adsorption edge of an ion shifts with changing ionic strength. Although qualitative

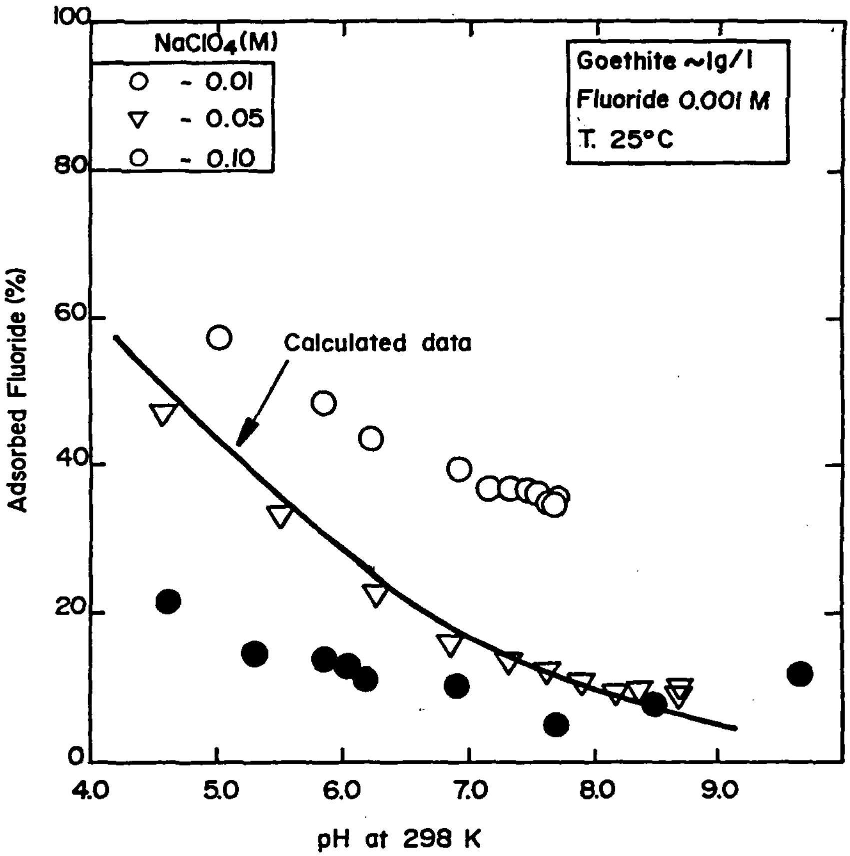

Figure 2 Adsorption of fluoride on goethite at different background ionic strengths' conditions.

in nature, this fact may be attributed largely to variations of activity coefficients in the anions and competition of electrolyte ions and adsorbing anions for surface sites in the interfacial region.

Generally, the adsorption of strongly bonding ions leaves a residual effect on the position of the adsorption edge for the changes of ionic strength, suggesting an innersphere surface complexation mechanism for adsorbing anions. In contrast, the adsorption edges shift significantly in the case of weakly bonded ions, suggesting an outer-sphere surface complexation mechanism. As depicted in Figure 2, data on ion adsorption onto goethite as a function of ionic strength, indicates an outer-sphere fluoride-surface complex formation mechanism. (The adsorption edge shifts by ~ 1 pH units at $50\%_{\text{adsorption}}$ for about a two-fold variations of the ionic strength).

Moreover, the pH of the equilibrium solution plays an important role in determining the retention of fluoride on geothite. Figures 1 and 2 show that when pH > 8.5, there is no significant retention of fluoride. As discussed in previous literature[14], two possibilities concerning the nature of the surface hydroxyl groups may be considered.

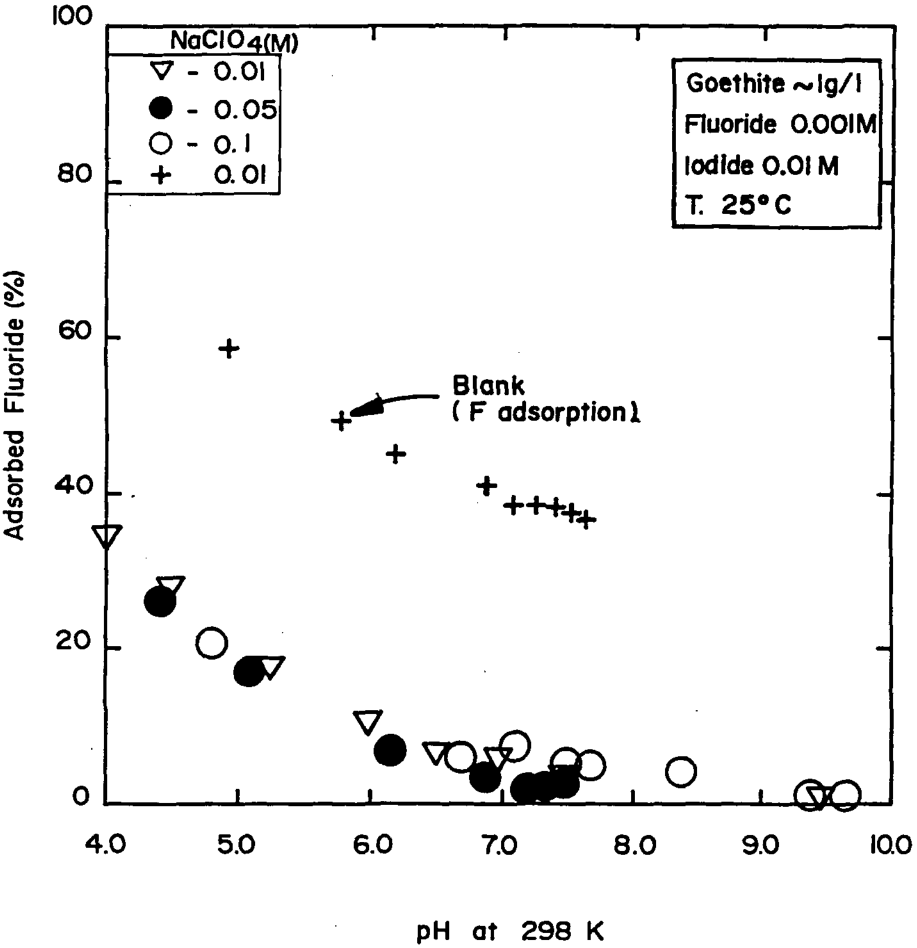

Figure 3 Adsorption of fluoride on goethite in the presence of different iodide ion concentrations.

First, the protonated hydroxyl sites are mainly responsible for the creation of these sites. In this case, adsorption should be considered mainly as being electrostatic. Second, the neutral surface hydroxyls are involved in the deposition by reacting with the ions to be deposited. Anion adsorption on sites created by deprotonated surface hydroxyls seems to be unlikely. Goethite has a zero point charge pH of 8.20 and therefore at near neutral pH values the surface may be dominanted by neutral and deprotonated hydroxyl sites leaving little room for negatively charged fluoride ions for adsorption.

Figure 3 shows the variation of fluoride adsorption density as a function of pH in the presence of excessive iodide concentrations (typically greater than 10 mM). Iodide shows a competing effect on fluoride adsorption sites, thus reducing the fluoride adsorption capacity of goethite by about 30% at 1:10 fluoride:iodide concentration ratio. It is interesting to note that the relative adsorption affinity of fluoride in the presence of iodide has been slightly affected due to the changes of swamping electrolyte concentrations in the reaction system (Figure 3). According to the observations made by Hayes *et al.*[8], this effect may be partly due to the change in bonding mechanism of fluoride complexation onto mineral surface in iodide mediated reaction systems(?). The data presented in this paper therefore indicate some other associated factor/s in the surface complex formation mechanism. However, in-situ spectroscopic data are required to confirm the speculated interpretations. The elucidation of binding mechanisms of fluoride onto goethite at varying concentrations of iodide is in progress at present.

Numerous chemical models[e.g.10,16] that describe the interaction of ions with oxide surfaces have been developed. Excellent reviews of the formulation of these models and their ability to fit experimental data have been published by Westall and Hohl[17] as well as by Morel *et al.*[18]. In the present work we have used a triple layer surface complexation model, because of its applicability to a broad range of pH, ionic strength and adsorbing ions, and further, because of its relative simplicity. The essential mathematical formulae required for chemical calculation is summarized in the section on methods and materials. Two problems that exist in modeling anion adsorption data are: (a) defining the total number of available sites, and (b) choosing the stoichiometry of the adsorption reactions. Data obtained from adsorption isotherms and from calculations on the size of anions relative to the area of surface site, suggest that an inorganic anion covers two to three surface sites, or alternatively, that all sites determined by crystallographic calculations are not available for anion adsorption. Therefore, the total adsorption sites have to be reduced by a factor of two in chemical modeling calculations. (This may affect the intrinsic binding constants. However the essential mechanisms of the calculations will remain the same). As shown below, various combinations of stoichiometries could be suggested to describe the adsorption of anion by surface sites.

$$>SOH + H^+_s + F^- = >SOH_2^+ - F^- \quad [1]$$
$$>SOH + H^+_s + F^- = >SOH - HF \quad [2]$$
$$>SOH + F^- = >SOH - F^- \quad [3]$$

However, it is important to calculate the relative contribution of the suggested surface complexes in interpreting the experimental data.

In this study, we have checked possible combinations, starting with all three reaction stoichiometries. A stepwise adjustment procedure associated with the computer algorithm (FITEQL or HYDRAQL) showed that only two species, namely [$>SOH_2^+ - F^-$] and [$>SOH - F^-$], are very significant in modeling fluoride adsorption at varying ionic strengths' in the absence of competing ions.

In all cases, the adsorbate concentration fits well with the experimentally derived data and agreement may be formally compared to that which has been reported in other instances of the application of the TLM to specific adsorption of anions. In modelling the competing-anion effect for fluoride binding sites on goethite, we chose the same surface-fluoride species as in mono-adsorbate systems reaction (1/3). However, the following stoichiometries were chosen one at a time to account competing effect of iodide.

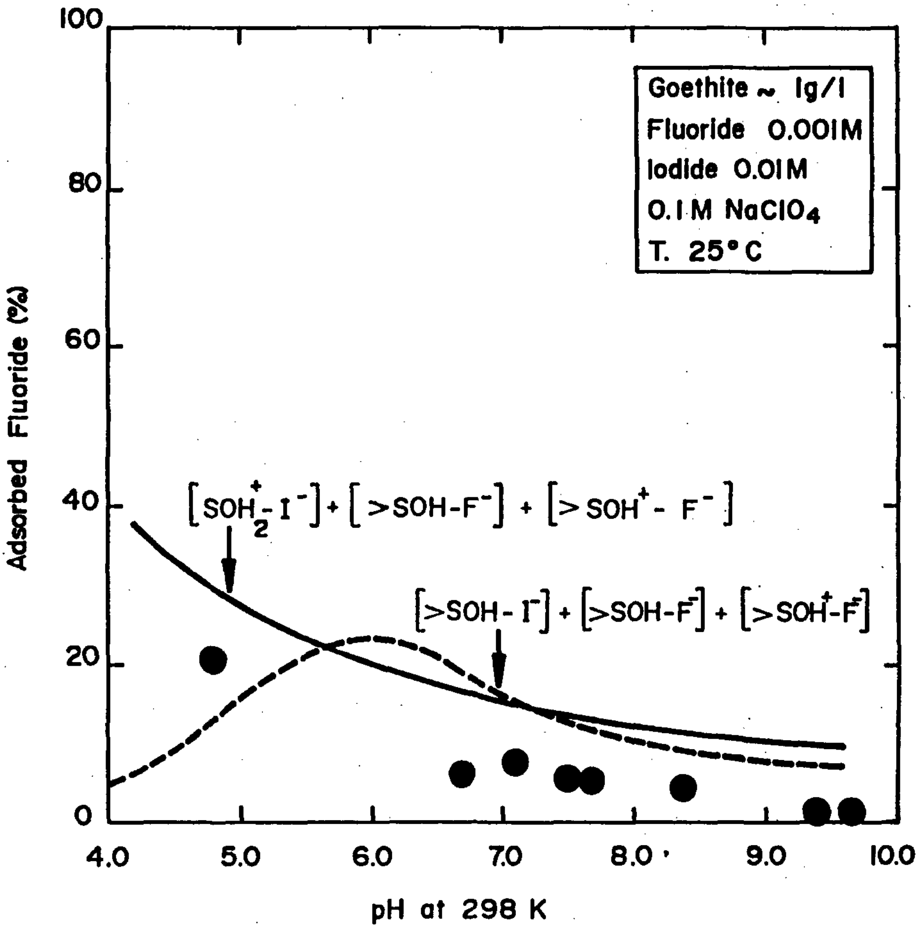

Figure 4 The competing effect of iodide on fluoride adsorption sites (solid line depict calculated data using TLM).

$$>SOH + H^+_s + I^- \quad = \quad >SOH_2^+ - I^- \qquad [4]$$

$$>SOH + I^- \quad = \quad >SOH\text{–}I^- \qquad [5]$$

As shown in Figure 4, the experimental data of fluoride adsorption fits to some extent with calculated values when the pH of the system is above 5.7. However, when the pH is less than this value, the model predictions do not agree with the experimental results. Therefore, in agreement with Goldberg *et al.*[19], the model calculations predict only the trend of the observed results. In a later study, Goldberg and Traina[20] noted that in modeling the ion adsorption in multi-adsorbate systems, the experimental data can be better represented by recalculating binding constants for multi-ion systems. Their explanation for this centered on the presence of selective adsorbed sites and surface heterogeneity in goethite. However in the present work, we have avoided this approach in modeling the experimental results in multi-ion systems.

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