Modeling of cadmium(II) adsorption on kaolinite-based clays in the absence and presence of humic acid

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Abstract

Cadmium adsorption on kaolinite-based clays in the absence and presence of humic acid was modeled with the aid of the FITEQL 3.2 computer program using a modified Langmuir approach for capacity calculations. Formation of surface–metal ion and surface–humate–metal ion complexes was assumed using the DLM approach. As Cd(II) adsorption was ionic strength-dependent, the adsorption experiments were carried out in solutions containing two different concentrations of an inert electrolyte (0.1 M and 0.005 M NaClO$_4$). The surface sites responsible for the adsorption were assumed to be the permanent charges, $\equiv S_1OH$ silanol groups and carboxyl groups having pK_a values close to that of the silanol groups, and $\equiv S_2OH$ aluminol groups and phenol groups with pK_a values close to that of the aluminol groups, because the studied clays (partly composed of clay soil) contained organic carbon. Cd^{2+} ions were assumed to bind to the surface in the form of outer-sphere $X_2^{2-}\cdot Cd^{2+}$ and inner-sphere $\equiv SOCd^+$ monodentate complexes. When humic acid was added, Cd(II) adsorption was modeled using a multi-site binding model by the aid of FITEQL3.2. The fit between model and experimental values was excellent in each case. Since the stability of the ternary surface complexes in the presence of humic acid was higher than that of the corresponding binary surface–cadmium ion complexes, the adsorption vs. pH curves were much steeper (and distinctly S-shaped) compared to the tailed curves observed in binary clay–cadmium ion systems. The clay mineral in the presence of humic acid probably behaved more like a chelating ion-exchanger for heavy metal ions than as a simple inorganic ion exchanger.
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Keywords: Cadmium(II); Kaolinite; Clays; Humic acid; Adsorption; Modeling; FITEQL; DLM

1. Introduction

Various methods such as hydrometallurgical technologies, ion exchange, electrodialysis, reverse osmosis, precipitation and adsorption have been used for heavy metal removal from environmental aqueous solution (La Grega et al., 1994). Effluents of metallurgical and chemical industries, ceramics, electrogalvanization and textile industries are potential sources of water pollution by cadmium ions. Cadmium ions cause serious cases of acute toxicity and diseases such as lung cancer and kidney failure. In Japan, a bone disease named 'itai-itai' emerged in the mid-fifties especially in children (Hagino and Kono, 1955) as a result of consumption of cadmium-contaminated rice as food, because the rice plant was watered with effluents from Cd–Ni battery factories. Prolonged exposure to cadmium ions may lead to bone diseases such as osteomalacia (showing a mixed pattern with osteoporosis) found responsible for

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itai-itai disease (Jarup, 2002). As cadmium is a highly toxic element for living organisms, its adsorption on soils and soil minerals has been the subject of many studies during the last decade (Ludwig and Schindler, 1995; Angove et al., 1997).

The clays readily adsorb heavy metal ions. Adsorption of metal ions from aqueous solution on oxides, clay minerals and clays has been a subject of interest in chemistry as well as in other research areas. It is considered that the adsorption of heavy metal ions and complexes on clay minerals occurs as a result of ion exchange, surface complexation, hydrophobic interaction, and electrostatic interaction (Turner et al., 1996; Nowack and Sigg, 1996; Jung et al., 1998; Kraepiel et al., 1999).

The electrokinetic potential of kaolinite and smectite dispersions with pH in 1 mM NaCl solution is pH-dependent for kaolinites but relatively unaffected by pH for smectites over a wide pH range (Sondi and Pravdic, 1998). The fraction of edge surfaces is about 12–14% for kaolinite, and close to 1% for smectites (Yariv and Cross, 1979; Sposito, 1984). Consequently, one can deduce that heavy metal ion adsorption by kaolinites and smectites results from pH-dependent inner-sphere surface coordination with the edge hydroxyl groups (Farrah et al., 1980; Papini and Majone, 2002) and outer-sphere ion exchange with the permanent negative surface sites (Kim et al., 1996; Turner et al., 1996; Jung et al., 1998; Kraepiel et al., 1999). The magnitude of surface charge and its origin (tetrahedral or octahedral) should determine the selectivity of the silicate surfaces for different metal ions (Sposito, 1989; Gier and Johns, 2000). In addition, the organic components of clays and soils having carboxyl, phenol or amine groups may take part in heavy metal ion retention by complexation.

Studies regarding the use of unconventional adsorbents such as red mud, fly ash, lignin, and peat for metal ion retention are found in literature (Apak et al., 1996, 1998a,b; Bailey et al., 1999). These adsorbents have high capacities for heavy metal ions. For example, bauxite waste-red muds have a high and pH-dependent capacity for Cd(II) adsorption (Barrow, 1982; López et al., 1998; Gupta and Sharma, 2002) and restrict Cd^{2+} leaching in red mud-treated soils (Lombi et al., 2003). Clay minerals play an important role in accumulation, adsorption/desorption, as well as exchange processes of metal ions. Cu(II), Cd(II), and Pb(II) adsorption isotherms on red mud and fly ash were established in previous studies (Apak et al., 1998a,b), and their adsorption on red mud was modeled using single- and double-site modified Langmuir isotherms (Apak et al., 1998a,b).

Modeling works include formation of binary and ternary surface complexes via coordinative covalent binding between the surface and metal ions. Surface complexation reactions involve metal ions, ligands, protons and surface sites. The differences between these models arise from the treatment of electrical double layer at the liquid–solid interface and the conditions set for the weakly bound ions. Therefore, each model uses different electrostatic correction factors in practising mass law equations. The simplest surface complexation model is non-electrostatic. This model ignores the nature of the interface between the solid and liquid, so it does not require an electrostatic correction factor.

Models explaining the adsorption of metal ions and in the presence of complexing agents on various adsorbents are widely reported (Park et al., 205–210, 1995; Park et.al., 447–458, 1995; Nagy and Kónya, 1998; Nagy et al., 1998). Cu(II), Cd(II), and Pb(II) adsorption on red mud in the presence of EDTA (as a widely encountered anthropogenic complexing agent in the environment) were investigated and modeled, and the corresponding stability constants for all binding modes were calculated (Güçlü and Apak, 2000, 2003). According to this study, the adsorption reactions for metal ions–EDTA may be simplified as:

i) formation of covalent bonds between the metal ion (M^{2+}) and surface; SOM^+ type inner-sphere complexes

ii) electrostatic binding of metal ion-EDTA (MY^{2-}) complexes to the surface; $SOH_2^+–MY^{2-}$ type outer-sphere complexes

iii) formation of hydrogen bonds between the carboxylate of the MY^{2-} complexes and surface hydroxyl groups; $SOHYM^{2-}$ type inner-sphere complexes.

Since metal ion–EDTA complexes can be characterized more easily than metal ion–humate complexes due to the polymeric nature of humic acids, modeling of the adsorption of M^{2+} ions on the hydrous-oxide surface in the presence of EDTA : H_2Y^{2-} may aid the understanding of metal ion–humate adsorption. To model adsorption processes, there are many programs such as FITEQL or MINEQL (Tiffreau et al., 1995; Turner et al., 1996; Boily and Fein, 1998; Weerasooriya et al., 1998; Kosmulski, 1999). These computer programs allow modeling of adsorption of metal ions and their complexes as well as of surface acidity properties of these sorbents.

Humic acids are complex aggregates of dark-colored amorphous high molecular weight substances extracted from the natural degradation products of plant residues.

Although considerable work about humic acid exists, only a few of them have dealt with humic acid adsorption on clay minerals. Humic acid is completely soluble only in strongly basic solution. Its solubility increases with increasing pH and decreases with increasing inert electrolyte concentration (Kipton et al., 1992). It contains carboxyl, amine, hydroxyl, and phenol groups, and is negatively charged in basic media (Brady, 1990). Humic acids may both enhance or diminish heavy metal ion adsorption depending on the relative stabilities of metal ion–humate and metal ion–humate–surface complexes as a function of pH (Apak, 2002). Humic acid forms negatively charged complexes with heavy metal ions (especially Fe(III)) as a result of phenolate and carboxylate ligands (Hiraide, 1992). In accord with HSAB (Hard and Soft Acids and Bases) theory, Cu(II) and Pb(II) ions react with humic acid via O and N donor atoms and form stable complexes (Plavsic et al., 1991). Most heavy metal ions are known to bind as inner-sphere complexes to the same type of sites in humic substances such as the carboxylate and phenolate groups irrespective of the type of metal and humic acid (Tipping et al., 2002). The acidity constants (pK_a) of a particular humic acid were reported as 3.94 for pK_{a1} (due to carboxylic acid groups), 5.49 for pK_{a2} (due to amine groups), and 8.29 for pK_{a3} (due to phenol groups) (Westall, 1982).

Kaolinite is an abundant clay mineral in Turkey (Bolle and Adatte, 2001), and is widely used in ceramics. Since most metal ions are adsorbed by smectites by ion-exchange, the surface of these minerals may easily be saturated with alkali and alkaline earth cations (which are more abundant in seawater) in estuarine sediments. On the contrary, kaolinites in such sediments may show a higher selectivity for transition and heavy metal ions due to the presence of pH-dependent adsorption sites. Thus, metal ion retention by estuarine sediments could be better modeled with kaolinites than smectites. Moreover, Davis has shown that the reactive edge sites of kaolinite may be coated with adsorbed organic matter (Davis, 1982), further enhancing metal ion adsorption capacity. Inorganic particles (e.g., kaolinite) coated with humic substances play an important role in the environmental behaviour of various ions (Takahashi et al., 1999).

The aim of this work is to provide a simplified approach to metal ion adsorption from solutions containing simple and hydrolyzed metal ions and humic acids on clay minerals, and thus to better understand real systems and heavy metal mobility in geochemical environments (Hizal and Apak, 2006). A simple SCM modeling the complexation of metal ions with humic substances may provide predictions on specification, reactivity, and transport of heavy metal ions (Zhou et al., 2005) through soil layers with groundwater movement. In contaminated areas with high concentrations of metal ions, addition of humic substances may provide useful remediation strategies based on complexation and/or mobilization of toxic metal ions (Zhou et al., 2005).

2. Analyses

2.1. Supply and preparation of the kaolins

We used three types of kaolins composed of identical components in different percentages. The kaolins were received from the ceramics–raw material storage site of Kalemaden Ceramic Factory at Omerli-Istanbul. The chemical analysis of the dry adsorbents yielded the following weight percentages:

Kaolin-I: SiO_2: 54.96%, Al_2O_3: 28.11%, TiO_2: 1.06%, Fe_2O_3: 2.93%, CaO: 0.06%, MgO: 0.99%, Na_2O: 0.27%, K_2O: 2.17%;

Kaolin-II: SiO_2: 45.49%, Al_2O_3: 38.12%, TiO_2: 0.17%, Fe_2O_3: 0.91%, CaO: 0.27%, MgO: 0.08%, Na_2O: 0.09%, K_2O: 0.22%;

Kaolin-III: SiO_2: 66.8%, Al_2O_3: 21.3%, TiO_2: 0.6%, Fe_2O_3: 1.8%, CaO: 0.1%, MgO: 0.6%, Na_2O: 0.1%, K_2O: 2.0%.

The kaolins were washed with 20% (by wt.) HNO_3 and 1 M NaOH, subsequently with distilled water until neutral, and dried at 80 °C. The specific surface areas were measured by the BET/N_2 adsorption (Hizal, 2001), and were found as 17.8 m^2 g^{-1} (Kaolin-I), 26.7 m^2 g^{-1} (Kaolin-II), and 14.1 m^2 g^{-1} (Kaolin-III). The kaolins consisted mainly of kaolinite as confirmed by XRD spectroscopy (diagram not shown; Rigaku Miniflex powder diffractometer, University of Notre Dame, Department of Environmental Geochemistry laboratories). Total organic carbon contents of these kaolins by elemental analysis were as 2052, 808, and 1288 ppm, respectively (Hizal, 2001). Potentiometric titrations were made at a solid-to-liquid ratio of 1 : 10 at 0.1 and 0.005 M $NaClO_4$ (ABU 91 autoburette radiometer titrator), as described earlier (Hizal and Apak, 2006).

2.2. Adsorption capacity for cadmium ions

Cd^{2+} stock solutions were prepared from cadmium nitrate such that the metal ion concentrations varied between 10 and 600 ppm (mg L^{-1}). Amounts of 1 g kaolin were dispersed in 50 mL of $Cd(NO_3)_2$ solution so as to maintain a solid / liquid ratio of 20 g/L, and contacted batchwise in a thermostatic water bath-agitator for 4 h at 25 °C without adding acid or base. All experiments were repeated at two ionic strength (0.1 and 0.005 M $NaClO_4$). After filtering the equilibrated

dispersion, the cadmium ion concentrations in the filtrate were measured with a flame atomic absorption spectrometer (Varian SpectrAA 220/FS AAS). The equilibrium pH of each sample was measured with a pH-meter (Metrohm Herisau E-512) equipped with a glass electrode calibrated with standard buffers.

2.3. Cadmium adsorption as a function of pH

Kaolin samples were dispersed in 10 ppm Cd^{2+} solutions maintaining a solid / liquid ratio of 50 g/L in the presence of 0.1 M $NaClO_4$ on a rotator for 15 h at 25 °C. The pH of samples were adjusted between 2 and 7 using 20% (by wt) HNO_3 and 1 M NaOH. After 15 h, the dispersions were filtered, and the equilibrium pH and cadmium ion concentration of each sample were measured in the filtrates.

2.4. Solubility of humic acid

A 0.1% (w/v) stock solution of humic acid was prepared by dissolving 0.5 g humic acid (Fluka, 97% pure) in NaOH solution at pH=12, and stirring on a magnetic stirrer for 15 h, then filtering through a Whatman blue-band filter paper. The pH of the samples with 0.004% humic acid in 10 mL volume was adjusted to the desired value using 20% HNO_3 and 1 M NaOH solutions without significant volume change. Samples were shaken for 15 h on a rotator, and then filtered through a blue-band filter paper. First, pH measurements were made in the equilibrated filtrate, and then the humic acid concentration were measured at 370 nm using a Varian Cary 1E UV–Vis spectrophotometer. All experiments were carried out in the presence of 0.1 M $NaClO_4$.

2.5. Humic acid adsorption at different pH

The kaolin dispersions (50 g/L) were reacted with 0.004% humic acid solution after pH adjustment. They were filtered 15 h later, pH was measured, and absorbance measurements (at 370 nm) were made in the filtrate, using a reference solution obtained by shaking kaolins in 0.1 M $NaClO_4$ for 15 h. In all cases, experiments were designed to differentiate true adsorption from precipitation i.e. considering the solubility of humic acid at the given pH.

2.6. Humic acid and cadmium adsorption at different pH

The kaolin dispersions (50 g/L) were reacted with 0.004% humic acid +10 ppm cadmium nitrate in 0.1 M $NaClO_4$ after pH adjustment. They were filtered 15 h later; the filtrates were divided into two parts, and pH and humic acid concentration measurements (with UV spectrophotometry) were made in one part of the filtrate. The other part was used for the determination of the Cd(II) concentration using FAAS with a precision between 0.2% (for pure Cd^{2+} standard solutions) and 2% (for filtrates of Cd^{2+}–humate–kaolin dispersions). All measurements were performed at room temperature.

3. Results and discussion

3.1. Cd^{2+} adsorption

The adsorption isotherms for Cd^{2+} showed Langmuirian character. Table 1 shows the maximum adsorption capacity calculated from the linearized Langmuir isotherm.

$$C_E/Q_E = 1/(Q_M \cdot K) + C_E/Q_M \tag{1}$$

where C_E is the equilibrium concentration of the cadmium ions (mmol L^{-1}), Q_E is the specific amount of cadmium ions adsorbed (mmol g^{-1}), Q_M is the maximum adsorption capacity (mmol g^{-1}), and K is the equilibrium constant (mmol^{-1} L).

Kaolin-I shows the maximum uptake among the kaolin samples because of its maximum organic carbon content (TOC: 2052 ppm) and relative abundance of Fe_2O_3. Adsorption capacities in 0.005 M $NaClO_4$ are almost three times greater than in 0.1 M $NaClO_4$ for all Cd(II)–kaolin systems. The surface area-normalized adsorption capacity (AC) at low ionic strength (Table 1) correlated positively with Fe_2O_3 content as well as with organic carbon content of the kaolins (separately), the linear correlation coefficients being $r=0.98$ and 0.97, respectively (i.e., Kaolin-I>Kaolin-III>Kaolin-II). The correlation coefficients at high ionic strength (0.1 M $NaClO_4$) were somewhat lower; $r=0.96$ and 0.94, respectively. However, three data points (i.e., 3 different kaolins) are not sufficient to test the linearity of the curves. Lackovic et al. (2003) has reported a site density of about 44 µmol/g of variable-charge SOH sites for kaolinite (Ajax Chemicals, Sydney), 6 µmol/g of which was occupied by Cd^{2+} at pH=5.5. The Cd^{2+} retention capacity of our kaolins (found with the aid of a Langmuir approach) for Kaolin II and III were almost identical with this amount at an ionic strength of 0.1, but the larger adsorption capacity of Kaolin I (i.e., 9 µmol/g)

Table 1
Adsorption capacities of Cd(II) on clays (in the units of µmol g^{-1}; µmol m^{-2}) in 0.1 and 0.005 M inert electrolyte ($NaClO_4$)

Metal	[$NaClO_4$]	Clay-I*	Clay-II*	Clay-III*
Cd(II)	0.1	9; 0.51	6; 0.22	6; 0.42
	0.005	27; 1.52	14; 0.52	16; 1.13

* True capacities were as (result=mean±std. dev.); the RSD for results were 2% at most, thus a capacity of 9 µmol g^{-1} corresponded to (9±0.2) µmol g^{-1} within 95% confidence level (no. of measurements: N=5).

may be related to organic carbon content (NOM) of this kaolin.

The surface acidity constants i.e., (pK_{a1}, pK_{a2}) of S$_1$OH and S$_2$OH sites as 1.5 and 4.5; 3.0 and 6.05, respectively, were roughly estimated within a range by potentiometric titration, and further refined with the aid of FITEQL. This is roughly in accord with the findings of Brady et al. (1996), Appel et al. (2003), and Siracusa and Somasundaran (1987) who reported the point of zero charge (PZC) for kaolinite in the range 3.9–4.3, 3.8–4.1, and 4.5–5.0, respectively. Actually, humic acid (HA) adsorption onto clay minerals is expected to change the surface properties (e.g., surface charge, zeta potential, and colloidal stability) (Kretzschmar et al., 1997; Tombacz et al., 1998; Takahashi et al., 1999) to such an extent that experimental determination of surface acidities is not a necessity in the FITEQL code. FITEQL, combining nonlinear least-squares fitting with a chemical equilibrium model, solves this

problem by minimizing the difference between experimental and predicted data using nonlinear regression analysis (Zhou et al., 2005). Thus it is possible to model complex adsorbents — even when they are not characterized to a high level (i.e., when all electrostatic parameters, surface acidities, and surface complexation constants are not experimentally found).

Adsorption (%) vs. pH curves are given in Fig. 1a. The maximum adsorption of cadmium ions takes place at pH between 3 and 4.5 for Kaolin-II and Kaolin-III, and between 3 and 5.5 for Kaolin-I. Considering that the first hydrolysis constant of Cd^{2+} is pK_{h1}=9.83, the degree of hydrolysis of the most concentrated Cd(II) solution tested (600 ppm, or 5.34 mM) is 4.4×10^{-3}%. Thus it may be assumed that Cd^{2+} binds as unhydrolyzed Cd^{2+} ion on negative surface sites. Results found with the aid of FITEQL3.2 support this assumption.

Because adsorption stoichiometry is important in determining adsorption mechanism, Kurbatov curves
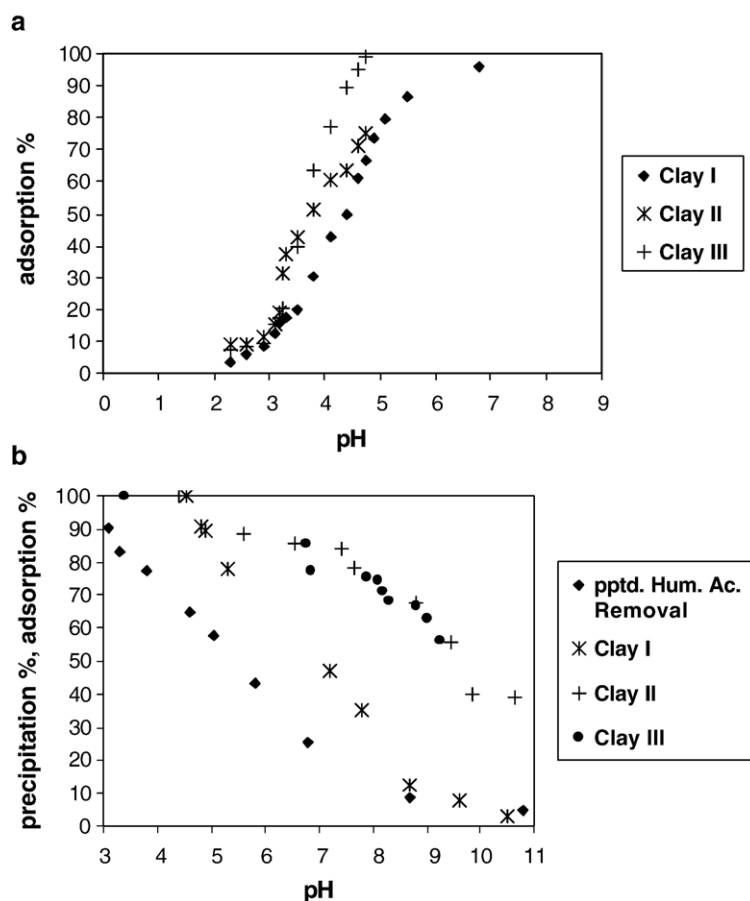

Fig. 1. (a) Cd(II) adsorption on kaolins as a function of pH. (b) Humic acid adsorption on kaolins as a function of pH considering the solubility of humic acid.

are used to find the proton exchange coefficient (Apak, 2002):

$$\text{Log}\frac{[\equiv\text{SOMe}^+]}{[\text{Me}^{2+}]} = \alpha\,\text{pH} + \text{Log}K_{\text{part}} \qquad (2)$$

where $[\equiv\text{SOMe}^+]$ is the concentration of the metal ion on the surface (mmol g^{-1}), $[\text{Me}^{2+}]$ is the molar concentration of the metal ions in solution, α is the stochiometric coefficient, and K_{part} is the partition coefficient of the metal ions between aqueous and solid phases. α gives the number of released protons ion per metal ion adsorbed. Monodentate inner-sphere surface binding on a $\equiv\text{S}_1\text{OH}$ site to form a $\equiv\text{S}_1\text{OCd}^+$ complex necessitates one H$^+$ release for each Cd^{2+} bound. A proton coefficient (α) less than unity indicates that surface reactions that do not release protons such as electrostatic binding or hydrophobic interaction possibly accompany monodentate surface-binding. $\alpha > 1$ may point out to simultaneously occurring monodentate and bidentate bonds. Cd(II) adsorption on the kaolins in the presence and absence of humic acid are lower than 1 (Table 2) indicating that surface complexation takes place simultaneously with electrostatic binding. On the other hand, the α values in the presence of humic acid are slightly higher than in its absence for all Cd(II)–kaolin systems. In general, the presence of humic acid enhances surface complexation. The variation of α values in two different ranges of pH, i.e., pH 2–3 and pH 4–6, for the Cd(II)–Kaolin III system may be ascribed to different binding modes at these pH ranges.

Humic acid adsorption decreases with increasing pH in a manner typical of "ligand-like adsorption" (Apak, 2002). As opposed to normal metal ion adsorption that increases with increasing pH, ligand-like adsorption of metal–EDTA complexes (MY^{2-}) onto goethite was first described by Nowack and Sigg (1996):

$$n\equiv\text{FeOH} + \text{MY}^{2-} + (m+n)\text{H}^+ ===$$
$$\equiv\text{Fe}_n\text{–YH}_m\text{–M}^{(2-n-m)-} + n\text{H}_2\text{O}$$
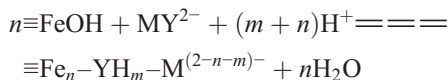
where adsorption is expected to increase with increasing H$^+$ concentration (decreasing pH). In our case at high

Table 2
α values for Cd(II)–Clay systems in the presence and absence of humic acid

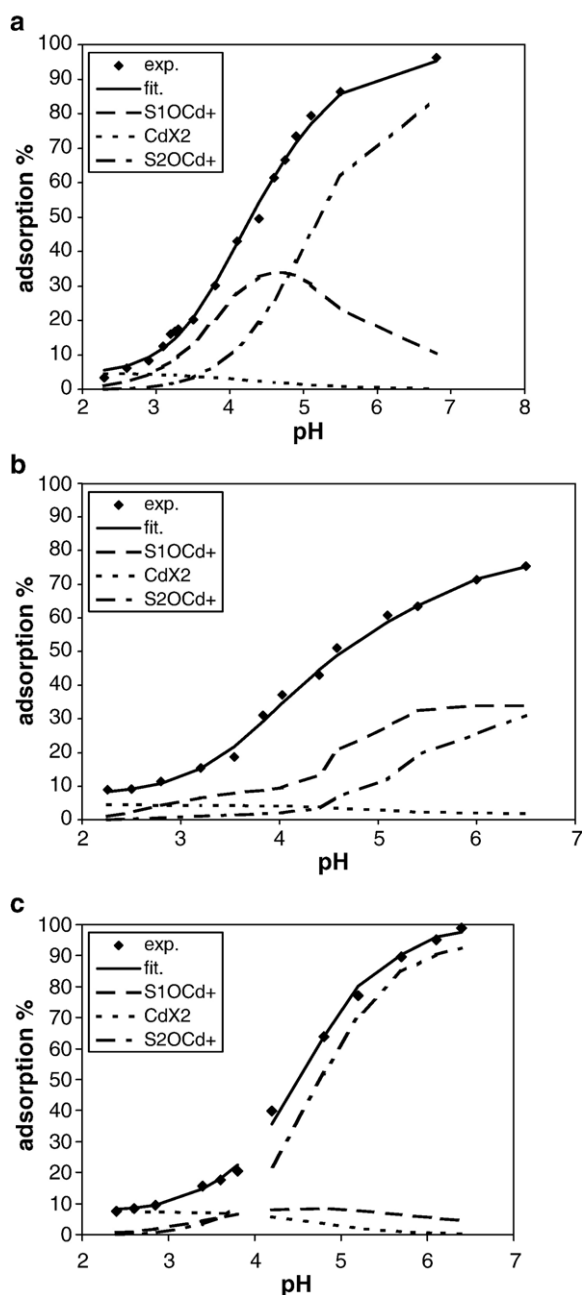|	Clay I	Clay II	Clay III
Cd(II)	$2 < \text{pH} < 6$ $\alpha = 0.45$	$2 < \text{pH} < 6$ $\alpha = 0.33$	$4 < \text{pH} < 6$ $\alpha = 0.66$
			$2 < \text{pH} < 3$ $\alpha = 0.85$
Cd(II)–HA	$4 < \text{pH} < 5$ $\alpha = 0.49$	$1 < \text{pH} < 3$ $\alpha = 0.07$	$4 < \text{pH} < 6$ $\alpha = 0.91$
		$4 < \text{pH} < 4.5$ $\alpha = 1.06$	
		$4.5 < \text{pH} < 6.5$ $\alpha = 0.46$	

Fig. 2. (a) pH vs. adsorption curve for Cd(II)–Kaolin-I system, modeled with FITEQL3.2. (b) pH vs. adsorption curve for Cd(II)–Kaolin-II system, modeled with FITEQL3.2. (c) pH vs. adsorption curve for Cd(II)–Kaolin-III system, modeled with FITEQL3.2.

pH, both the adsorbent surface and humic acid become negatively charged, and consequently repel each other. At lower pH, the uncharged surface functional groups and humic acid can attract each other via hydrogen bonds. However, there is significant adsorption at high pH (Fig. 1b). Thus a further mechanism accompanies
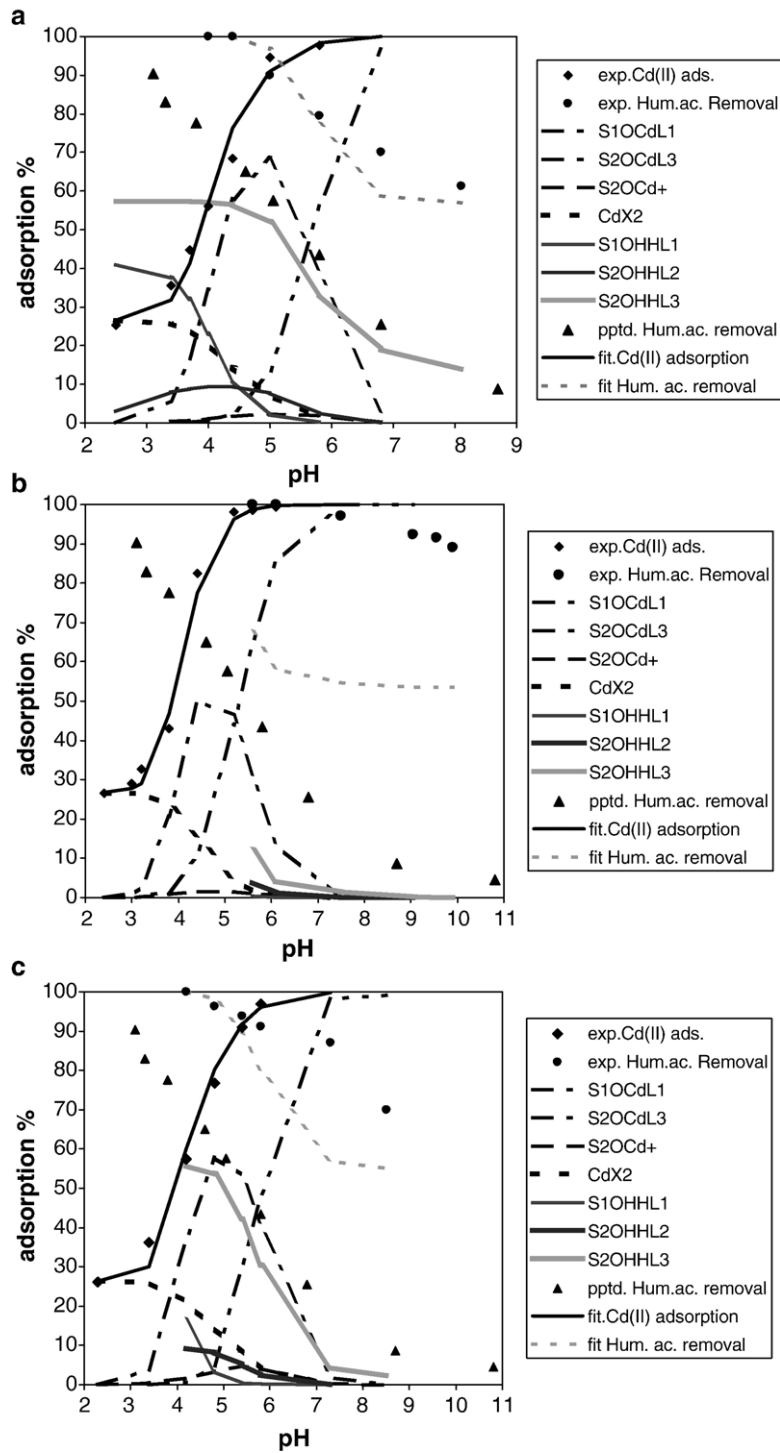
Fig. 3. (a) The Cd(II)–humic acid–Kaolin I; species distribution according to FITEQL3.2. (b) The Cd(II)–humic acid–Kaolin II; species distribution according to FITEQL3.2. (c) The Cd(II)–humic acid–Kaolin III; species distribution according to FITEQL3.2.

humic acid uptake. Van der Waals interaction was shown to have the largest relative contribution to natural organic matter (NOM) adsorption on montmorillonite from a CaCl$_2$ solution (Arnarson and Keil, 2000). Fig. 1b shows the humic acid adsorption by considering the humic acid solubility at different pH. Fig 2a,b,c involve curves concerning the modeling of Cd^{2+}–kaolin binary systems. A humic acid mass-balance would yield an equation of the form: HA$_{removed}$=HA$_{pptd}$+ HA$_{adsorbed}$. A few examples of the research of Fein et al. (Fein et al., 1999; Boily and Fein, 2000; Wightman and Fein, 2001) indicate that "only by comparing the amount of humic acid in solution in an adsorptive substrate or metal-bearing system with that in a humic acid-only system can we quantify the effects of other components on humic acid removal from solution," and consequently, they report their "humic removal" curves always together with a humic acid solubility curve (as a function of pH) as a polynomial fit to the 'humic only' data set. Our 'model of HA adsorption' (Fig. 3a,b,c) is only based on adsorptive removal. Only when adsorption of humate is added to precipitation, we obtain the experimental removal data points. As seen in Fig. 1b, Kaolins I and III exhibit nearly the same adsorption, and their adsorption capacities exceed that of Kaolin II which has minimum of total organic carbon content among the kaolins studied. Thus, humic acid probably not only reacts with silanol and aluminol groups of the surface, but also interacts with the organic components of the kaolin mineral by H-bonds and van der Waals interactions. In fact, it is known from the literature that the organic carbon fraction of many adsorbents, even existent in minor proportions relative to other inorganic constituents, may play a major role in the selective adsorption of organic compounds and their metal complexes (Apak, 2002).

3.2. Modeling of surface complexation

Surface binding constants and molar concentration of surface hydroxyl groups were calculated by FITEQL 3.2 (Tables 3 and 4). It was initially assumed that Cd^{2+}, CdOH$^+$, and Cd$_2$OH^{3+} species are represented in aqueous

Table 3
Log K values calculated by the aid of FITEQL3.2

	Log K_{S1OCd+}	Log K_{S2OCd+}	Log K_{CdX2}	WSOS/DF	Data points
I	−0.17	−1.74	4.74	1.23	17
II	−0.15	−1.48	5.04	1.47	13
III	0.67	−2.62	5.04	1.71	12

Table 4
Molar concentration of surface hydroxyl groups calculated using FITEQL3.2

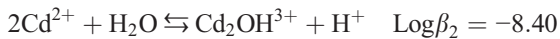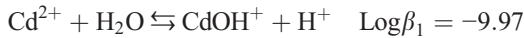|	TOH$_{S1OH}$	TOH$_{S2OH}$	TOH$_{NaX}$	WSOS/DF	Data points
I	9.67×10^{-5}	1.04×10^{-3}	1.03×10^{-4}	1.24	17
II	1.04×10^{-4}	9.71×10^{-5}	9.94×10^{-5}	1.44	13
III	4.4×10^{-4}	3.07×10^{-2}	1.09×10^{-4}	0.93	12

Cd(II) solutions. Complexation equilibria and formation constants of metal hydroxo complexes as extracted from the literature (Pretorius and Linder, 2001) are shown below. The diffuse layer model (DLM) was chosen because the number of parameters required for the model is less (Langmuir, 1997) than that of the triple layer model (TLM), the stoichiometry of the equilibrium problem for the DLM (after Goldberg, 1995) is formulated much simpler than for the TLM, and it leads to better results than the constant capacitance model (CCM) (Hohl and Stumm, 1976). In our modeling approach, we used a high electrolyte concentration (0.1 M NaClO$_4$) so that ion-exchange adsorption onto the kaolinite surface sites would be minimized. The cation exchange capacity of kaolinite is low (Heidmann, 2004), so that the exchange sites could be well saturated with the sodium ions, resulting in inner-sphere surface complexation as the predominant mode of cadmium adsorption, in accord with the basic assumptions of DLM. For an adsorbent containing carboxylic and phenolic groups, and oxidic surfaces similar to that of our kaolinite–humic acid system, electrostatic effects were taken into account using a DLM mathematical treatment of interfacial electrostatics (Puziy et al., 2001). DLM surface complexation modeling was previously shown to describe Cu^{2+} binding to natural organic matter (NOM) with a minimum number of adjustable parameters (i.e. 5) (Ravat et al., 2000). In fact, we used the CCM with a capacitance of 1.6 F m^{-2} close to the literature value (Schindler et al., 1987), with good agreement with the DLM model.

FITEQL input values for the electrical double layer model are shown in Table 5, and FITEQL 'Screen II: Species' of the original program is given in Table 6 to
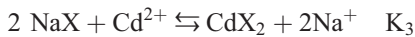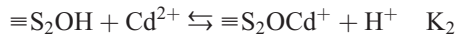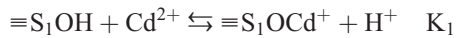
Table 5
FITEQL input values for EDL model

EDL model	Diffuse layer model
Specific surface area	17.8, 26.68, and 14.13 m^2 g^{-1} respectively
Concentration of suspended solid	50 g/L
Concentration of z : z electrolyte	0.1 M
Charge of z : z electrolyte	1

depict acidity, hydrolysis, and stability constants of concerned species in binary and ternary surface complexation.

$$Cd^{2+} + H_2O \leftrightarrows CdOH^+ + H^+ \quad Log\beta_1 = -9.97$$

$$2Cd^{2+} + H_2O \leftrightarrows Cd_2OH^{3+} + H^+ \quad Log\beta_2 = -8.40$$

Possible reactions for Cd(II) retention in the absence of humic acid are:

$$\equiv S_1OH + Cd^{2+} \leftrightarrows \equiv S_1OCd^+ + H^+ \quad K_1$$

$$\equiv S_2OH + Cd^{2+} \leftrightarrows \equiv S_2OCd^+ + H^+ \quad K_2$$

$$2\ NaX + Cd^{2+} \leftrightarrows CdX_2 + 2Na^+ \quad K_3$$

The formation constants of $\equiv S_1OM$ surface–metal complexes are larger than those of $\equiv S_2OM$ species in all systems (Table 3). Fig. 2a–c indicate that $\equiv S_1OM$ and MX_2 species are responsible for adsorption at pH ≤ 4.8. At pH >4.8, $\equiv S_2OM$ species become dominant. This observation explains the metal ion adsorption by aluminol and phenol groups which are activated at higher pH (Apak, 2002). It is clear that the Cd(II) binding sites (possibly silanol and –COOH deprotonated at lower pH) are occupied first with a higher

overall binding constant. These reactions explain the rather low α values (Table 2) in the absence of humic acid. The equilibrium constants of H^+-releasing surface complexation reactions are smaller than that of CdX_2 formation, yielding α values lower than unity.

Inspection of Fig. 1a shows that Cd(II) adsorption onto Kaolin-I reaches a maximum in a wider pH range than on the other kaolins. FITEQL modeling in Fig. 2a shows that $\equiv S_1OH$ and $\equiv S_2OH$ surface sites consecutively become Cd(II) adsorption sites of Kaolin I, i.e., the surface species $\equiv S_1OCd^+$ shows a maximum at pH$=4.8$, a pH value where the $\equiv S_2OCd^+$ species has only reached about half of its maximum. This situation is not found for the other kaolins, where either both $\equiv S_1OCd^+$ and $\equiv S_2OCd^+$ species show a parallel rise with pH (Fig. 2b), or $\equiv S_2OCd^+$ is alone responsible for the adsorption at weakly acidic to neutral pH (Fig. 2c). Thus, Kaolin-I has a stronger multisite adsorption behaviour than the other two kaolins, resulting in a wider adsorption vs. pH profile (Fig. 1a). The relative abundance of $\equiv S_2OH$ surface sites with respect to that of $\equiv S_1OH$ sites is maximum in Kaolin III (Table 4), which explains the predominant role of $\equiv S_2OCd^+$ at weakly

Table 6
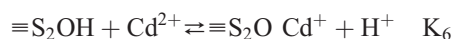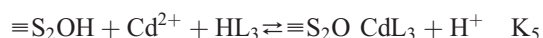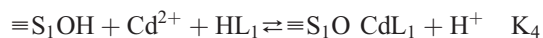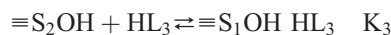Screen II: "Species" in FITEQL for Clay I–Humic acid–Cd(II) system

	Log K	PSI	Cd(II)	HL^1	HL^2	HL^3	XOH	YOH	Yads.	Cdads.	H$^+$	Na$^+$	NaX
Cd(II)	0.00	0	1	0	0	0	0	0	0	0	0	0	0
CdOH$^+$	−9.97	0	1	0	0	0	0	0	0	0	−1	0	0
[Cd$_2$OH]$^{3+}$	−8.40	0	2	0	0	0	0	0	0	0	−1	0	0
CdL$_3$	−5.00	0	1	0	0	1	0	0	0	0	−1	0	0
HL$_1$	0.00	0	0	1	0	0	0	0	0	0	0	0	0
HL$_2$	0.00	0	0	0	1	0	0	0	0	0	0	0	0
HL$_3$	0.00	0	0	0	0	1	0	0	0	0	0	0	0
L$_1$	−3.94	0	0	1	0	0	0	0	0	0	−1	0	0
L$_2$	−5.49	0	0	0	1	0	0	0	0	0	−1	0	0
L$_3$	−8.29	0	0	0	0	1	0	0	0	0	−1	0	0
(XOH$_2$)$^+$	1.50	1	0	0	0	0	1	0	0	0	1	0	0
XOH	0.00	0	0	0	0	0	1	0	0	0	0	0	0
XO$^-$	−4.50	−1	0	0	0	0	1	0	0	0	−1	0	0
XOML$_1$	1.30	0	1	1	0	0	1	0	1	1	−2	0	0
XOHHL$_1$	5.00	0	0	1	0	0	1	0	1	0	0	0	0
YOH	0.00	0	0	0	0	0	0	1	0	0	0	0	0
YO$^-$	−6.05	−1	0	0	0	0	0	1	0	0	−1	0	0
(YOH$_2$)$^+$	3.00	1	0	0	0	0	0	1	0	0	1	0	0
YOHHL$_1$	6.60	0	0	1	0	0	0	1	1	0	0	0	0
YOHHL$_2$	2.40	0	0	0	1	0	0	1	1	0	0	0	0
YOML$_3$	0.80	0	1	0	0	1	0	1	1	1	−2	0	0
YOM	−2.50	1	1	0	0	0	0	1	0	1	−1	0	0
H$^+$	0.00	0	0	0	0	0	0	0	0	0	1	0	0
Na$^+$	0.00	0	0	0	0	0	0	0	0	0	0	1	0
NaX	0.00	0	0	0	0	0	0	0	0	0	0	0	1
CdX$_2$	6.00	0	1	0	0	0	0	0	0	0	0	−2	2
OH$^-$	−13.78	0	0	0	0	0	0	0	0	0	−1	0	0

acidic to neutral pH (Fig. 2c). The permanent negative sites are responsible for Cd(II) adsorption (as adsorbed CdX_2 species) only at distinctly acidic pH (Fig. 2a–c).

In the absence of HA, we modeled Cd(II) adsorption on kaolinite with one type of ion-exchange sites and two different pH-dependent sites, S_1OH and S_2OH as S_1OCd^+ and S_2OCd^+. Ganor et al. also considered silanol and aluminol groups as responsible for pH-dependent adsorption of metal ions (Ganor et al., 2003). Srivastava et al. modeled Cd(II)–kaolinite with one type of ion-exchange (X^-) and one type of pH-dependent sites (SOH) with formation of monodentate and bidentate Cd^{2+} complexes $(X_2Cd$ and $(SO)_2Cd)$ (Srivastava et al., 2004). However, in the latter modeling, Cd(II) adsorption on different sites of kaolinite in the single-element system did not show an exact fit. Experimental isotherms of Cd(II) adsorption on kaolinite by Lackovic et al. showed significant deviations from the fit when Cd(II) adsorption was modeled with the aid of one outer-sphere $X_2^{2-}Cd^{2+}$ and one inner-sphere $(SO)_2Cd$ surface species (Lackovic et al., 2003). This may result from the rather unrealistic assumption of bidentate Cd-binding to a single SOH site compared to our statistically more probable model concerning monodentate-binding to surface hydroxyl groups of different character.

3.3. Modeling of in the presence of humic acid

Simultaneous humic acid and Cd(II) adsorption on kaolins significantly increased compared to the separate experiments. If HL_1, HL_2, and HL_3 symbolize humic acid with carboxyl, amine, and phenol groups, the adsorption may be represented by the following equilibria:

$$\equiv S_1OH + HL_1 \rightleftarrows \equiv S_1OH\,HL_1 \quad K_1$$

$$\equiv S_2OH + HL_2 \rightleftarrows \equiv S_1OH\,HL_2 \quad K_2$$

$$\equiv S_2OH + HL_3 \rightleftarrows \equiv S_1OH\,HL_3 \quad K_3$$

$$\equiv S_1OH + Cd^{2+} + HL_1 \rightleftarrows \equiv S_1O\,CdL_1 + H^+ \quad K_4$$

$$\equiv S_2OH + Cd^{2+} + HL_3 \rightleftarrows \equiv S_2O\,CdL_3 + H^+ \quad K_5$$

$$\equiv S_2OH + Cd^{2+} \rightleftarrows \equiv S_2O\,Cd^+ + H^+ \quad K_6$$

$$2NaX + Cd^{2+} \leftrightarrows CdX_2 + 2Na^+ \quad K_7$$
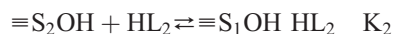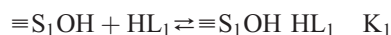
The reported pK_a values (e.g., 3.0 and 6.05 for S_2OH sites) agree with the acidity constants of HL_1 and HL_2 sites reported to be 2.5 and 6.1 by Wightman and Fein (2001). Thus, a model with two discrete edge sites (in addition to the permanent sites) can be used even in the presence of HA in the FITEQL Screen II (Table 6); the acidity constants of humic acid for HL_1, HL_2, and HL_3

were 3.94, 5.49, and 8.29. In spite of the difficulty indicated by Kinniburgh et al. (1996) to distinguish carboxyl- and phenol-type sites merely on the basis of their acidity, the silanol and aluminol sites of kaolinite could approximately be merged with the carboxyl and phenol sites of HA, respectively. This approach is expected to better serve the purpose of modeling complex systems. The fact that adsorption breakthrough occurred over a wide pH range is also an indication that 'single (variable-charge) site, single pK_a' models would not be appropriate.

Fein and coworkers have clearly indicated (Boily and Fein, 2000; Wightman and Fein, 2001) that effective modeling of the metal–humate system cannot be made because of the inavailability of formation constants, and that a surface complexation model (SCM) cannot be applied to complex polymeric molecules of unknown structure. Nierop et al. (2002) further have pointed out that calculation of the overall stability constants of Cu (II)–DOM (dissolved organic matter, composed of humic substances and their fractions) shows a large uncertainty which may explain the inconsistency of information existing in literature. In the speciation diagrams of divalent metal ion like Mn^{2+}, Co^{2+}, and Zn^{2+} in solution containing also humate and inorganic species, M^{2+} and M-humate predominate at low pH, their abundancies being almost equal at a pH around 4; other hydroxide or carbonate species are effective only above pH 8 (Takahashi et al., 1999). The ternary complexes are formed with bulky and polyfunctional ligands of humic acid, and the stoichiometry 1:1:1 metal ion–humate–surface would be sterically favoured (Boily and Fein, 2000). As it is not possible to experimentally determine reaction stoichiometries in a complex mixture of ligand sites, 1 : 1 molar stoichiometry has traditionally been assumed in metal–humic models and is usually observed for simplicity (U.S.-EPA, 1999). Therefore, this stoichiometry of ternary complex formation with HA was adopted in our modeling.

As seen in Fig. 3a–c, $\equiv S_1OCd^+$ species do not exist, formation of $\equiv S_2OCd^+$ species significantly decreases, and formation of CdX_2 species significantly increases especially at lower pH values, and humic acid and the cadmium–humate complex are adsorbed simultaneously. It is noticeable that species having close pK_a and similar functional groups (such as S_1OH with HL_1, and S_2OH with HL_2 and HL_3) have a tendency to interact with each other. In the presence of humic acid, the silanol+carboxyl groups (S_1OH) completely lose their importance in Cd(II) retention, and the observed cadmium adsorption is attributed to the formation of S_2OCd, S_1OCdL_1, and

S_2OCdL_3 surface complexes in weakly acidic to neutral solution, and Cd^{2+} on permanent sites at lower pH. Because most S_1OH sites are occupied by HL_1 species and the conditional stability constants of Cd(II)-humates decrease in acidic solution, Cd^{2+} ions are forced to interact with permanent charges (X^-) at low pH. Thus, formation of CdX_2 increases in the presence of humic acid compared to that in its absence. The curves also show that both calculated results (using FITEQL 3.2) (Westall, 1982) fit the experimental data (considering humic acid solubility). Thus, the used model successfully interprets the experimental results.

The α values are still <1, but greater than those in the absence of humic acid (Table 2), because the number of reactions releasing protons increase in the system. Since the ternary complexes are more stable than the binary complexes, formation of the ternary complexes increases especially at pH >4, with CdX_2 formation up to pH=5.5. The ideal case of $\alpha=1$ is not be reached in any pH range.

Electrostatic binding between Cd(II) and the permanent charges is pH dependent (Figs. 2 and 3). The permanent negative sites do not bear protons and therefore should not be influenced by pH changes, but the hydrated Cd(II) ions form polyhydroxo complexes, and the electrostatic interaction with the permanent negative sites should have an indirect pH dependence. In both binary and ternary systems, the relative contribution of X^- sites to metal adsorption decreases as pH increases.

Enhancement of metal ion adsorption on kaolinite by dissolved organic matter (e.g., fulvic acid) was also noticed by other authors (Heidmann et al., 2005). Enhancement was strongest at low pH, where adsorbed fulvic acid contributed to high-affinity metal ion binding sites of kaolinite. Humic acid clearly enhanced Cd^{2+} adsorption on kaolinite (Arias et al., 2002). In our study, we arrived to similar findings, e.g., distinct behaviour of Cd^{2+} adsorption in the presence of HA; Cd^{2+} adsorption rose from ca. 10% to ca. 25% at pH 2, and almost all Cd^{2+} ions were adsorbed around pH 6. Zhou et al. (2005) have shown that humic acids still carry a negative charge even at pH 2. Linear adsorption models concerning metal–clay–humic (or fulvic) acid dispersions may slightly underestimate adsorption of a given element (e.g., Pb^{2+} in kaolinite–fulvic acid dispersions) (Heidmann et al., 2005), because the total metal ion adsorption was assumed to be equal to the sum of metal ions adsorbed by kaolinite and metal ions adsorbed by fulvic acid. In fact, adsorbed humic substances strongly alter the surface charge, zeta potential and colloidal stability of mineral particles (Heidmann, 2004), and

therefore kaolinite (with adsorbed HA) should be treated as a particular adsorbent as we did in our FITEQL modeling.

4. Conclusion

The adsorption of Cd(II) on three kaolins has been interpreted by the modified Langmuir multi-site models. The ≡SOH surface sites with acidity constants pK_{a1} and pK_{a2} react with Cd(II) ions to form ≡SOM^+ inner-sphere complexes. Simultaneously, Cd(II) ions interact with the permanent surface charges. At pH higher than the PZC of the kaolinites, maximum adsorption was reached. FITEQL modeling assuming three types of binding sites successfully described the observed Cd(II) adsorption on the kaolins without humic acid.

In the presence of humic acid, Cd(II) ions, Cd(II)–humate complexes and humic acid were adsorbed simultaneously. The observed cadmium adsorption is explained as the sum of the formation of binary ≡S_2OCd and ternary ≡S_1OCdL_1 and ≡S_2OCdL_3 surface complexes and of CdX_2 at low pH values.

The clay mineral in the presence of humic acid probably behaved more like a chelating agent for heavy metal ion than a simple inorganic ion exchanger. Since the stability of the dominating surface complexes in the presence of humic acid was higher than that of the corresponding binary metal ion complexes, the adsorption vs. pH curves were much steeper (and distinctly S-shaped) compared to the curves observed in the binary systems. In all cases, the assumed species were shown by FITEQL modeling to describe the observed adsorption data. Thus the essentially complex cadmium humate adsorption as a function of pH from solutions containing simple and hydrolyzed metal ions and humic acids on kaolin has been described by simple terms in groundwater and clay soils, which can clarify heavy metal mobility in the environment.

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