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Surface Complexation Model for the Heavy Metal Adsorption on Natural Sediment

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Surface complexation models (SCMs) have been successfully used to describe metal ion adsorption on pure mineral materials. However, such models have rarely been applied to model adsorption on natural materials. In this study, the surface complexation model approach was used to describe the surface properties and adsorption behavior of natural aquatic sediment. Three typical versions of the surface complexation model were used: constant capacitance model (CCM), diffuse layer model (DLM), and triple layer model (TLM). All the model parameters were determined on the basis of the experimental data of the potentiometric titration and the metal adsorption isotherm using LeAn River (China) sediment. The experimental data of the adsorption edges were used to verify the performance of the models. This work indicated that all three models can simulate the experimental results very well. In predicting the adsorption behavior of the sediment sample, the relative errors of these three models were quite close. The results illustrate that SCMs can be used to successfully model natural materials.

Introduction

The behavior, transport, and ultimate fate of heavy metals in aquatic environment depend largely on their sorption reactions with sediment particles (*1*−*4*). Thus, it is very important to investigate such reactions. Different empirical approaches, in particular the measurement of adsorption isotherms and the corresponding partitioning parameters, have commonly been used in the studies of the adsorption behavior of natural sediments or soils (*5*−*10*). However, limitations of these empirical ways have been observed (*1*, *11*−*13*). Extensive studies have been made on surface complexation models (SCMs) to describe the adsorption of heavy metals on pure mineral surfaces, especially on pure hydrous oxide solid surfaces; the results are quite promising (*14*−*23*). It has also been hoped that SCMs can be used with natural materials, but unfortunately, there have been very few studies that apply SCMs to natural materials and to sediments in particular.

Mouvet and Bourg (*24*) were the first to use the chemical equilibrium models to quantitatively describe the adsorption data of metals to river sediment. They reported that the adsorption constants of the metals are directly proportional to their first hydrolysis constants. They concluded that to a certain degree the chemical equilibrium program can be used to predict the speciation of Cu, Ni, Pb, and Zn in a river. Fu and Allen (*25*) studied the Cd adsorption on an oxic sediment sample by carrying out both acid−base titration experiments and Cd adsorption experiments with the sediment sample. They used a multisite binding model that contained the effect of pH by considering the titration data against their adsorption data. The results derived from the model were close to that from the experiment. They suggested that the adsorption behavior of natural sediment can be modeled via one or two surface reactions. Charlet (*26*) and Osaki et al. (*27*, *28*) used the concept of triple layer SCMs and constant capacitance SCMs to study the behavior of metal adsorption on oxic sediment. Wang (*29*) tried successfully to apply the diffuse layer SCMs to describe his metal adsorption data. Some researchers have also used SCMs in the area of soil science. Goldberg (*11*, *12*) was the first person to extend the use of CCM to describe *o*-phosphate adsorption by noncalcareous mineral soils. Goldberg believed that CCM did the best job of describing *o*-phosphate adsorption by noncalcareous soils, including the effect of pH. Using SCMs to describe the adsorption behavior of pure clay minerals has been reported (*30*−*32*). Although these studies have employed SCMs to describe adsorption, SCMs have not been widely used with natural materials because of insufficient or missing data, particularly a data base of model constants and pertinent information regarding surface properties of natural sediment (*21*−*29*). Obviously, more work is needed in this field.

Theoretically, it is not quite clear yet which of the three frequently used surface complexation models (CCM, DLM, and TLM) is best in reflecting the chemical principles in describing the adsorption processes in a natural system (*20*, *33*−*36*). Dzombak and Morel (*20*) carefully evaluated the distinguishing aspects of these different versions of surface complexation models. It was shown that all three SCMs can simulate the experimental data of cation adsorption on pure metal hydroxide solid very well (*1*, *35*−*37*). However, no comparison of the performance of these three models in describing adsorption on natural sediments has been reported.

The purpose of this study was to use the SCM approach to describe the adsorption of heavy metals to natural river sediments. Generally speaking, SCMs can be applied in two different ways to composite materials. The first is to treat the composite material as an integrated whole with adsorption described as complexation with average surface functional groups. The second is to consider the main composites that are supposed to dominate adsorptive interactions. Initially the first approach was chosen for this work. A river sediment sample that was collected from LeAn River in Jiangxi Province, China, was used. Potentiometric titration and adsorption experiments were conducted to provide the data set to calibrate the model parameters. The effectiveness of the three SCMs in interpreting the experimental data were tested and compared.

Materials and Methods

Samples. The sediment sample was free of pollution as demonstrated by previous desorption tests (*38*). The sample was air-dried, and particles larger than 200 mesh were removed by a nylon sieve. An X-ray fluorescence spectrometer (3080E3, RIGAKU Industrial Co., Japan) was used to analyze its mineral composition. An X-ray diffraction spectrometer (HZG-4x, DanDong Analytical Equipment Co., China) was used to analyze the clay composition. The N_2/

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TABLE 1. Element Content of Sample As Measured by X-ray Fluorescence Spectrometry

element	Ca (%)	Mg (%)	Na (%)	K (%)	Si (%)	Fe (%)	Al (%)	Mn (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
amount	0.26	0.58	0.34	2.02	29.53	4.14	8.68	1207	56	36.2	156

TABLE 2. Intrinsic Surface Constants of Sediment Sample

	solution methods	graphic methods			FITEQL 2.0 optimization					
	model type	CCM			TLM	CCM			DLM	TLM
	ionic strength	0.1	0.01	0.001		0.1	0.01	0.001	0.01	0.01
intrinsic constants	pK_{a1}^{int}	3.31	2.97	2.80	2.80	3.17	3.01	2.73	1.49	2.73
	pK_{a2}^{int}	4.27	4.80	5.07	5.37	4.25	4.93	5.35	4.73	5.35
	$pK_{Na^+}^{int}$				3.27					4.76
	$pK_{NO_3^-}^{int}$				4.06					3.00
error analysis	$\sigma_{pK_{a1}^{int}}$					0.208	0.231	0.310	7.274	
	$\sigma_{pK_{a2}^{int}}$					0.879	0.066	0.057	0.039	
	$\sigma_{pK_{Na^+}^{int}}$									0.293
	$\sigma_{pK_{NO_3^-}^{int}}$									0.054
	V_Y					1.32	0.935	0.924	5.004	2.641
capacity	C_1 (F/m^2)					1.76	1.66	1.45		1.60
	C_2 (F/m^2)									0.20

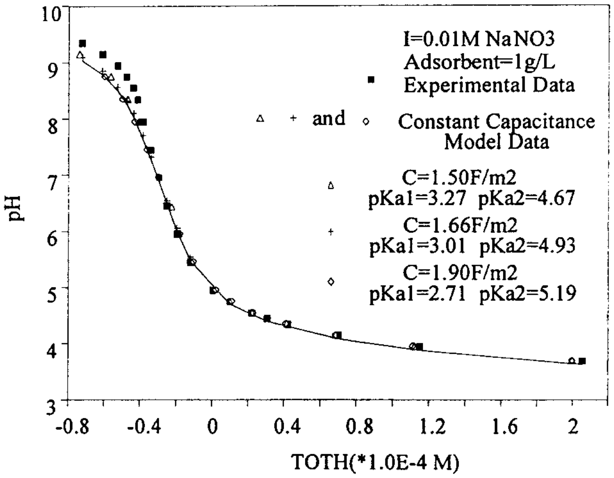

FIGURE 1. Fitting titration curves by the constant capacitance model. Each fitting curve is calculated based on the corresponding p*K* and *C* for that of ionic strength. The sample is from the LeAn River.

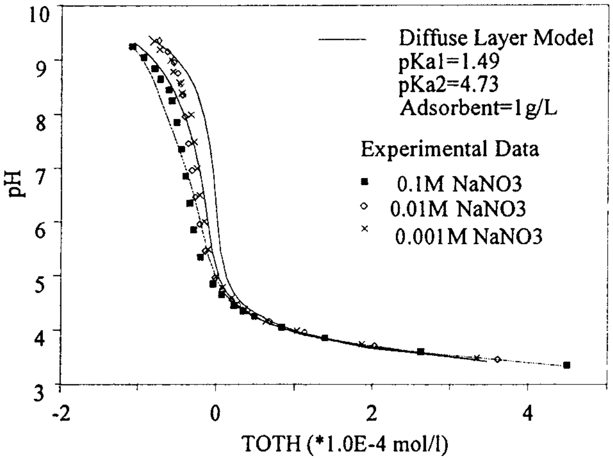

FIGURE 2. Fitting titration curves by the diffuse layer model. Parameters are derived from the data of 0.01 mol/L ionic strength. The sample is from the LeAn River.

BET method (ASAP-2000, Micromeritics) was used to determine the specific area of the sample. The organic content of the sample was analyzed by using the standard $K_2Cr_2O_7$ oxidation method (*37*). The sediment stock suspension was made by adding 10 g of sediment to 1 L of triple distilled water and was kept in a refrigerator for at least 2 weeks before the titration and adsorption experiments started.

Potentiometric Titration. The potentiometric titration experiment was done in a 100-mL Erlenmeyer flask. A 10-mL stock sediment suspension was added to the flask to give a sediment concentration of 1 g/L. $NaNO_3$ was added to make the ionic strength of the suspension 0.1, 0.01, and 0.001 mol/L, respectively. Triple distilled water was added to give a final volume of the suspension of 100 mL. HNO_3 was added to give a suspension pH value of less than 3. The sample was stirred for 1 h with a magnetic stirrer and was equilibrated for 30 min to get a stable pH. Thereafter, NaOH was micro-added until the suspension pH was greater than 10; this was monitored using a Metrohm 682 automatic titroprocessor. During the titration process, the suspension was continually bubbled with N_2 to exclude the effect of CO_2, and the temperature was held at 25 °C. The reference blank was prepared in the same manner as the sample except that no HNO_3 was added and only the supernatant of the suspension was titrated. The surface charges of the sample at different pH and ionic strengths were calculated based on eq 1. The data sets of pH value versus surface charge (σ_H) were obtained and used to derive surface site density, pH_{pzc}, and also the surface acidic constants:

$$\sigma_H = [(V_{HCl}N_{HCl} - V_{NaOH}N_{NaOH})_{Sample} - (V_{HCl}N_{HCl} - V_{NaOH}N_{NaOH})_{Blank}]/W \quad (1)$$

where σ_H is the surface charge (mol/g); *V* is the volume of acid or base added (mL); *N* is the concentration of acid or base added (mmol/L); *W* is the amount of sediment sample (g).

Adsorption. Cu and Cd were selected as the absorbates. The adsorption experiments were conducted under two different conditions. One employed a constant pH with a range of metal concentrations from which the adsorption isotherms were obtained. The other one used an array of pH value with several fixed metal concentrations from which the adsorption edge curves were obtained. The experiments were carried out in a series of 100-mL plastic bottles. Each bottle had 10 mL of sediment stock suspension added to make the solid concentration 1 mg/L. The pH of the suspension was adjusted by adding HNO_3 or NaOH. The suspension ionic strength was adjusted by adding $NaNO_3$ to

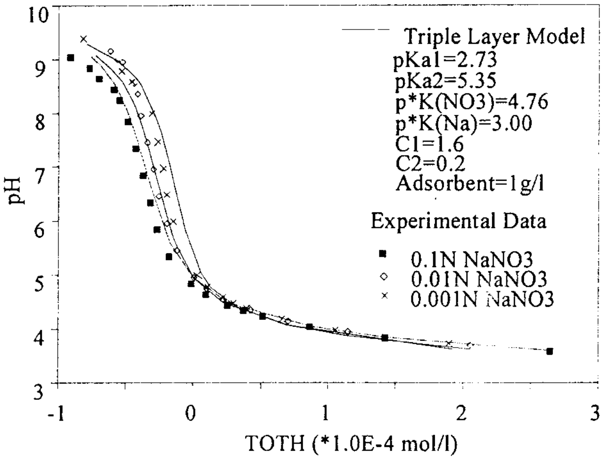

FIGURE 3. Fitting titration curves by the triple layer model. Parameters are derived from the data of 0.01 mol/L ionic strength. The sample is from the LeAn River.

0.01 mol/L to make it close to the ionic strength of natural waters. The Cu or Cd concentration of the suspension was adjusted to the designed values using standard Cu or Cd solutions. The samples were then shaken for 3 h in a reciprocating shaker and were equilibrated for 24 h at 25 °C. Part of the supernatant was used for pH measurement, and part of the supernatant was filtrated through a 0.45-μm membrane for metal concentration measurement using a PE-3100 atomic absorption spectrometer. The data of the adsorption isotherms were used to calibrate the adsorption parameters for the models by using the FITEQL 2.0 program (*40*). The data of the pH edges were used to verify the performance of the established models.

Parameter Estimation Methods. There are two important steps when using a surface complexation model. One is to properly choose the models that relate to the assumptions of the electrical double layer and the calculation method. The other is to determine the model parameters correctly. In this work, three frequently used surface complexation models are considered. The mass law equation and the static electronic expressions of these three models can be found in the literature (*14*–*20*). Both the graphical extrapolation method, which has been illustrated clearly in literature (*14*–*20*), and the nonlinear least squares optimization procedure with the FITEQL 2.0 program were employed to analyze the data. They are referred to as the graphical method and the computer method, respectively, in the following discussion.

Results and Discussion

Sample Characteristics. The results of X-ray fluorescence analysis are listed in Table 1. The clay (<2 mm) content of the sediment sample is mainly composed of 71% illite, 15% kaolinite, and 14% chlorite. Particles smaller than 2 mm comprised 19% of the total particle size spectrum. The specific area of the sample was 13.3 m^2/g. The total number of surface sites (N_s) is obtained by extrapolating a plot of the distribution coefficient ($K_d = \sigma_H/[H^+]$) vs σ_H (*26*). Three N_s values were obtained from three sets of titration data at different ionic strengths. The average of the three values was 7.9×10^{-5} mol sites per gram. The pH$_{pzc}$ of 4.2 was obtained from the crossover point of the three titration curves at different ionic strengths.

Surface Acidic Properties and Constants. The titration data were arranged in the format of data input for FITEQL, which is total H$^+$ (TOTH) concentration vs pH. TOTH was calculated from the titration data by using the BASIC computer program given by Dzombak and Morel (*20*). The data sets of pH vs TOTH for different ionic strengths are drawn point by point in Figures 1–3. It can been seen that the sample is negatively charged over a large pH range.

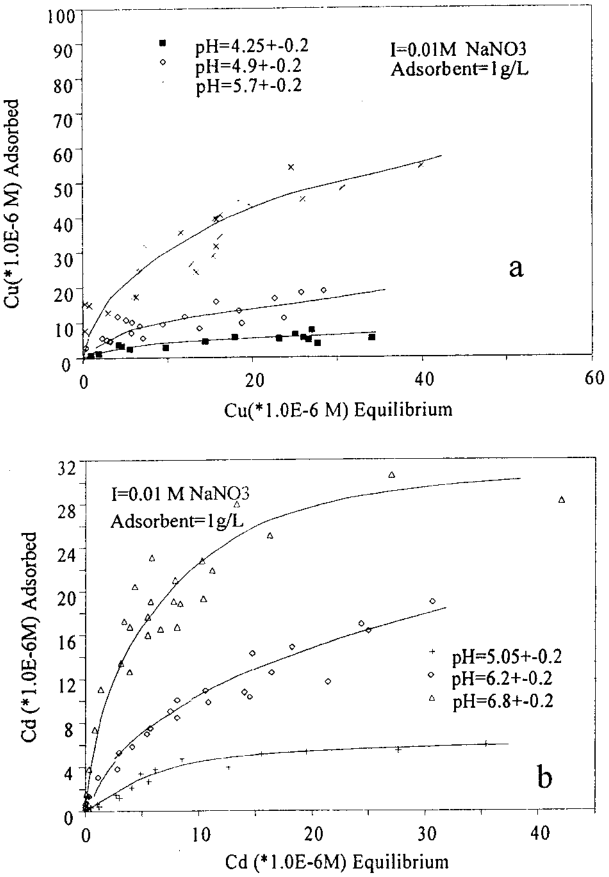

FIGURE 4. Adsorption isotherms of the sediment sample for Cu (a) and Cd (b). The sample is from the LeAn River.

TABLE 3. Intrinsic Surface Complexation Constants of the Sediment Sample

adsorbate	constants	CCM	DLM	TLM
Cu(II)	log $K_{M^{2+}}{}^{int}$	−0.766	−1.247	0.058
	log $K_{MOH^{+}}{}^{int}$			−4.599
Cd(II)	log $K_{M^{2+}}{}^{int}$	−1.960	−2.585	−0.455
	log $K_{MOH^{+}}{}^{int}$			−6.385
	C_1 (F/m^2)	1.66		1.60
	C_2 (F/m^2)			0.20

As mentioned above, the sediment is considered as an integrated whole with an average surface functional group (expressed as SOH). The surface protonation and deprotonation of the sediment are expressed as eqs 2 and 3.

$$SOH_2{}^+ = SOH + H^+ \qquad K_{a1}{}^{int} \qquad (2)$$

$$SOH = SO^- + H^+ \qquad K_{a2}{}^{int} \qquad (3)$$

For different surface complexation models, the considerations in calculating acidic constants are different, and this has been expounded clearly by a number of researchers (*20, 24, 25, 29, 30*). These calculations were tried for the natural sediment sample. It is obvious that the derived parameters are very much model specific; in other words, different models yield different parameter sets of p*K* and/or capacitance, *C*.

Constant Capacitance Model. Theoretically, only one plane in the intersurface is considered in this model. All the specific adsorbed ions are assigned into the surface plane, and they contribute to σ_0 and experience the potential ψ_0.

The electrical double layers are Helmholtz type. It is like a capacitor with a pair of plates in parallel and with a fixed electrical capacitance (*C*) for each of the corresponding combinations of temperature, ionic strength, and the electrolyte property (*1, 24, 25, 29, 30*). The model has three specific parameters (C, pK_{a1}^{int}, and pK_{a2}^{int}). In this study, both the graphical method and the computer method are employed to evaluate the surface characteristic constants. Three sets of parameters including an electric capacity (C) and two intrinsic acidity constants (pK_{a1}^{int} and pK_{a2}^{int}) are obtained respectively from the three data sets of different ionic strengths. These two methods produce very similar results as shown in Table 2. The capacitance value required to do FITEQL 2.0 optimization was taken from the graphical method.

The derived parameters are incorporated into the model to reproduce the titration curves as depicted in Figure 1. It is obvious that the results calculated by the model matched well with the experimental results.

Diffuse Layer Model. This model assigns two planes in the interfacial region: a surface plane for adsorption of H^+, OH^-, and all specifically adsorbed species, and a diffuse layer plane representing the closest distance of approach for all counterions. The distribution of ions, charge, and potential in the diffuse layer is described by the Poisson–Boltzmann equation. The overall relationship between surface charge and the potential is given by the Gouy–Chapman equation (*1, 29, 30*). As indicated by Dzombak and Morel (*20*), DLM uses only two constants (pK_{a1}^{int} and pK_{a2}^{int}) to express the surface characteristics at variable ionic strengths. In this work, the acidity constants are extracted by using FITEQL 2.0 with the titration data at 0.01 mol/L ionic strength. The parameters are listed in Table 2. In turn, the parameters are used in the model to reproduce a titration curve for each of the three data sets at the different ionic strengths. The results are shown in Figure 2. It can be seen that the model calculation results match with the experimental data points very well. This confirms that in DLM the influences of ionic strength are already imbedded into the model itself; therefore, the model applies in different solution conditions.

Triple Layer Model. In this model, there are three planes in the interfacial region: a surface plane for adsorption of H^+, OH^-, and strongly adsorbed ions; a near-surface plane (the β-plane) for weakly adsorbed ions; and a diffuse layer plane, representing the closest distance of approach of dissociated charge. One distinctive advantage of TLM is that it takes the influence of electrolyte ions into account in the calculations so that the model parameters such as pK_{a1}^{int}, pK_{a2}^{int}, $pK_{NO_3^-}^{int}$ and $pK_{Na^+}^{int}$ are independent of electrolyte concentration. As a result, the TLM can interpret data over a wide range of ionic strengths. Six parameters (C_1, C_2, pK_{a1}^{int}, pK_{a2}^{int}, $pK_{NO_3^-}^{int}$, and $pK_{Na^+}^{int}$) are required for this model. In this work, pK_{a1}^{int} and pK_{a2}^{int} are evaluated by the graphical method, whereas $pK_{NO_3^-}$ and pK_{Na^+} are evaluated with both the graphical and the computer methods for the 0.01 mol/L ionic strength titration data. Simultaneous optimization of the values of pK_{a1}^{int}, pK_{a2}^{int}, $pK_{Na^+}^{int}$, and $pK_{NO_3^-}^{int}$ by using FITEQL 2.0 were tried but failed. $pK_{NO_3^-}^{int}$ and $pK_{Na^+}^{int}$ were predicted by using FITEQL 2.0 while treating the pK_{a1}^{int} and the pK_{a2}^{int} values from the graphical method. The parameters derived from the 0.01 mol/L ionic strength experimental data were then put back into the TLM to reproduce the titration curves. The results are very close to titration experimental data of all three different ionic strengths in Figure 3. This proves the effectiveness of the model in interpreting the data over a wide range of ionic strengths. However, since this model requires that the values of more parameters be determined than is required for the other models, application is more difficult.

Adsorption Properties and Constants. Langmuir adsorption isotherms for the adsorption of Cu and Cd on the sediment at different pH values are shown in Figure 4. For both Cu and Cd, there is a maximum adsorption at each pH. The adsorption increases for Cu when the pH increases from 4.25 to 5.7 and for Cd when the pH increases from 5.05 to 6.8.

The adsorption of heavy metals (M^{2+}) on the sediment surface is expressed in eqs 4 and 5. Based on the theoretical hypotheses of CCM, DLM, and TLM (*1, 20*), only eq 4 is used in the CCM and DLM calculations, while both eqs 4 and 5 are used in the TLM calculation.

$$SOH + M_S^{2+} = SO^- - M^{2+} + HS^+ \qquad (4)$$

$$SOH + M_S^{2+} + H_2O = SO^- - MOH^+ + 2H_S^+ \qquad (5)$$

The data of the isotherms together with the intrinsic surface constants listed in Table 1 are used to determine the intrinsic adsorption constants by using FITEQL 2.0 for the three surface complexation models. For each model, one set of constants is obtained for each isotherm at a fixed pH. Three adsorption isotherms are obtained. Thus, three sets of constants are derived for each of the models. The values of the constants listed in Table 3 are the average of the three related numbers calculated by using Dzombak and Morel's method (*20*). Comparing the intrinsic complexation constants of Cu and Cd in Table 2, we find that Cu has a higher affinity with this river sediment than does Cd.

Performance of the Models in Data Interpreting. The surface complexation models, which have been viewed as mechanistic models (*1, 20*), should be effectively used to describe the adsorption behavior in the different conditions from those used for parameter extraction. As a verification step for the models, the parameters derived from the adsorption isotherms obtained at several fixed pH values were incorporated into the three surface complexation models to reproduce the pH edge curves, which are over a

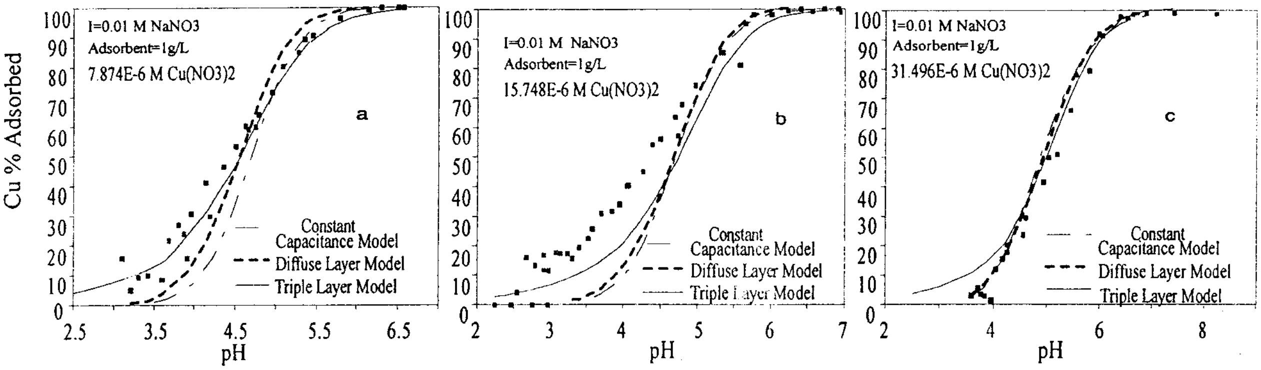

FIGURE 5. Fitting curves for the adsorption edges of Cu with the three surface complexation models for LeAn River sediment sample.

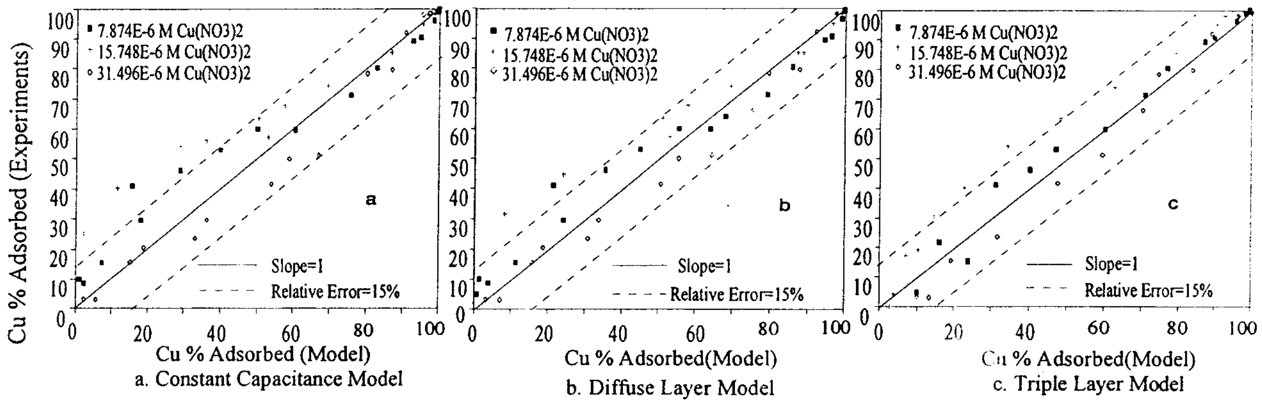

FIGURE 6. Relative error analysis for the fits of Cu adsorption pH edges.

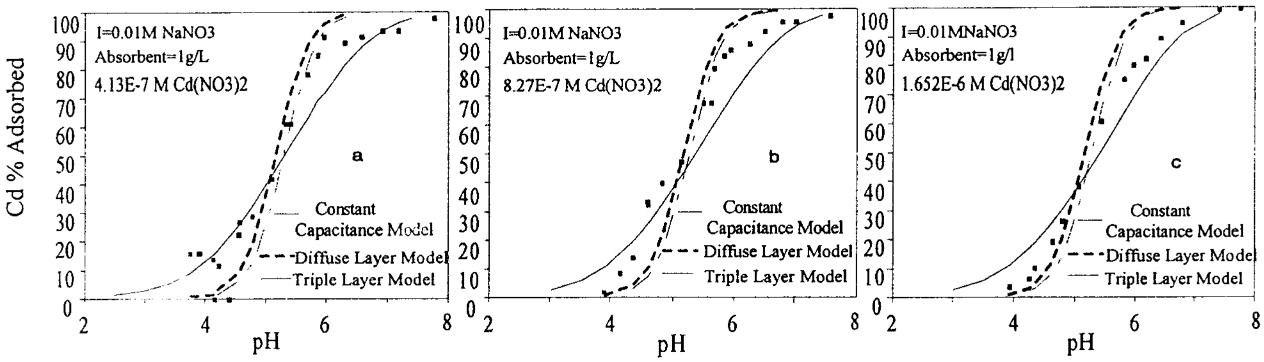

FIGURE 7. Fitting curves for the adsorption edges of Cd with the three surface complexation models for LeAn River sediment sample.

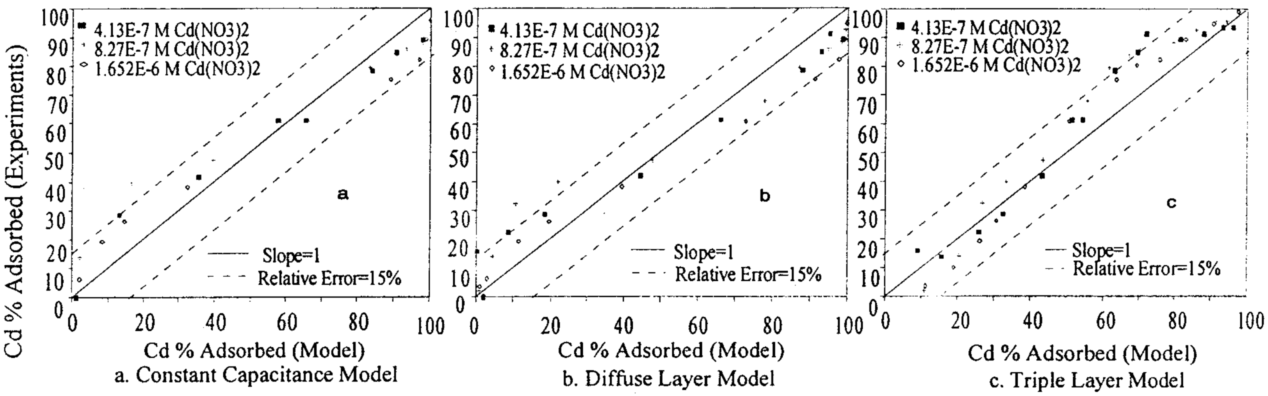

FIGURE 8. Relative error analysis for the fits of Cd adsorption pH edges.

wide range of pH, by using the MICROQL program (*41*). Figures 5 and 7 show the experimental data and the model fitting curves for Cu and Cd adsorption pH edges with different Cu and Cd concentrations. Figures 6 and 8 show the relative errors of each of the fitting results for all three models.

Model calculation results as well as the experimental results shown in Figures 5–8 indicate that the adsorption of the metals on the river sediment sample is strongly pH dependent. A large percentage of the adsorption of the metals occurs in a narrow range of pH. With the increase of the total metal concentration, the pH adsorption edge shifts to a high pH range, which is equivalent to the reduction of the adsorption affinity.

From the results shown in Figures 5–8, it has been concluded that all three models can interpret the experimental data of the pH adsorption edges for Cu and Cd very well, which means that all three surface complexation models apply very well in describing the adsorption behavior of the natural sediment. In this case, the relative errors are within 15%. Although this does not tell which model is correct in a mechanistic sense, it indicates that the SCMs can be used to describe adsorption to natural sediments.

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