

# Heavy metal adsorption on the Le An River sediment —The adsorption model\*

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**Abstract**—In this study, the surface properties and adsorption properties of the Le An River sediment were modelled via surface complexation approach. The model parameters were determined based on the data of our potentiometric titration experiments and the metal adsorption experiments with the Le An River sediment samples. Consequently, the surface complexation models for the natural sediment, in our case the Le An River sediments, which can interpret the experimental data very well were successfully established. Three typical surface complexation models that is the constant capacitance model, the diffuse layer model and the triple layer model, were considered in this research. This work indicated that the consistency and the interdependency among model parameters together with the selection of the surface adsorbed species should be emphasized.

**Keywords**, surface complexation model; Le An River; sediment; potentiometric titration; adsorption.

## 1 Introduction

The adsorption behavior of the river sediment with the micro-pollutants has a significant influences on the environmental quality of a river (Stumm, 1987; Luoma, 1983). The Le An River on which we have done our research is in Jiangxi Province, China. The largest open-cast copper mine of China—Dexing Copper Mine is close to the upstream of the river. As a result, there have been somewhat pollution problem with the heavy metals. Thus, for the assessment of the pollution situation of the river and the establishment of the area heavy metal sediment criteria to avoid further pollution, it is crucial to investigate the adsorption behavior of the river sediment.

The current most promising model for describing the adsorption processes is the surface complexation model that was put forward by Stumm *et al.* (Stumm, 1970) and has been studied intensively through years (Hohl, 1976; Huang, 1977; Davis, 1978; Hayes, 1991; Dzombak, 1990). However, the application of this model to the natural sediments which are complicated in composition have been lacking (Fu, 1992). Besides, it is still controversial

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that among three often used surface complexation models, that is the constant capacitance model, the diffuse layer model and the triple layer model, which one is better in terms of reliability and applicability.

The principle idea of the surface complexation model is to view the adsorption reactions of the surface hydroxyl groups with ions in solution happened on solid surface as an analogous to the formation of soluble complexes in that they are described by mass law equations. The major difference between the surface reactions and the reactions in solutions is that all reactions occurred on surface are influenced by the electrostatic effects caused by the surface charge which are taken into account by applying a coulombic correction factor, derived from electric double layer theory, to surface complexation mass law. Equation(1) shows the equation for the description of surface reactions. Furthermore, the reaction of surface hydroxyl groups with the hydrogen ions and other ions are specially termed as intrinsic acidity constant and the intrinsic surface complexation constant separately ( Dzombak, 1990; Westal, 1986; 1987; Stumm, 1976).

$$K^s = K^{int} \exp(-ZF\psi/RT). \quad (1)$$

A number of surface complexation models have been proposed. The often used models are the constant capacitance model, the diffuse layer model and the triple layer model. Differences among the various models are the different assumptions of the physical pictures of the solid/water interface(location and hydrated state of adsorbed ions; spatial distribution of solution counterions), the geometric model of the interface which must be assumed in order to determine the coulombic correction factor. Dzombak reviewed these distinguishing aspects of the surface complexation critically(Dzombak, 1990). Unfortunately, so far, it is still impossible to go into details of the structure of the solid surface. The controversy among different models may be continued until a realistic method can be invented to express the surface characteristics clearly.

Therefore, the purposes of this study are to investigate the adsorption of the heavy metals with Le An River sediments via the approach of surface complexation models, broaden the application area of the surface complexation models to natural sediments and tentatively make a comparison among the three models in terms of the model ability in interpreting the experimental data not in terms of the mechanism of the surface chemistry.

## 2 Materials and methods

### 2.1 Samples

The surface sediment samples used in this research were collected from the down stream of the Le An River. Samples were air-dried and sieved through a 200 mesh nylon sieve. The sediment samples were analyzed with the X-ray differential spectrograph for their clay compositions and with  $N_2$ /BET method for their specific areas. Sediment stock solutions were made with these samples in 10g/L concentration at least two weeks before the titration and adsorption experiments and kept in refrigerator.

### 2.2 Potentiometric titration

The potentiometric titration experiment was done in a 100ml Erlenmeyer flask by first acidifying the suspension of sediment sample with  $\text{HNO}_3$  to reach  $\text{pH} < 3.0$  and then micro-adding  $\text{NaOH}$  till  $\text{pH} > 10$  using Metrohm 682 Automatic Titroprocessor. The concentration of the sediment suspension was 1g/L.  $\text{NaNO}_3$  was used as the supporting electrolyte to adjust the ionic strength of the sample suspension at 0.1, 0.01, and 0.001 separately. The sample was continually bubbled with  $\text{N}_2$  to exclude the trouble of the  $\text{CO}_2$  and temperature was controlled at about  $25^\circ\text{C}$  during the micro-titration process. The medium alone was also titrated as the blank reference.

### 2.3 Adsorption

Cu and Cd are the main pollutants from Dexing Copper Mine and were investigated in this research as the adsorbates in the experiments. The adsorption experiments were conducted in the conditions of both the constant pH at different metal concentrations from which the adsorption isotherms were obtained and an array of pH at a fixed metal concentrations from which the adsorption edge curves were obtained. The experiments were proceeded in a series of 100ml plastic bottles. After adjusting the pH at various values with  $\text{HNO}_3$  or  $\text{NaOH}$ , the sediment concentration at 1g/L by adding the 10g/L stock suspension of the sediment samples, the ionic strength at 0.01 mol with  $\text{NaNO}_3$ , the Cu or Cd concentrations at a certain values with the standard Cu or Cd solutions, the samples were shaken for 3 hours and equilibrated for 24 hours at  $25^\circ\text{C}$ . Then part of the supernatant was used for pH measurement and part of the supernatant was filtrated through a  $0.45\mu$  membrane for metal concentration measurement with PE-3100 Atomic Adsorption Spectrometer.

## 3 Results and discussion

### 3.1 Sample characteristics

The X-ray analysis results indicate that the major clay components ( $< 2\mu\text{m}$ ) in the sample are 71% of Illite, 15% of Kaolinite and 14% of Chlorite. The specific area of the sample is  $13.3\text{m}^2/\text{g}$ .

### 3.2 Surface constants

The surface charges of the samples at different pH and ionic strength are calculated from the difference between the amount of base consumed by the blank reference and the sample suspension. The data set of the surface charge versus pH at the different ionic strengths are used first to derive the surface site density and the  $\text{pH}_{\text{pzc}}$ . The results are  $N_s = 7.9 \times 10^{-5}$  mol sites per gram and  $\text{pH}_{\text{pzc}} = 4.2$  respectively. The data sets are consequently used in the determination of the surface constants in the following discussion.

The key point in the applications of surface complexation model lies in first, which model should be chosen that relates to the assumptions for the electrical double layer and the calculation method; second, how to get the parameters properly. In this research, three often used surface complexation models are put into consideration. The mass law equations and the static electronic expressions of these three models being used in the following discussion are listed in the appendix. Both the graphical extrapolation method (Stumm, 1987; 1970;



model to fit the titration curves. It is obvious in Fig. 2, all the three fitting curves computed with the three sets of the parameters agree with the same set of data relatively well. It means that the parameter set is not unique for describing the same data satisfactorily. Accordingly, it shows that the parameters are poorly model constrained but somewhat subjective influenced. Besides, which sets of parameters is better than the others can not be indicated yet. These remains as a problem to be investigated in model application.

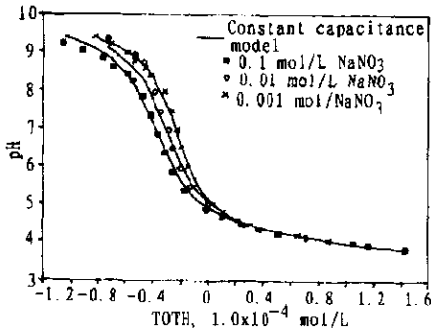


Fig. 1 Fitting titration curves by the constant capacitance model

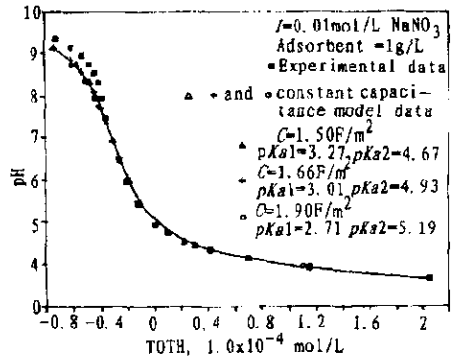


Fig. 2 Fitting the titration curve at ionic strength of 0.01 by the constant capacitance model with three different sets of parameters. It shows the importance of the interdependency among parameters and the indefinite nature of the parameter set.

### 3. 2. 2 Diffuse layer model

Three sets of acidity constants are extracted with Fiteql from the titration data at ionic strength of 0.1, 0.01 and 0.001 mol NaNO<sub>3</sub> are listed in Table 1. Furthermore, the three sets of parameters are used to interpret the experiment titration data obtained at the same three ion strength respectively (Fig. 3a). In turn, the parameters from the data at the ionic strength of 0.01 are put into the model to reproduce the titration curves for the data at the three ionic strength. The results are shown in Fig. 3b. It can be seen that the two kinds of

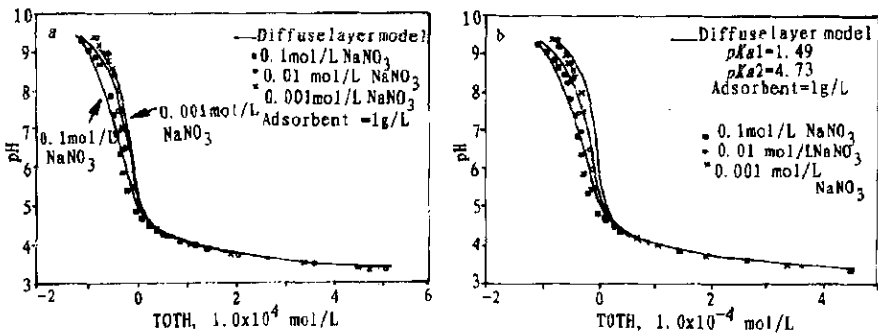


Fig. 3 Fitting titration curves by the diffuse layer model

- a. Parameters deriving from one ionic strength of for reproducing the data at the same ionic strength
- b. Parameters from ionic strength of 0.01 for reproducing the data at three different ionic strengths

result are good. It confirms that with diffuse layer model, the influences of the ionic strength is already incorporated into the model itself and the model can be applied to different solution conditions. On the other hand, in the computation process with diffuse layer model, no capacitance value need to be chosen. The values is already fixed by the theory. As indicated by Dzombak(Dzombak, 1990), diffuse layer model use only two constants ( $pK_{a1}^{int}$  and  $pK_{a2}^{int}$ ) to express the surface characteristics. This avoid intuitively picking up a value for the electrical capacitance and simplify the calculation process. More work is necessary to study the applicability of diffuse layer model to different kinds of river sediment and to establish the constants data base.

### 3.2.3 Triple layer model

$pK_{a1}^{int}$  and  $pK_{a2}^{int}$  are evaluated by the graphical method. The  $pK_{NO_3}^{-int}$  and  $pK_{Na^+}^{int}$  are evaluated with both the graphical and the computer methods. Simultaneously optimizing  $pK_{a1}^{int}$ ,  $pK_{Na^+}^{int}$  and  $pK_{NO_3}^{-int}$  values with Fiteql,  $p$  tried but failed. When the  $pK_{NO_3}^{-int}$  and  $pK_{Na^+}^{int}$  are predicated with Fiteql, the  $pK_{a1}^{int}$  and  $pK_{a2}^{int}$  from graphical method are taken as known parameters and the titration data at ionic strength of 0.01 are the input data. The deriving parameters are listed in Table 1. One distinctive advantage of the triple layer model is that it takes the influence of the electrolyte ions into account in model calculation so that the model parameters  $pK_{a1}^{int}$ ,  $pK_{a2}^{int}$ ,  $pK_{NO_3}^{-int}$  and  $pK_{Na^+}^{int}$  are independent of the electrolyte concentration. As a result, the triple layer model can interpret the data over a wide range of ionic strength. Our results show that the model combined with the intrinsic constants derived from experimental data in 0.01mol NaNO<sub>3</sub>, successfully fit the titration experiment data at ionic strength of 0.1, 0.01 and 0.001(Fig. 4). But on the other hand, this model

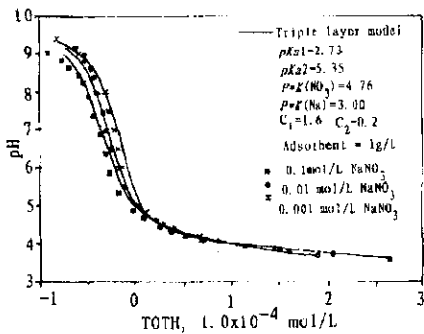


Fig. 4 Fitting titration curves by the triple layer model

introduces more parameters need to be determined which makes the model appear complicated and increases the difficulties in the process of the parameter estimation. Other point should be stated here is that the value of two electrical capacitances should be chosen in the computation process with Fiteql. This would result in the same situation in terms of the indefinite nature of the parameters as discussed above for the constant capacitance model. In our case, the results from our graphical method helps this choice. But it has been noticed as something from intuition and it is still a point need to be studied.

### 3.3 Adsorption constants

The adsorption isotherms for Cu and Cd adsorption to the samples are those of Langmuir type(Fig. 5 and Fig. 6). The data from these isotherms together with the intrinsic surface constants listed in Table 1 are used to determine the intrinsic adsorption constants by Fiteql with the three kinds of surface complexation models. To each model, one set of constants are obtained for each isotherm at each fixed pH condition. Thus, three sets of con-

stant are derived for each kind of model. The constant values listed in Table 2 are the average of the relative three numbers. Comparing the intrinsic complexation constants of Cu and Cd in Table 2, we find that Cu possesses a higher affinity than Cd to this river sediment.

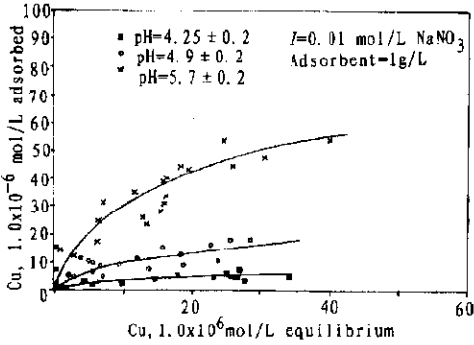


Fig. 5 Adsorption isotherms of the sediment sample for Cu

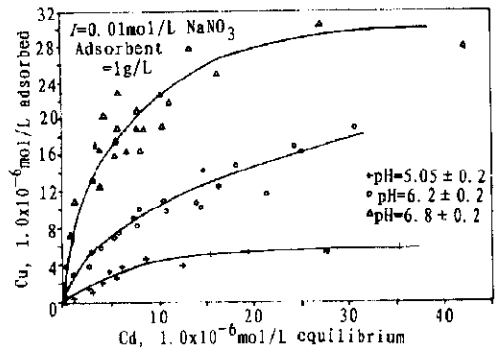


Fig. 6 Adsorption isotherms of the sediment sample for Cd

Table 2 Intrinsic surface complexation constants

Adsorbate	Constants	Capacitance	Diffuse layer	Triple layer
		model	model	model
Cu( I )	$\log K_{M^{2+}int}$	-0.766	-1.247	0.058
	$\log K_{MOH^{+}int}$			-4.599
Cd( I )	$\log K_{M^{2+}int}$	-1.960	-2.585	-0.455
	$\log K_{MOH^{+}int}$			-5.385
	$C_1(F/m^2)$	1.66		1.60
	$C_2(F/m^2)$			0.20

### 3.4 Data interpreting capacity of the model

The surface complexation models which have been viewed as mechanistic model (10) should has the ability of interpreting the adsorption data which are independence of the data used for the model calibration. As a step of the verification of the models, the parameters derived from the adsorption isotherms obtained in several fixed pH are combined into the three surface complexation models, separately, to reproduce the pH edge curves which are in wide pH range with Microql program. Fig. 7 and Fig. 9 show the fitting curves for Cu and Cd adsorption pH edges at different Cu and Cd concentrations with the three models. Fig. 8 and Fig. 10 show the relative estimating errors of each fitting result for the three models.

Model calculation results as well as the experiment results shown in Fig. 7 — Fig. 10 indicate that the adsorption of the metals to the river sediment sample is strongly pH dependent. A big percent of the adsorption of the metals occurs in a narrow pH range. With the increase of the total metal concentration, the pH adsorption edge shift to the high pH range, which is equivalent to the reduction of the adsorption affinity. From the results shown in Fig. 7 — Fig. 10, we can conclude that all three models which obtained their constants

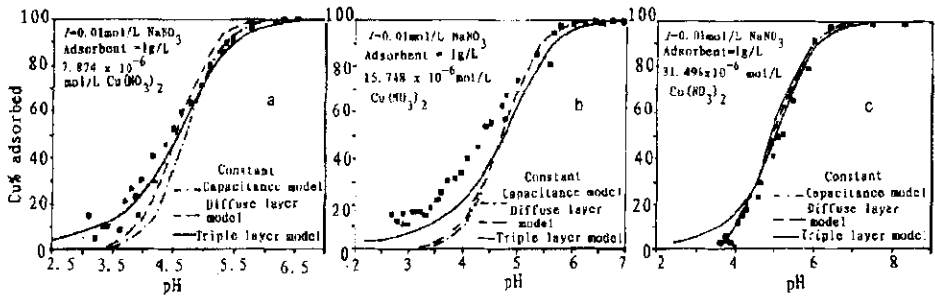


Fig. 7 Fitting curves for the adsorption edges of Cu with the three surface complexation models

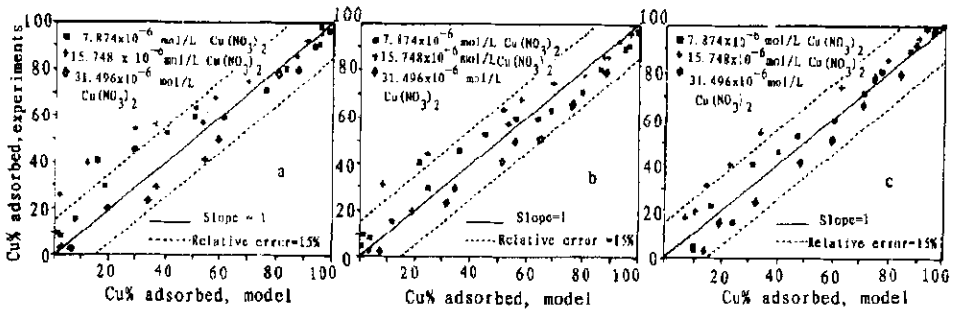


Fig. 8 Relative error analysis for the fits of Cu adsorption pH edges

- Constant capacitance model
- Diffuse layer model
- Triple layer model

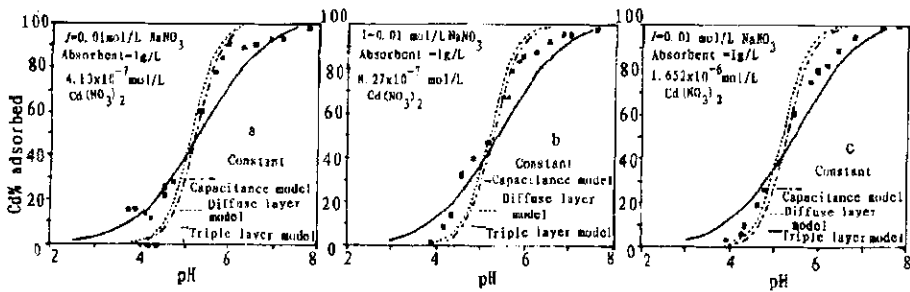


Fig. 9 Fitting curves for the adsorption edges of Cd with the three surface complexation models

through the above discussion process can interpret the experimental data of the pH adsorption edges for Cu and Cd satisfactorily, which means that all the three surface complexation models can be applied to the description of the adsorption behavior of the natural sediment satisfactorily. In this case, the relative estimation errors are within 15%. But this does not help to decide if the assumptions for the geometric form of the interface that is intended to determine the coulombic correction factor of the electrostatic influence in each model are correct. This does not help to explain which model is better than the others in mechanistic



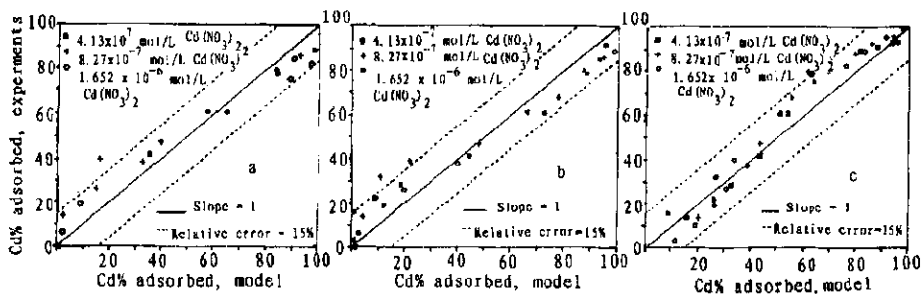


Fig. 10 Relative error analysis for the fits of Cd adsorption pH edges  
 a. constant capacitance model;  
 b. diffuse layer model;  
 c. triple layer model

sense.

Considering the model calibration process together with the model verification results in this research, the following points should be emphasized in the application of surface complexation models to natural sediment. One is the interdependency and consistency among model parameters. As state above, in the parameter estimation process, several parameters such as the  $C$ ,  $pK_{a1}^{int}$  and  $pK_{a2}^{int}$  are covaring adjustable parameters. The value for  $C$  need to be given with in a certain range by the researchers. For each giving  $C$ , a corresponding set of  $pK_{a1}^{int}$  and  $pK_{a2}^{int}$  values are derived while each combination of the relevant parameters can interprt the same titration experimental data relatively well. Consequently, for each set of the surface parameters ( $N_s$ ,  $A$ ,  $C$ ,  $pK_{a1}^{int}$  and  $pK_{a2}^{int}$ ), a corresponding set of adsorption constants come out. The relevant parameters must be put together in model calculation. For giving an evidence to this, in relative to three sets of the surface parameters (Fig. 2), three corresponding adsorption constants by constant capacitance model are extracted from the adsorption isotherm data of Cu. The adsorption pH edge data are simulated by combining these three sets of parameters ( $C$ ,  $pK_{a1}^{int}$ ,  $pK_{a2}^{int}$  and  $K_{M^{2+}int}$ ) into the constant capacitance model and the results are shown in Fig. 11. As we can see that all three sets of parameters can describe the adsorption behavior well. Thereafter, another point emerges. That is the indefinite nature of the parameters as cited above for the surface characteristic parameters and how to evaluate which set of the parameters are the best in terms of "close to realities". This point has been and remains to be a problem in the application of surface complexation models. The importance of the interdependency of parameters and the indefinite nature of the parameters are more obvious for the constant capacitance model and the triple layer model because one or two capacitance values have to be given to some extent by the intuition and experience of the researchers. In this aspect, the diffuse layer model shows the advantages of simplicity and being out of the subjective influence of the researchers.

The third point should be emphasized is the selection and the assignment of the location of the adsorption species. Till now, it is still impossible to accurately identify the nature of the surface complexes, but the species of these complexes have to be assumed in model calcu-

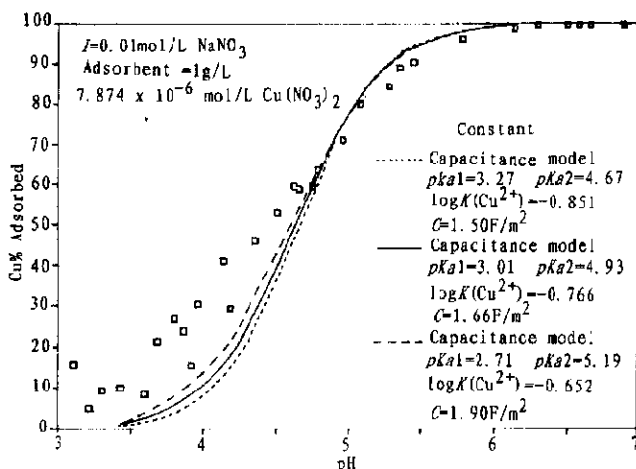


Fig. 11 Fitting the Cu adsorption pH edges by the combination of the three sets of parameters into the constant capacitance model, which shows the importance of the interdependency among parameters and the indefinite nature of the parameters

lation. The value of the intrinsic adsorption constants depends on the choice of the surface species and their locations. In this work, only simplest monodentate surface complex of free metals ( $\text{SO}^- \text{-M}^{2+}$ ) is considered for the constant capacitance model and the diffuse layer model. For the triple layer model, the monodentate surface complex of both free metals ( $\text{SO}^- \text{-M}^{2+}$ ) and the monohydroxyl metal ions ( $\text{SO}^- \text{-MOH}$ ) are considered according to the method of Davis *et al.* (Davis, 1978a; 1978b). All the results from all three model calculations agree with the experimental data satisfactorily. But the choice of the surface species remains to be a problem.

#### 4 Conclusions and recommendations

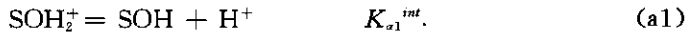
Surface complexation approach is successfully practised in this research to the description of the adsorption behavior of heavy metals with the natural sediments. Through this work, the following conclusions and recommendations are reached. All three surface complexation models that is the constant capacitance model, the diffuse layer model and the triple layer model, studied in this research can be satisfactorily applied to the description of the adsorption process of the natural sediment, in our case, the Le An River sediment with heavy metals. Each model has its specific strengths and shortcomings. However, unfortunately, which model is the best in terms of "close to the reality" remains to be a problem to solve. In addition, the interdependency and consistency of the model parameters should be strongly emphasized in application of the surface complexation models especially for the constant capacitance model and the triple layer model. In this consideration, the diffuse layer model shows its attributes of simplicity and being out of the subjective influence. Another

point is that the choice of the adsorption species affects the parameters values. Also to several aspects, the parameter set is not unique but somewhat indefinite. For the application of the surface complexation models, more research work is necessary to establish the data base.

The significant purpose of the introduction of the surface complexation model to interpret the adsorption phenomenon of natural sediment is what we hope, to some extent, the model can predicate the adsorption data fairly well to widespread range through effort. However, there is a long way to go to meet the goal. We are continuing this work in two aspects. One is that instead of employing the approach of the black-box model in this research, we are trying to investigate the adsorption behavior of the main component of the sediment samples separately in order to establish a grey-box type model to describe the natural system more precisely. The second is to study more sediment samples to add the information to the constant data base for the application of the models.

**Appendix**—Surface complexation models cited in this paper

Adsorption of H<sup>+</sup> ions (for all models):



Acidity constants:

$$K_{a1}^{int} = \frac{\{\text{SOH}\}[\text{H}^+]_s}{\{\text{SOH}_2^+\}} \quad (\text{a3})$$

$$K_{a2}^{int} = \frac{\{\text{SO}^-\}[\text{H}^+]_s}{\{\text{SOH}\}} \quad (\text{a4})$$

$$[\text{H}]_0 = [\text{H}^+] \exp(-e\phi_0/kT). \quad (\text{a5})$$

Where and in the following, { }, concentration of surface species; [ ], concentration in bulk solutions; the subscript s, define the concentration near the surface.

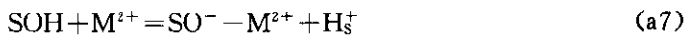
**The constant capacitance model and the diffuse layer model:**

Total surface site concentration,

$$N_s = B(\{\text{SOH}_2^+\} + \{\text{SOH}\} + \{\text{SO}^-\}), \quad (\text{a6})$$

where and in the following,  $B = 10^6 F/A$ ;  $F$ , Farady constant, (coul/mol);  $A$ , surface area of the adsorbent, cm<sup>2</sup>/L

Metal adsorption,



$$K_M^{int} = \frac{\{\text{SO}^- - \text{M}^{2+}\}[\text{H}^+]_s}{\{\text{SOH}\}[\text{M}^{2+}]_s} \exp(e\phi_0/kT). \quad (\text{a8})$$

Relationship between the surface charge and potential:

The constant capacity model:

$$\sigma_H = C\phi_0. \quad (\text{a9})$$

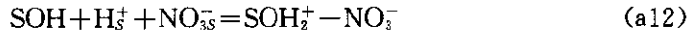
The diffuse layer model:

$$\sigma_d = 0.11741^{1/2} \sinh(ZF\phi_0/RT). \quad (\text{a10})$$

**The triple layer model:**

Adsorption of electrolyte,





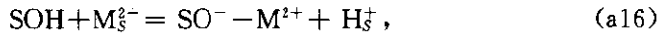
$$K_{\text{Na}^+}^{\text{int}} = \frac{\{\text{SO}^- - \text{Na}^+\} [\text{H}^+]}{\{\text{SOH}\} [\text{Na}^+]} \exp[(e\varphi_\beta - e\varphi_0)/kT], \quad (\text{a13})$$

$$K_{\text{NO}_3^-}^{\text{int}} = \frac{\{\text{SOH}\} [\text{NO}_3^-] [\text{H}^+]}{\{\text{SOH}_2^+ - \text{NO}_3^-\}} \exp[(e\varphi_\beta - e\varphi_0)/kT], \quad (\text{a14})$$

Total surface site concentration,

$$N_s = B(\{\text{SOH}_2^+\} + \{\text{SOH}_2^+ - \text{NO}_3^-\} + \{\text{SOH}\} + \{\text{SO}^-\} - \{\text{SO}^- - \text{Na}^+\}), \quad (\text{a15})$$

Adsorption of metal ions;



$$K_{\text{M}^{2+}}^{\text{int}} = \frac{\{\text{SO}^- - \text{M}^{2+}\} [\text{H}^+]}{\{\text{SOH}\} [\text{M}^{2+}]} \exp[(2e\varphi_\beta - e\varphi_0)/kT], \quad (\text{a18})$$

$$K_{\text{M(OH)}^+}^{\text{int}} = \frac{\{\text{SO}^- - \text{MOH}^+\} [\text{H}^+]}{\{\text{SOH}\} [\text{M}^{2+}]} \exp[(e\varphi_\beta - e\varphi_0)/kT], \quad (\text{a19})$$

Relationship between the surface charge and potential.

$$\varphi_0 - \varphi_\beta = \sigma_H / C_1 \quad (\text{a20})$$

$$\varphi_\beta - \varphi_a = (\sigma_H + \sigma_B) / C_2 = \sigma_d / C_2, \quad (\text{a21})$$

$$\sigma_d = 0.1174I^{1/2} \sinh(ZF\varphi_1/2RT). \quad (\text{a22})$$

## References

- Davis JA, James RO, Leckie JO. *J Colloid Interface Sci*, 1978; 63:480
- Davis JA, Leckie JO. *J Colloid Interface Sci*, 1978; 67:90
- Dzombak DA, Morel FMM. *Surface complexation modelling, hydrous ferric oxide*. New York: John Wiley, 1990
- Fu G, Allen HE. *Water Res*, 1992; 26:225
- Hohl H, Stumm W. *J Colloid Interface Sci*, 1976; 55:281
- Huang CP, Elloitt. *Journal WPCF*, 1977; (5):745
- Hayes KF, Leckie JO. *J Colloid Interface Sci*, 1991; 142:448
- Luoma SN, Davis JA. *Marine Chemistry*, 1983; 12:159
- Stumm W. *Aquatic surface chemistry*. A Willey-Interscience Publication. 1987
- Stumm W, Huang CP, Jenkins SR. *Croat Chem Acta*, 1970; 42:223
- Stumm W, Hohl H, Dalng F. *Croatica Chemica Acta*, 1976; 48(4):491
- Wesrall J. *Reactions at the oxide-solution interface*. In: *Geochemical process at mineral surfaces* (Ed. by JA Davis *et al.*). Washington DC: American Chemical Society. 1986

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