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Surface Speciation Modeling of Heavy Metals in Kaolin: Implications for Electrokinetic Soil Remediation Processes

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Abstract. The driving mechanisms for flux occur at interface between the soil particles and solution during electrokinetic soil remediation and the nature of this interface affects the electrokinetic response of the system. The pH-dependent adsorption of heavy metal contaminants by kaolin and the sensitivity of kaolin zeta potential to the aqueous phase properties are two important aspects that complicate the metal movement during electrokinteic soil remediation. This paper addresses these aspects and presents an electrostatic adsorption model that describes the behavior of kaolin surface for Cr(VI), Cr(III), Ni(II), and Cd(II) under various chemical conditions. This study showed that the aqueous properties: pH, ionic strength and the presence of the heavy metals Cr(VI), Cr(III), Ni(II), and Cd(II) in the system affect the zeta potential of kaolin surface. The zeta potential of kaolin shifts to a more negative value if the system pH increases. However, it shifts to a more positive value if the system ionic strength or metal concentration increases. It was found that the amount of the heavy metal adsorbed by kaolin has a pronounced sensitivity to the pH. As a result of the adsorption modeling, the constant capacitance protonation-dissociation intrinsic constants of kaolin are: $\mathrm{pK}_{+}^{\mathrm{int}} = -3.8 \pm 0.5$ and $pK_{-}^{\mathrm{int}} = 9.4 \pm 0.5$. The ion-kaolin surface complexation constants ($\mathrm{pK}^{\mathrm{int}}$) of Cr(VI), Cr(III), Ni(II), and Cd(II) are: -12.5 ± 0.5, -5.0 ± 1.0, 2.6 ± 0.6, and 3.3 ± 1.0, respectively.

Keywords: kaolin, electrophoresis experiments, equilibrium constants, electrostatic adsorption models, electrokinetic remediation

Introduction

The mobility and reactivity of heavy metals in soils are critically dependent on the aqueous speciation, controlling their solubility and adsorption behavior. Evaluation of remediation strategies for heavy metal-contaminated soils requires that the partitioning of contaminants between the pore water and the soil solids is understood. Modeling of the surface speciation can be used to predict the trends in adsorption behavior of heavy metals in soils with master variables such as pH and redox status. Application of sound thermodynamic principles to adsorption reactions provides a modeling framework that is theoretically rigorous, which can be applied for even complex adsorption reactions (Grenthe and Puigdomenech, 1997).

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Adsorption/desorption process is one of the important physico-chemical processes affecting the transport of the heavy metals during electrokinetics (Reddy et al., 2001; Reddy and Parupudi, 1997). This importance stems from the fact that the pH and solution chemistry change throughout the soil during electrokinetics, affecting the adsorption/desorption process. The electrostatic adsorption models such as diffuse-layer model and triple-layer model consider simultaneously such important system properties as changes in pH, aqueous complex formation and solution ionic strength (solution speciation). Unfortunately, the input data for the electrostatic adsorption models (i.e., capacitances, protonation-dissociation constants, ion surface complexation constants) for different solid surfaces, specially soils, are very scarce. Most of the studies on surface behavior have worked with synthetic particles such as hydrous ferric oxide (HFO) to eliminate the variability in the system. Dzombak and Morel (1990) have reported diffuse-layer model parameters for the adsorption of 20 divalent cations and 14 anions by hydrous ferric oxide (HFO). Hohl et al. (1980), James and Parks (1982), and Stumm (1992, 1993) discussed and found the diffuse-layer model parameters for different ions adsorbed by oxides of Al, Si, and Ti. Smith and Jenne (1991) have published a set of intrinsic constants for triple-layer model of adsorption by ferric oxyhydroxide solids and by birnessite. The lack of data for electrostatic adsorption model parameters of soil surfaces necessitates one to conduct experiments using the specific soil and heavy metals of concern to determine these parameters.

Another important aspect that complicates movement of heavy metals in soils during electrokinetic remediation process is the change in electroosmotic flow magnitude and direction. Moreover, electroosmotic flow, the movement of the pore water under electric field, depends upon zeta potential of the soil surface, which is defined as the potential existing between the shearing surface in the diffuse double layer and the liquid. The values of zeta potential (ζ) reported to range from $+50\,\text{mV}$ to $-50\,\text{mV}$ (Yeung, 1994). During electrokinetic remediation, the zeta potential greater than zero (mV) is shown to induce electroosmotic flow towards the anode and the zeta potential less than zero is shown to induce electroosmotic flow towards the cathode (Eykholt and Daniel, 1994). The zeta potential of most charged particles is dependent on solution pH, ionic strength, types of ionic species, temperature, and type of clay minerals (Eykholt, 1992; Shapiro and Probstien, 1993; Vane and Zang, 1997). During electrokinetics, both the pH and the solution speciation change throughout the soil. As a result, the zeta potential changes spatially. Consequently, the electroosmotic conductivity also changes spatially and temporally. Only recently, theoretical models for electrokinetic processes included the zeta potential as a variable. For example, the electrokinetic model developed by Shapiro and Probstien (1993) considered ζ to be a constant parameter over the entire soil sample. Eykholt (1992), and Eykholt and Daniel (1994) applied the pH-dependent zeta potential to the modified Helmoholtz–Smoluchowski's model to predict the magnitude and direction of electroosmotic flow in kaolin soil. However, these investigations neglected the effects of the presence of contaminants in the pore fluid on zeta potential. Jacobs et al. (1994) stated that the assumption of constant or only pH-dependent electroosmotic flow for purposes of electrokinetic modeling is not accurate for situations where the electroosmotic contribution to contaminant mass transport is significant and aqueous and clay properties are variable.

This paper addresses two important aspects during the electrokinetic process, namely, the pH changes and the solution speciation effects on the clay surface behavior. Specifically, this paper evaluates the effect of pH, ionic strength, and ionic species on zeta potential and models the adsorption behavior of kaolin surface for the heavy metals Cr(VI), Cr(III), Ni(II), and Cd(II) in order to incorporate such aspects in electrokinetic modeling in future work. This paper presents a four-fold work: (1) characterization of the surface charge behavior of kaolin particles by performing potentiometric titration experiments, (2) quantifying the influence of the aqueous phase properties (pH, ionic strength and metal type and concentration) on kaolin particles' zeta potential by performing electrophoresis experiments, (3) quantifying the influence of pH of the aqueous phase on the adsorption of the heavy metals: Cr(VI), Cr(III),Ni(II), and Cd(II) to the kaolin surface by performing adsorption batch experiments, and (4) modeling the adsorption behavior of kaolin surface for Cr(VI), Cr(III), Ni(II), and Cd(II) by estimating their constant capacitance intrinsic adsorption constants (protonation-dissociation and ion-surface complexation constants) by applying the chemical equilibrium models, FITEQL 4.0 and MINEQL+, to the titration and adsorption data.

Theoretical Background

Electroosmosis

In basic terms, electrokinetic remediation involves applying either a low DC current (on the order of milliamps per square centimeter of the cross-sectional area of the electrodes) or a low potential gradient (on the order of a few volts per centimeter of distance between the electrodes) to the electrodes that are inserted into the ground. Depending on the physico-chemical processes that occur at the electrodes and in the soil such as electrolysis, adsorption-desorption, precipitation-dissolution, and oxidation-reduction, three major mechanisms are responsible for the transport of the contaminants: electroosmosis, electromigration, and electrophoresis. The contaminants are transported to the cathode or anode depending on the nature of their charge, either cationic or anionic; and are extracted by different methods such as electroplating or adsorption onto the electrode, precipitation or co-precipitation at the electrode, pumping water near the electrode, or complexing with ion-exchange resins (Acar and Alshawabkeh, 1993; Lindgren et al., 1992).

Electroosmosis is the movement of an electrolyte solution relative to a stationary charged surface due to an applied electric field. The Helmholtz-Smoluchowski theory is the most commonly adopted theoretical description for electroosmosis. This theory introduces the coefficient of electroosmotic permeability, k_e ($\mathrm{m^2\,V^{-1}\,s^{-1}}$), as the volume rate of fluid flowing through a unit cross sectional area due to a unit electrical gradient. The electroosmotic flow rate in one dimension along the soil sample, J_w^e, is given by the empirical relation:

$$J_w^e = k_e \frac{d\phi_e}{dx} = \frac{\varepsilon\varepsilon_o\zeta}{\eta} n \tag{1}$$

where ε is the permittivity of the medium (farad $\mathrm{m^{-1}}$), ε_o is permittivity of the vacuum (8.854×10^{-12} C/V *m*), n is the porosity ($m^3\,m^{-3}$), ζ is the zeta potential (V), and η is the viscosity ($\mathrm{kg\,s\,m^{-2}}$).

Electroosmosis depends on zeta potential, which is defined as the potential existing between the rigid and movable parts of the double layer. Zeta potential is generally negative for water saturated silts and clays and in the range −10 to −100 mV (Probstein and Hicks, 1993). Electroosmotic flow occurs towards cathode when zeta potential is negative. If the concentration of the electrolyte concentration increases or pH of the medium decreases, zeta potential becomes positive, reversing the direction of the electroosmosis.

Adsorption Models

Ion adsorption phenomena at the soil particle-solution interface have been represented by empirical and chemical models (Grenthe and Puigdomenech, 1997). Empirical models are simplified representations of reality considering only the characteristics important to given problem. Empirical models useful for description of adsorption data are the distribution coefficient, the Freundlich isotherm equation, and the Langmuir isotherm equation (Al-Hamdan, 2002). The parameters of these empirical models are only valid for the conditions under which the experiment was conducted and prediction under changing solution composition is not possible.

Surface complexation models (electrostatic models) are discrete site models that provide molecular descriptions of adsorption phenomena using an equilibrium approach and are designed to calculate values for thermodynamic properties such as activity coefficients and equilibrium constants (Langmiur, 1997). Surface complexation models define surface species, chemical reactions, mass and charge balances and constitute a family of models having similar characteristics. This model family includes the constant capacitance model, the diffuse double layer model, the triple-layer model, the Stern variable surface charge-variable surface potential model, and the one-pK model. The major advancement of electrostatic models is the consideration of charge on both the adsorbate ion and the adsorbent surface, in other words, they can consider simultaneously such important system properties as changes in pH, aqueous complex formation and solution ionic strength (solution speciation), and acid-base and complexation properties of one or more sites on several sorbing surfaces simultaneously. Westall and Hohl (1980) provides a detailed discussion of the presently available surface complexation/electrostatic models.

The constant capacitance and diffuse-layer models have many similarities and are commonly used. Both models define specific adsorption of all ions on the same plane. Also, their mass action and charge balance equations are identical (except for the numerical value of the equilibrium constants). The difference in these two models is in the function relating total surface charge σ_o to surface potential ψ_o (Langmuir, 1997). For the diffuse-layer model,

$$T_{\sigma_o} = 0.1174 I^{1/2} \sinh(Z\varphi_o F/2RT) \tag{2}$$

where Z is the valency of the symmetrical electrolyte, I is the ionic strength, F is the Faraday constant, R is the ideal gas constant, T is the absolute temperature, and ϕ_0 is the surface potential in volts. The constant capacitance model is a special case of the diffuse-layer model for solutions of high ionic strength and surfaces of low potential (Langmuir, 1997). In such systems, the above equation can be approximated by

$$T_{\sigma_o} \approx C\varphi_o \tag{3}$$

where C is a constant capacitance term.

These T_{σ_o} expressions for the two models are used to evaluate the charge balance (difference) equations (Y_σ) that are defined for the electrostatic components and have the form

$$Y_\sigma = \sum_i a_{i\sigma} C_i - T_\sigma \tag{4}$$

where $a_{i\sigma}$ is the stoichiometry of the electrostatic component pertaining to σ in species i, and C_i is the concentration of species i.

Both constant capacitance and diffuse-layer models treat metal surface reactions as complexation reactions analogous to the formation of complexes in solution. Surface sites are represented as SOH groups where S's are metals associated with the solid structure and located at the solid-liquid interface. The protonation and dissociation reactions of the surface functional group, SOH, are represented by:

$$\mathrm{SOH} + \mathrm{H_s^+} \leftrightarrow \mathrm{SOH_2^+} \tag{5}$$

$$\mathrm{SOH} - \mathrm{H_s^+} \leftrightarrow \mathrm{SO^-} \tag{6}$$

where $\mathrm{H_s^+}$ is the hydronium ion near the surface, and the intrinsic equilibrium constants for these reactions are:

$$K_+(\mathrm{int}) = \frac{[\mathrm{SOH_2^+}]}{[\mathrm{SOH}][\mathrm{H^+}]} \exp[F\varphi/RT] \tag{7}$$

$$K_-(\mathrm{int}) = \frac{[\mathrm{SO^-}][\mathrm{H^+}]}{[\mathrm{SOH}]} \exp[-F\varphi/RT] \tag{8}$$

Typical surface complexation reactions for specific ion adsorption for the constant capacitance model are:

$$\mathrm{SOH} + \mathrm{M}^{m+} \leftrightarrow \mathrm{SOM}^{(m-1)} + \mathrm{H^+} \tag{9}$$

$$2\mathrm{SOH} + \mathrm{M}^{m+} \leftrightarrow (\mathrm{SO})_2\mathrm{M}^{(m-2)} + 2\mathrm{H^+} \tag{10}$$

$$\mathrm{SOH} + \mathrm{H}_n\mathrm{L} \leftrightarrow \mathrm{SH}_{n-i}\mathrm{L}^{(1-i)} + \mathrm{H_2O} + (i-1)\,\mathrm{H^+} \tag{11}$$

$$2\mathrm{SOH} + \mathrm{H}_n\mathrm{L} \leftrightarrow \mathrm{S_2H}_{n-j}\mathrm{L}^{(2-j)} + 2\mathrm{H_2O} + (j-2)\,\mathrm{H^+} \tag{12}$$

where M is a metal ion, m^+ is the charge on the metal ion, L is the ligand, n is the number of protons present in undissociated form of the ligand, $1 \leq i \leq n$, and $2 \leq j \leq n$ and is equal to the number of proton dissociations undergone by a ligand. The intrinsic equilibrium constants describing the above reactions are:

$$K_\mathrm{M}^1(\mathrm{int}) = \frac{[\mathrm{SOM}^{m-1}][\mathrm{H^+}]}{[\mathrm{SOH}][\mathrm{M}^{m+}]} \exp[(m-1)F\varphi/RT] \tag{13}$$

$$K_\mathrm{M}^2(\mathrm{int}) = \frac{[(\mathrm{SO})_2\mathrm{M}^{m-2}][\mathrm{H^+}]^2}{[\mathrm{SOH}]^2[\mathrm{M}^{m+}]} \exp[(m-2)F\varphi/RT] \tag{14}$$

$$K_\mathrm{L}^i(\mathrm{int}) = \frac{\left[\mathrm{SH}_{(n-i)}\mathrm{L}^{1-i}\right][\mathrm{H^+}]^{i-1}}{[\mathrm{SOH}][\mathrm{H}_n\mathrm{L}]} \exp[(1-i)F\varphi/RT] \tag{15}$$

$$K_\mathrm{L}^j(\mathrm{int}) = \frac{\left[\mathrm{S_2H}_{(n-j)}\mathrm{L}^{2-j}\right][\mathrm{H^+}]^{j-2}}{[\mathrm{SOH}]^2[\mathrm{H}_n\mathrm{L}]} \exp[(2-j)F\varphi/RT] \tag{16}$$

In the diffuse double layer model, the surface reaction for specific ion adsorption includes the same reactions as the constant capacitance model except that in the diffuse-layer model no bidentate (Eqs. (10)) or binuclear (Eqs. (12)) surface complexes are defined for metals or ligands, respectively. Also, surface complexation with metal ions is considered to occur on two types of sites: high-affinity "strong" sites, $\mathrm{S^sOH}$, and low-affinity "weak" sites, $\mathrm{S^wOH}$. The adsorption reaction on both sets of sites is analogous to the following equations:

$$\mathrm{S^sOH} + \mathrm{M}^{m+} \leftrightarrow \mathrm{S^sOM}^{(m-1)} + \mathrm{H^+} \tag{17}$$

$$\mathrm{S^wOH} + \mathrm{M}^{m+} \leftrightarrow \mathrm{S^wOM}^{(m-1)} + \mathrm{H^+} \tag{18}$$

And for ligand exchange the adsorption reactions considered in the diffuse-layer model are

$$\mathrm{SOH} + \mathrm{L}^{l-} + \mathrm{H}^+ \leftrightarrow \mathrm{SL}^{(l-1)-} + \mathrm{H_2O} \quad (19)$$

$$\mathrm{SOH} + \mathrm{L}^{l-} + 2\mathrm{H}^+ \leftrightarrow \mathrm{SL}^{(l-2)-} + \mathrm{H_2O} \quad (20)$$

The intrinsic equilibrium constants describing the above reactions are:

$$K_{\mathrm{L}}^{1}(\mathrm{int}) = \frac{[(\mathrm{SL}^{(l-1)-})]}{[\mathrm{SOH}][\mathrm{L}^{l-}][\mathrm{H}^+]} \exp[-(l-1)F\varphi/RT] \quad (21)$$

$$K_{\mathrm{L}}^{2}(\mathrm{int}) = \frac{[(\mathrm{SL}^{(l-2)-})]}{[\mathrm{SOH}][\mathrm{L}^{l-}][\mathrm{H}^+]^2} \exp[-(l-1)F\varphi/RT] \quad (22)$$

Experimental Methodology

Materials

Kaolin, a commercial-grade soil consisting mainly kaolinite clay mineral obtained from American Clay Minerals Society has been used in this study. Its properties are summarized in Table 1. Four heavy metals were selected for this study: trivalent chromium Cr(III), hexavalent chromium Cr(VI), cadmium Cd(II), and nickel Ni(II). The source of these metals were: chromic chloride ($CrCl_3 \cdot 6H_2O$, certified Fisher Chemical) for Cr(III), potassium dichromate (K_2CrO_4, ACS certified) for Cr(VI), nickel chloride ($NiCl_2 \cdot 6H_2O$, technical Fisher Chemical) for Ni(II), and cadmium chloride ($CdCl_2 \cdot 2.5H_2O$, ACS certified) for Cd(II). Nitric acid (ACS PUL certified) and sodium hydroxide (ACS certified) were used as titrants to change the pH conditions of the system. Also, sodium nitrate (ACS certified) was used as a background electrolyte. In addition to these chemicals, deionized water was used.

Table 1. Summary of properties of kaolin soil.

Property	Result
Mineralogy	Kaolin: 100% Muscovite: trace Illite: trace
Particle Size Distribution (ASTM D 422)	
Gravel	0%
Sand	4%
Silt	18%
Clay	78%
Atterberg Limits (ASTM D 2487)	
Liquid Limit	50.0%
Plastic Limit	27.4%
Plasticity Index	22.6%
Specific Gravity (ASTM D 854)	2.60
Hydraulic Conductivity (ASTM D 2434)	1.3E-07 cm/sec
Cation Exchange Capacity (ASTM D 9081)	1.0–1.6 meq/100g
pH (ASTM D 4972)	4.9
Organic Content (ASTM D 2974)	Near 0%
USCS Classification (ASTM D 2487)	CL

Surface Charge Experiments

The pH-dependent surface charge of kaolin was investigated by conducting potentiometric batch tests. The batch titration of the kaolin was performed using 125 mL bottles containing 10 mL of kaolin suspension (100 g/L), and a predetermined amount of $NaNO_3$ for various initial ionic strength settings (i.e., 2 ml of 0.25 M $NaNO_3$ will yield $I = 0.01$ M in 50 ml sample). A total of 30 samples were prepared and their pH was changed by adding varying amounts of 0.1 M HNO_3 or 0.1 M NaOH solution. The first half of batch samples contained 1,000, 900, 800, 700, 600, 500, 400, 300, 250, 200,150,100,75, 25, and 10 μL of 0.1 M NaOH, while the other half of batch samples contained similar amounts of 0.1 M HNO_3. One control sample was prepared with no acid or base additions. The volumes of acid or base additions were carefully monitored by the use of an adjustable volume pipette which can deliver the desired solution in 0.002 mL increments. Each sample was then diluted to a final volume of 50 mL with deionized water.

Finally, after all the additions were made, the samples were tightly capped and shaken overnight on a shaker at room temperature. After equilibrating, suspension pH of each sample was measured and the pH data of the entire batch was plotted against moles of acid (or base) added. The process was repeated for three ionic strengths (0.001 M, 0.01 M, 0.1 M $NaNO_3$). Samples were tested in duplicates to ensure reproducibility. The data was analyzed based on the principle of electroneutrality (i.e., the sum of the negative charges is equal to the sum of all positive charges). This analysis resulted a surface charge for each point from the titration curves to generate new curves. Plotting the surface charge versus pH yields three lines intersecting at the point of zero charge (pH_{PZC}).

Table 2. Electrophoresis experimental program.

Test series	Soil type	pH	Ionic strength	Metal concentration	Objective
I	Kaolin	(2–12)	0.001 M KCl	None	To study the effect of pH on zetal potential under different ionic strengths
	Kaolin	(2–12)	0.01 M KCl	None	
	Kaolin	(2–12)	0.1 M KCl	None	
II	Kaolin	4	0.01 M KCl	Cr(VI) = 1,10,100, and 1000 mg/L	To study the effect of metal concentration on zeta potential
	Kaolin	4	0.01 M KCl	Cr(III) = 1,10,100, and 1000 mg/L	
	Kaolin	4	0.01 M KCl	Ni(II) = 1,10,100, and 1000 mg/L	
	Kaolin	4	0.01 M KCl	Cd(II) = 1,10,100, and 1000 mg/L	
III	Kaolin	4	0.01 M KCl	Cr(VI):Ni(II):Cd(II) = 10:5:2.5 [Cr(VI) = 1,10,100, and 1000 mg/L]	To study the effect of metal existence as combined on zeta potential

Electrophoresis Experiments

Electrophoresis experiments were conducted to determine zeta potential of kaolin soil. Three series of experiments were conducted on the tested soil. Table 2 summarizes the objective and variables of each test series. The first test series was conducted to study the effect of pH on zeta potential under different ionic strengths ($I_1 = 0.001\,\text{M}$, $I_2 = 0.01\,\text{M}$ and $I_3 = 0.1\,\text{M KCl}$). The second series was conducted to study the effect of metal concentration of Cr(VI), Cr(III), Ni(II), and Cd(II), individually, on zeta potential. In the tests of second series, the pH of the suspension was 4, the ionic strength was 0.01 M KCl, and the metal concentrations were 1, 10, 100, and 1000 mg/L. The third test series was performed to study the effect of multiple metals together in the suspension. The suspension pH was maintained to be 4, the ionic strength was 0.01 M KCl and the concentration ratio of Cr(VI):Ni(II):Cd(II) in the suspension was 10:5:2.5. In all the electrophoresis tests, the suspension was 0.1 g of soil to 1 L of solution. The suspension pH was adjusted by drop wise addition of HCl or KOH solution and measured with an Orion pH-triode probe calibrated with pH = 4.00, 7.00, and 10.00 standards.

The zeta potential of each soil suspension sample was measured using the zeta meter LAZER ZEE$^{\text{tm}}$ Model 500. For each test series, duplicate suspensions were prepared to determine precision and repeatability of test results.

Adsorption Experiments

The EPA batch-type test procedure was followed to determine the adsorption of heavy metals on soils (USEPA, 1992). This procedure takes into consideration of many factors that affect the adsorption behavior such as adsorbent preparation, solution pH, method of mixing, separation method, soil to solution ratio, and equilibrium time. The experimental program of adsorption behavior of heavy metals on kaolin surface is outlined in Fig. 1.

Batch adsorption tests for kaolin soil were conducted for six different soil to solution ratios (1:4, 1:10, 1:40, 1:60, 1:100, and 1:200 (mass/volume)) with a constant solution volume (50 mL) and highest concentration of solute (10^3 mg/L). Nickel was used as a representative solute for finding the soil to solution ratio and the

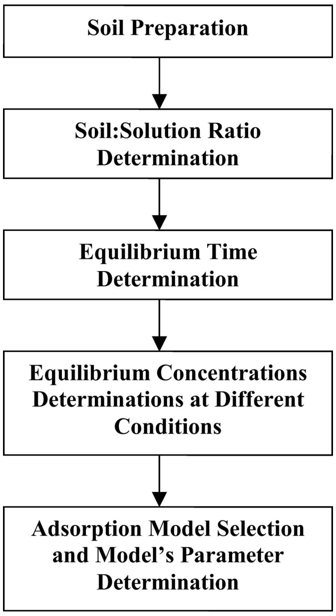

Figure 1. Experimental program for adsorption behavior of kaolin surfaces to heavy metals.

adsorption equilibrium time. The soil to solution ratio, indicating between 10 to 30% adsorption of the highest solute concentration, was selected and then used to determine the adsorption equilibrium time. The equilibrium time is the minimum amount of time required to establish a rate of change of solute concentration in solution equal to or less than 5% per 24-h interval using the selected soil to solution ratio and the maximum initial concentration of the solute (USEPA, 1992).

With the constant soil to solution ratio of 1 to 10 and known equilibrium time of 24 h, batch adsorption tests were conducted with eight different initial concentrations (5, 15, 30, 50, 100, and 250 mg/L) for each studied metal (Cr(VI), Cr(III), Ni(II), and Cd(II)) at six different constant pH conditions (2, 3, 4, 5.5, 6, and 8). The pH of the samples was adjusted by using 0.1 M HNO_3 or 0.1 M NaOH. All samples contained 0.1 M $NaNO_3$ as a background electrolyte so that pH adjustments would not alter the background ionic strength. Samples were shaken at room temperature (22 °C) for 24 h (i.e., estimated adsorption equilibrium time) then centrifuged at 3500 rpm for 20 min and filtered using Wattman filter paper. The metal ion concentration in the supernatant was determined using an Atomic Absorption Spectrophotometer (AAS). The amount of metal adsorbed per mass of dry soil was determined by:

$$\frac{x}{m} = \frac{C_o - C}{m} V \tag{23}$$

where x/m is amount of metal adsorbed per unit mass of soil, C_o is initial metal concentration before exposure to soil, C is metal concentration after exposure to soil at equilibrium, and V is volume of metal solution added to the reaction container.

Finally, following the same procedure mentioned above, a total of five batch tests with Cr(VI), Ni(II), and Cd(II) combined together in the kaolin suspension (100 mg/L) for different pH conditions (2, 3, 4, 5, 6, 7, 8, 9, and 10) were conducted. The initial concentrations of the Cr(VI), Ni(II), and Cd(II) in all the five tests were: 100, 50, and 25 mg/L, respectively. These tests were performed to investigate effects of coexisting multiple metals on the adsorption of individual metal and validation of adsorption models under multiple contaminant conditions.

Results and Discussion

Surface Charge Measurements

Figure 2 shows the pH of the kaolin suspension versus the mole of acid or base added to the suspension. Based on the principle of electroneutrality, the titration data in Fig. 2 was analyzed to yield the surface charge of kaolin versus pH. The scale was shifted such that the surface charge was equal to zero at the intersection of these curves (see Fig. 3). Figure 3 implies that the point of zero charge is 3.2, and a specific cationic adsorption by the kaolin surface exists when pH is higher than 3.2

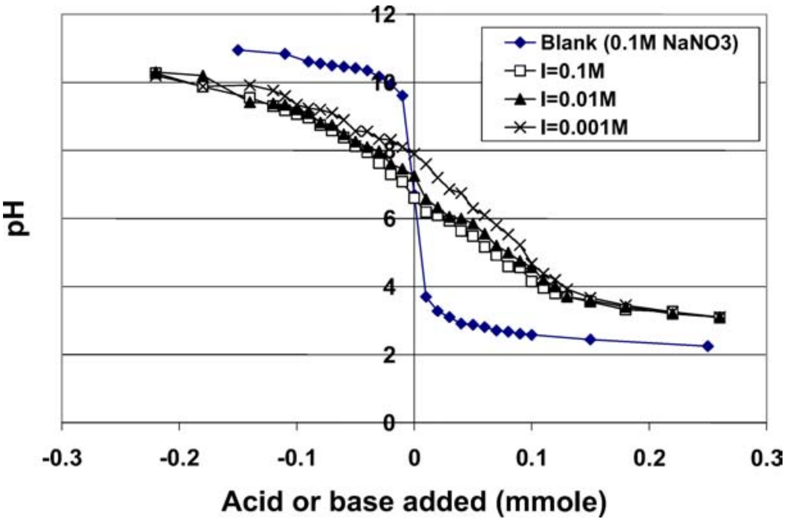

Figure 2. Acid base titration curves of kaolin at various ionic strengths (suspension is 100 g/L).

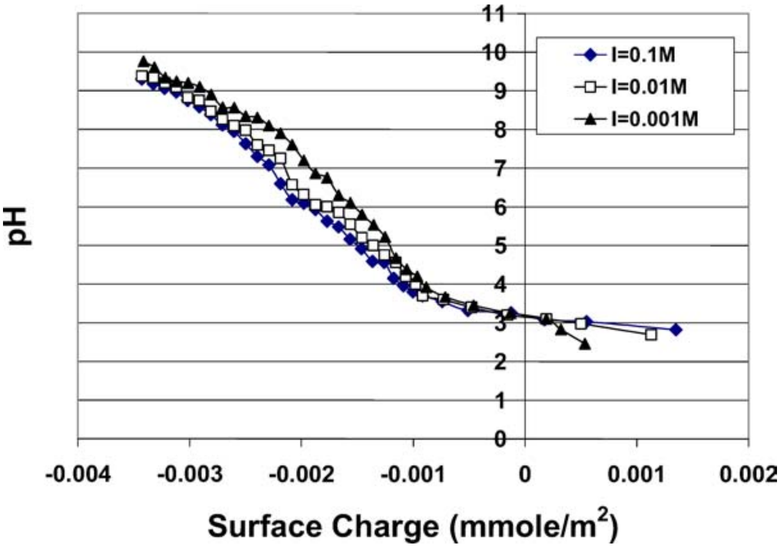

Figure 3. Surface charge of kaolin versus pH at various ionic strengths (obtained from batch titration data).

and a specific anionic adsorption exists when pH is less than 3.2.

Zeta Potential Measurements

The effect of pH on the zeta potential of kaolin is presented in Fig. 4. The zeta potential of kaolin was found to be strongly affected by pH, ranging from −0.75 mV at pH = 2.0 and 0.001 M ionic strength to −60.4 mV at pH = 12.0 and 0.001 M ionic strength. By analyzing the data, it is found that the zeta potential of kaolin is logarithmically related to the pH at ionic strength of $I = 0.001$ M as follows:

$$\zeta_{\mathrm{pH}} = -33.63 \ln \quad \mathrm{pH} + 23.96 \quad R^2 = 0.968 \quad (24)$$

where ζ_{pH} is the zeta potential of kaolin at specific pH value (pH > 1), mV.

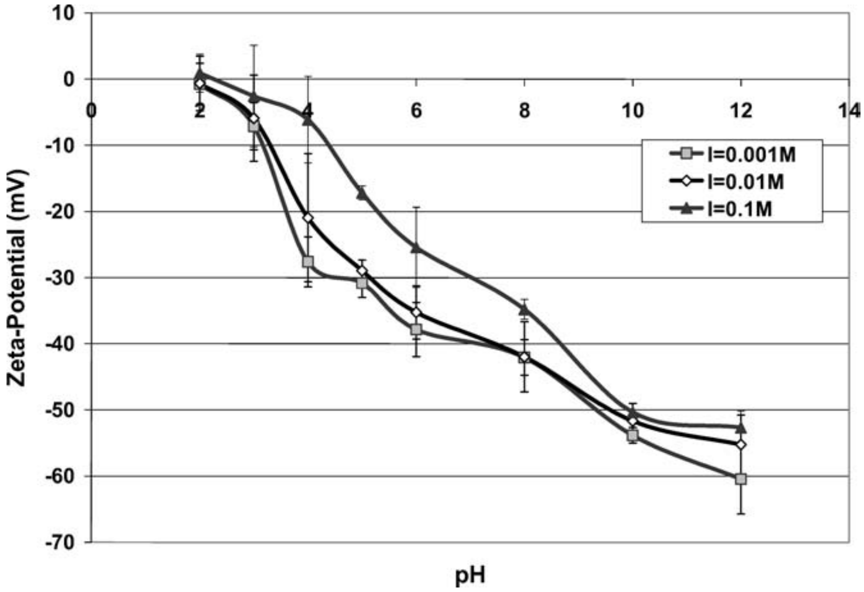

Figure 4. Effect of pH and electrolyte concentration on zeta potential of kaolin (0.1 g/L suspension at 25°C).

Kaolin exhibited some sensitivity to background electrolyte concentration as shown in Fig. 4. An increase in the ionic strength shifts the pH-dependent zeta potential curve to a more positive value. This is attributed to the fact that an increase in the ionic strength compresses the diffuse layer, causing a change in the surface potential value at the shear plane (i.e., zeta potential). The results suggest that zeta potential change, $\Delta\zeta_I$, is related to the ionic strength ($I > 0.001$ M) as follows:

$$\Delta\zeta_I = 90I + 0.7 \quad R^2 = 0.973 \tag{25}$$

where I = ionic strength of the suspension, mole/L.

The electrophoresis experiments show that the zero point of charge (pH_{ZPC}) of kaolin is 2 to 2.5. This value differs from the value that resulted from the potentiometric titration experiments (i.e., 3.2). This difference may be attributed to the fact that the procedures in the potentiometric titration experiments assume that the only reactions in the system involve the hydronium or hydroxyl ions either sorbing to or desorbing from the surface, and that no reactions exist in the aqueous bulk solution.

The presence of heavy metals in the suspension strongly affects the zeta potential of kaolin. Figure 5 shows that as the heavy metal concentration increases in the suspension, at fixed pH and ionic strength, the absolute magnitude of zeta potential reduces to reach a metal concentration point where the zeta potential sign reverses and continues to increase as the metal concentration increases. In other words, as the metal concentration increases in the suspension, the zeta potential value becomes more positive. These results suggest that at a pH of 4 and 0.01 M ionic strength, the influence on zeta potential of kaolin by Cr(III) is stronger than that of Cr(VI), Ni(II), or Cd(II), while Cr(VI), Cd(II) and Ni(II) each shows almost the same effect on the zeta potential of kaolin at a pH = 4. This implies that at pH = 4 the adsorption affinity of Cr(III) to the kaolin surface is highest among the studied metals and Cr(VI), Ni(II), and Cd(II) have almost the same affinity at that pH. The results suggest that the change in zeta potential of kaolin at pH = 4 is logarithmically related to the metal concentration as follows:

$$\Delta\zeta_{\mathrm{Cr(VI)}} = 5.3 \ln C_{\mathrm{Cr(VI)}} - 2.42 \quad R^2 = 0.998 \tag{26}$$

$$\Delta\zeta_{\mathrm{Cr(III)}} = 5.56 \ln C_{\mathrm{Cr(III)}} + 15.90 \quad R^2 = 0.985 \tag{27}$$

$$\Delta\zeta_{\mathrm{Ni(II)}} = 6.13 \ln C_{\mathrm{Ni(II)}} - 0.366 \quad R^2 = 0.988 \tag{28}$$

$$\Delta\zeta_{\mathrm{Cd(II)}} = 6.94 \ln C_{\mathrm{Cd(II)}} - 5.05 \quad R^2 = 0.962 \tag{29}$$

where C_i is the concentration of the metal (i) in mg/L ($C_i > 1$ mg/L)

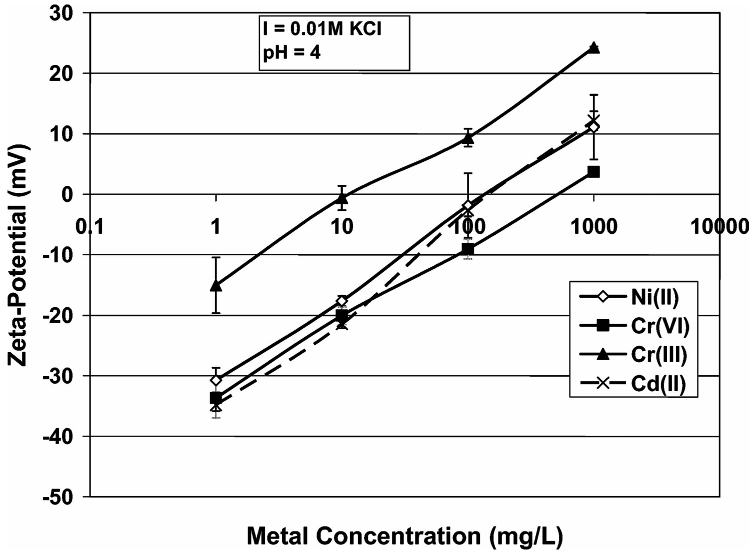

Figure 5. Effect of metal concentration on zeta potential of kaolin (all samples at pH = 4.0; 0.1 g/L suspension; and 25°C

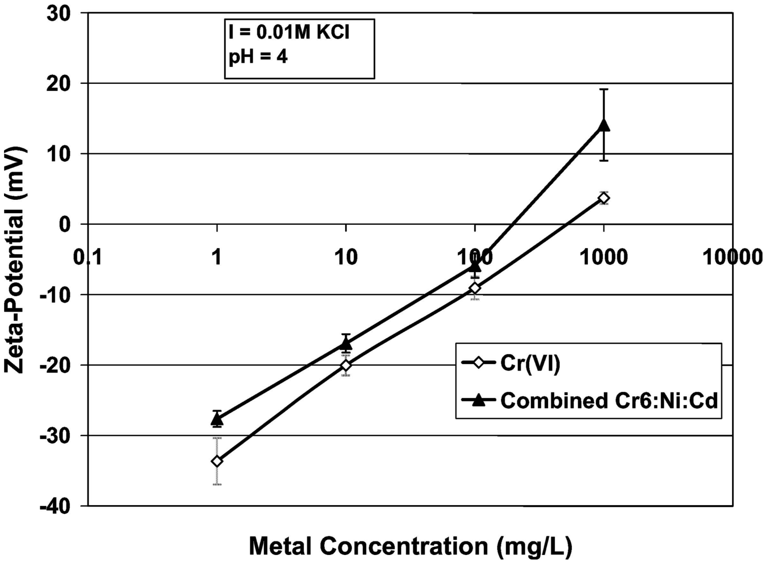

Figure 6. Effect of Cr(VI) as a single or combined with other metals on zeta potential of kaolin (all samples at pH = 4.0; 0.01 M KCl; 0.1 g/L suspension; 25°C; and Cr(VI):Ni(II):Cd(II) of 10:5:2.5).

The presence of multiple heavy metals strongly affects the zeta potential of kaolin as shown in Figs. 6–8. The presence of the other metals will increase the electrostatic interaction in the system and cause a competitive adsorption behavior of the metals to the kaolin surface, leading to a change in the zeta potential value. This change depends on the ion type as well as ionic concentrations in the suspension.

Adsorption Measurements

As shown in Fig. 9, as the soil to solution ratio of kaolin increases, the concentration of the nickel in the solution decreases, implying that the amount of the nickel adsorbed to the soil increases. Figure 9 shows that at the soil to solution ratio of 1 to 10 about 30% of nickel is adsorbed by kaolin. Therefore, the soil to solution

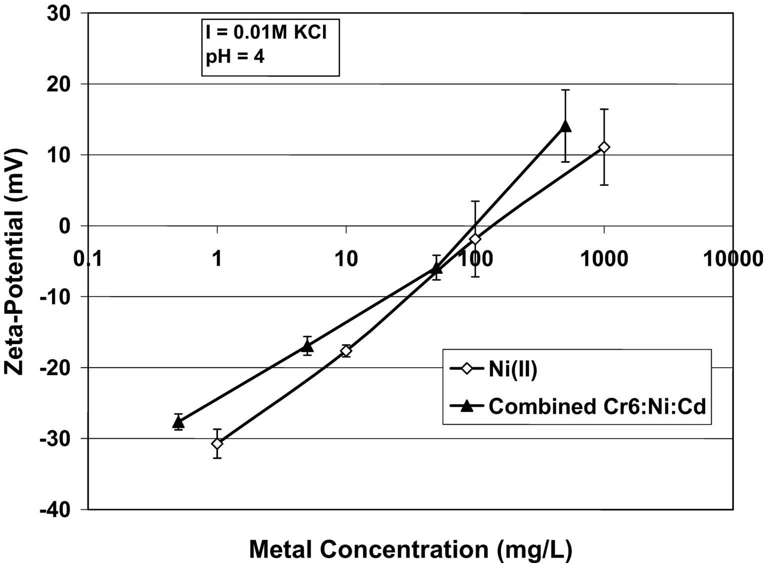

Figure 7. Effect of Ni(II) as a single or combined with other metals on zeta potential of kaolin (all samples at pH = 4.0; 0.01 M KCl; 0.1 g/L suspension; 25°C; and Cr(VI):Ni(II):Cd(II) of 10:5:2.5).

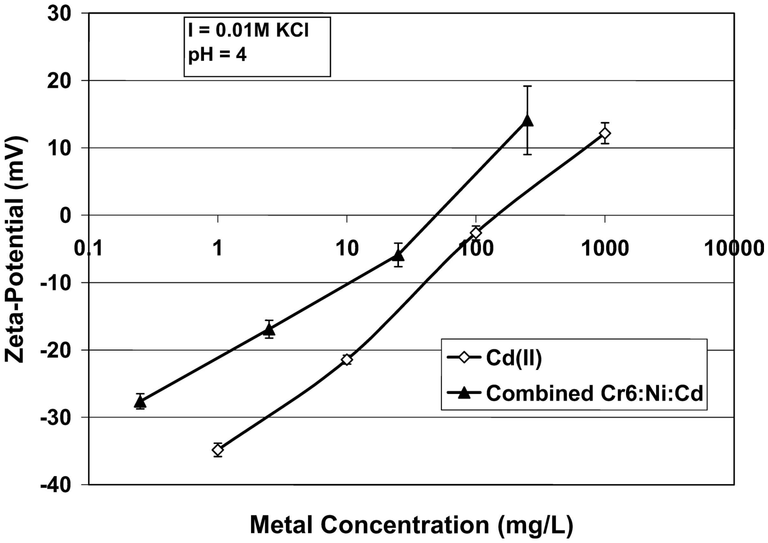

Figure 8. Effect of Cd(II) as a single or combined with other metals on zeta potential of kaolin (all samples at pH = 4.0; 0.01 M KCl; 0.1 g/L suspension; 25°C; and Cr(VI):Ni(II):Cd(II) of 10:5:2.5).

ratio used for the adsorption batch tests in this study was 1 to 10 (USEPA, 1992).

Figure 10 shows that for kaolin, as the equilibrium time increases, the concentration of the nickel in the solution decreases, implying that the amount of the nickel adsorbed to the soil increases. However, the change in the nickel concentration in the solution with time decreases as the equilibrium time increases. The minimum amount of time at which the rate of change of nickel concentration in the solution equal to or less than 5% per 24-interval was 24 h. Therefore, the selected equilibrium time for the adsorption batch tests was 24 h.

Figures 11–14 represent the adsorption isotherms of kaolin for hexavalent chromium, trivalent chromium, nickel, and cadmium, respectively. The results indicate

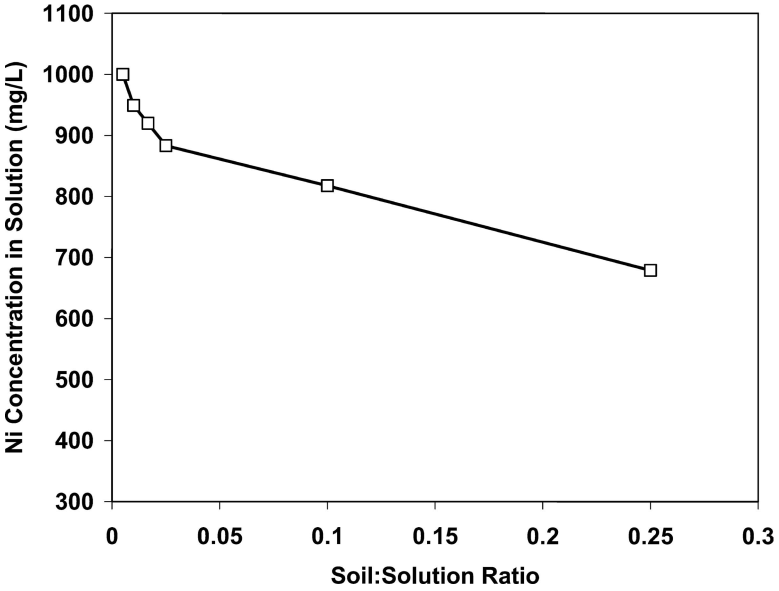

Figure 9. Distribution of nickel concentration after 24 hours of contact time with kaolin as a function of soil to solution ratio at 22°C.

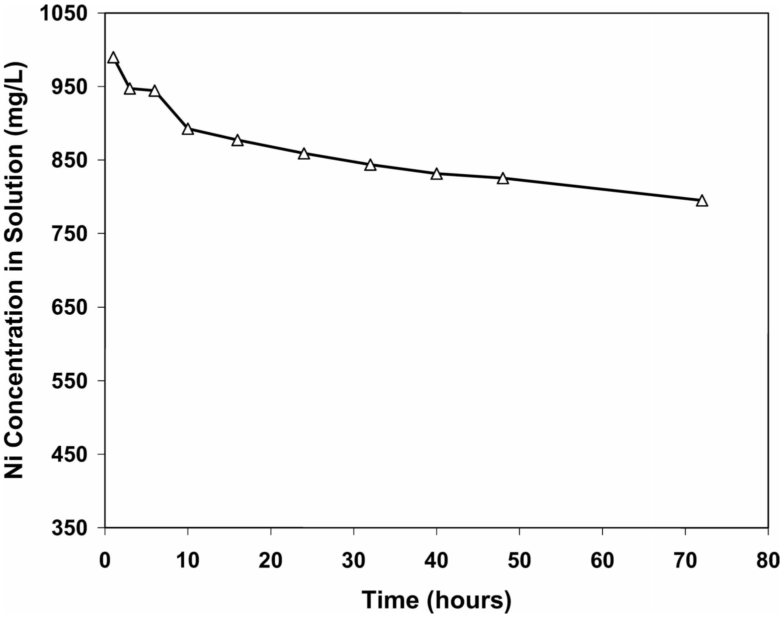

Figure 10. Distribution of nickel concentrations by kaolin as a function of contact time at 22°C and 1:10 soil to solution ratio.

that pH has a pronounced effect on the amounts of heavy metal adsorbed by the kaolin. The adsorption of trivalent chromium, nickel, and cadmium by kaolin increases as the pH increases, while adsorption of hexavalent chromium decreases as the pH increases. For each pH condition (isotherm), the percentages of metal adsorbed by kaolin (i.e., mass adsorbed of metal divided by its initial mass) was averaged. Figure 15 shows the average percentage of Cr(VI), Cr(III), Ni(II), and Cd(II) adsorbed by kaolin. These results suggest that, in an acidic environment ($3 < pH < 7$), the overall adsorption affinity by kaolin of Cr(III) > Ni(II) > Cd(II) ≫ Cr(VI).

Adsorption Modeling

The selection of adsorption model depends on the system behavior. If the system does not display a pH dependent behavior, then the adsorption model

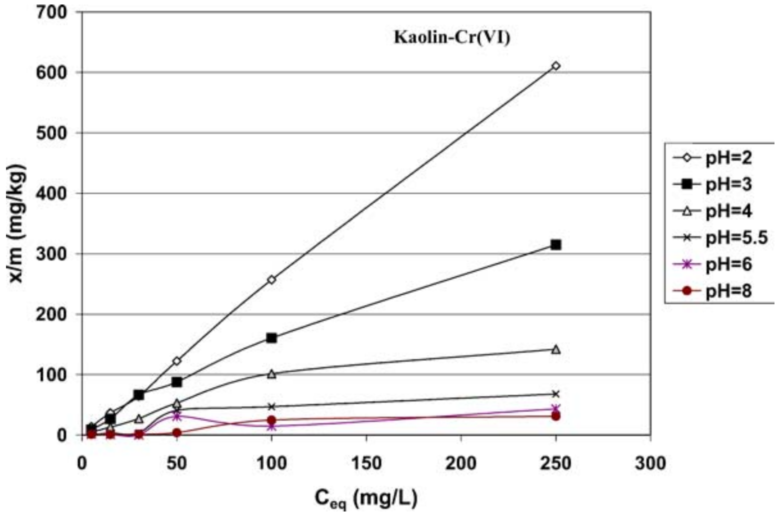

Figure 11. Adsorption of hexavalent chromium by kaolin as a function of pH at 22°C and ionic strength of 0.1 M.

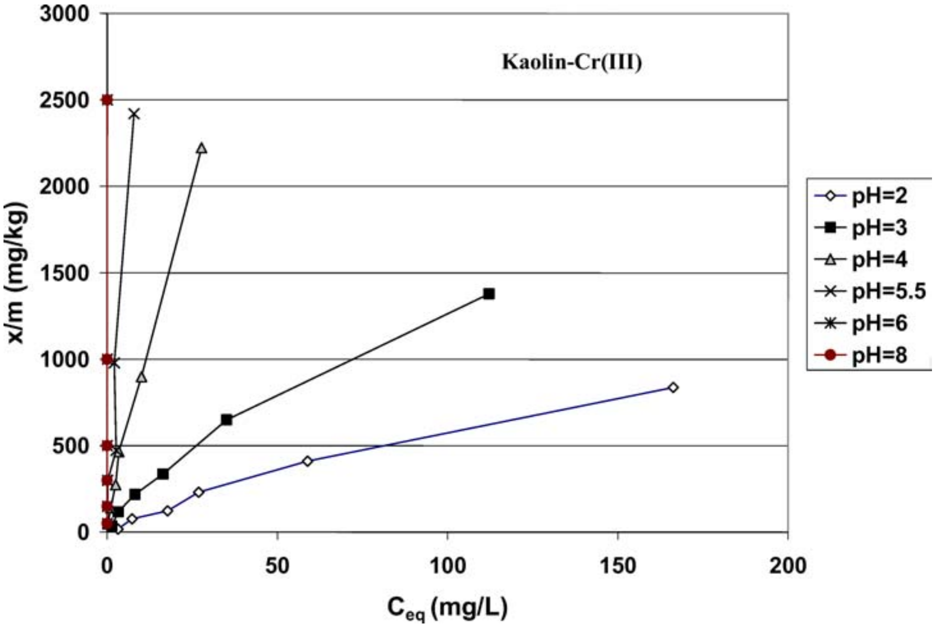

Figure 12. Adsorption of trivalent chromium by kaolin as a function of pH at 22°C and ionic strength of 0.1 M.

depends on the shape of the resulting adsorption curves. However, if the system displays pH dependent adsorption behavior, then one needs to use one of the electrostatic models (i.e., constant capacitance, diffuse layer, or triple layer). Results of this study have shown that pH significantly affects the adsorption behavior of heavy metals by kaolin. Therefore, electrostatic models, such as constant capacitance and diffuse-layer models, should be used to describe the adsorption behavior of metals in kaolin.

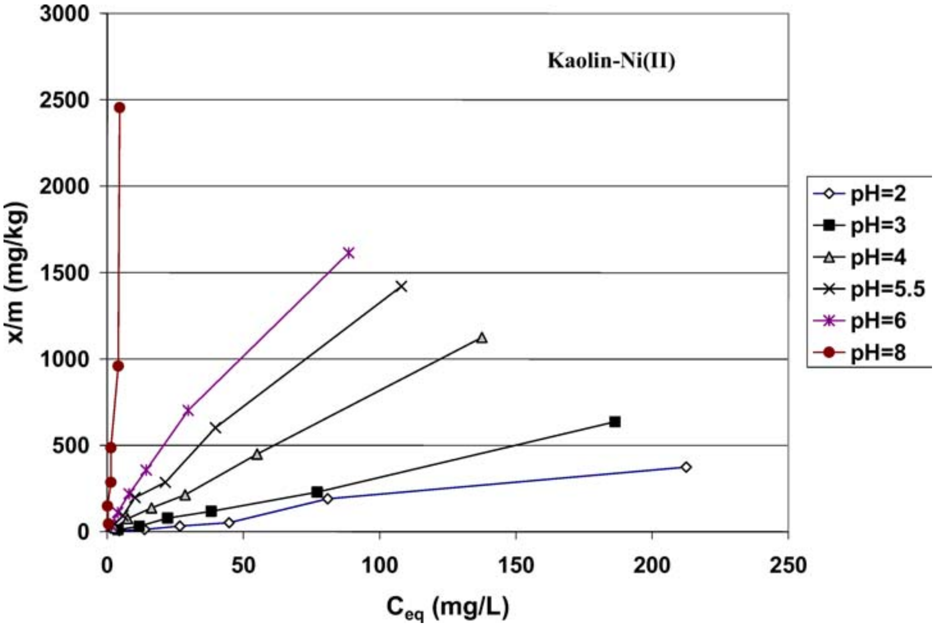

Figure 13. Adsorption of nickel by kaolin as a function of pH at 22°C and ionic strength of 0.1 M.

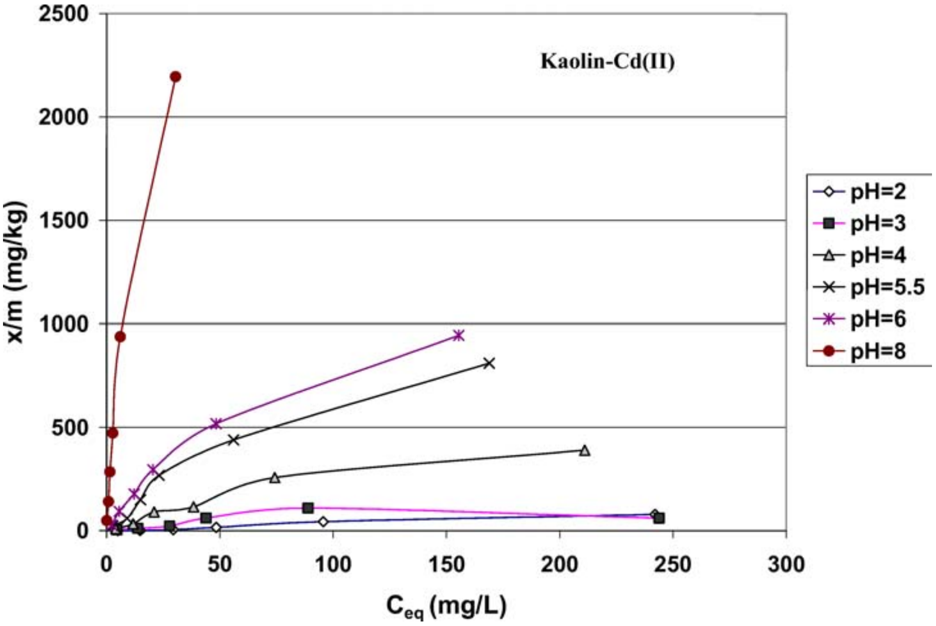

Figure 14. Adsorption of cadmium by kaolin as a function of pH at 22°C and ionic strength of 0.1 M.

A constant capacitance model which requires minimum number of model parameters was selected for this study. The model parameters include the protonation-dissociation constants, the ion surface complexation constants, and the constant capacitance term. These parameters for the studied soil and contaminant systems were estimated based on FITEQL 4.0 (a computer program for determination of chemical equilibrium constants from experimental data) developed by Herbelin and Westall (1994) as well as by

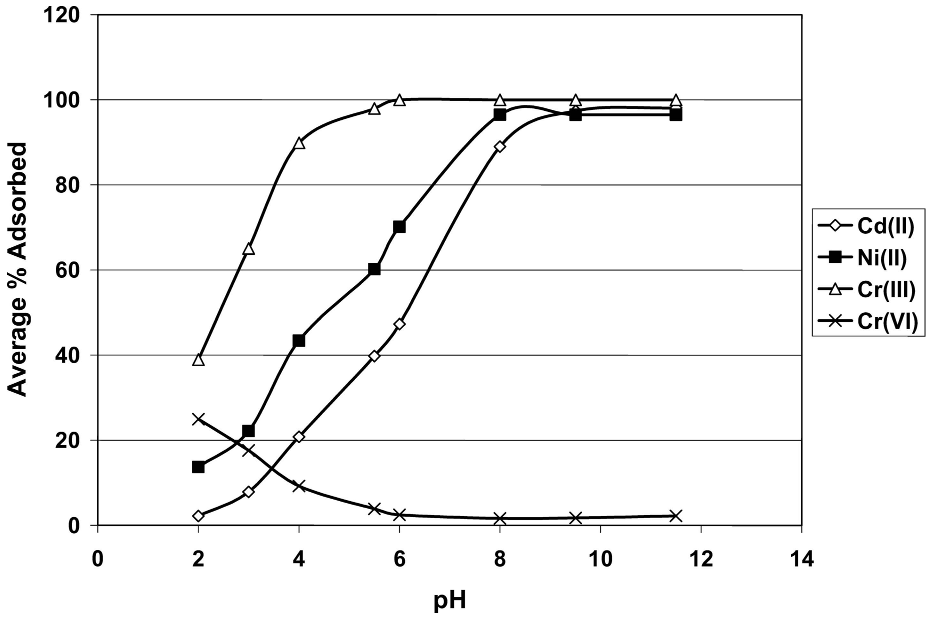

Figure 15. Average percentage of Cr(VI), Cr(III), Ni(II), and Cd(II) adsorbed by kaolin.

Table 3. Constant capacitance model parameters for kaolin.

Surface area (S_A)		$24\,m^2/g$
Surface site density (N_S)		2.35 sites/nm^2
Constant capacitance (C)		$1.0\,F/m^2$ if $I = 0.1\,M$ $0.7\,F/m^2$ if $I = 0.01\,M$ $0.5\,F/m^2$ if $I = 0.001\,M$
Intrinsic constants:		
Ion	Intrinsic Constant Expression	Log K^{int}
H^+	$SOH + H^+ \leftrightarrow SOH_2^+$	3.8 ± 0.5
	$SOH - H^+ \leftrightarrow SO^-$	-9.4 ± 0.5
Cd^{2+}	$SOH + Cd^{2+} \leftrightarrow SOCd^+ + H^+$	-3.3 ± 1.0
Ni^{2+}	$SOH + Ni^{2+} \leftrightarrow SONi^+ + H^+$	-2.6 ± 0.6
Cr^{3+}	$SOH + Cr^{3+} \leftrightarrow SOCr^{2+} + H^+$	5.0 ± 1.0
CrO_4^{2-}	$SOH + CrO_4^{2-} + 2H^+ \leftrightarrow SOH_2HCrO_4$	12.5 ± 0.5

matching the predicted results using MINEQL$^+$ (the chemical equilibrium model) developed by Schecher and McAvoy (1994) with the potentiometric titration and adsorption experimental results. Table 3 summarizes the protonation-dissociation values and the ion surface complexation constants for Cr(III), Cr(VI), Ni(II), and Cd(II). The model parameters also included the surface area (S_A) and surface site density (Ns) values and these values as reported by Davis and Kent (1990) for kaolin were adopted. The constant capacitance (C) value was found to be dependent on the ionic strength. The values of S_A, Ns and C are shown in Table 3.

A comparison of experimental adsorption results for Cr(VI), Cr(III), Cd(II), and Ni(II) by kaolin, along with the adsorption model results are shown in Fig. 16. Since at pH_{zpc} the net surface potential and net surface charge are zero and $[SOH_2^+] = [SO^-]$, then Eqs. (3a) and (b) can be combined to get that $pH_{ZPC} = 0.5(pK_+^{int} + pK_-^{int})$. Therefore, the resulting model gives a pH_{ZPC} value of 2.8 ± 0.5 for kaolin. This value is consistent with the resulting values in both the titration and electrophoresis experiments. Although the fit of the model to the data was generally good, this model has simplifications. This model is based on the assumption that ion adsorption takes place at one set of homogenous reactive surface functional groups. This is clearly a simplification since clay minerals and most soil particles are complex multisite mixtures. However, surface

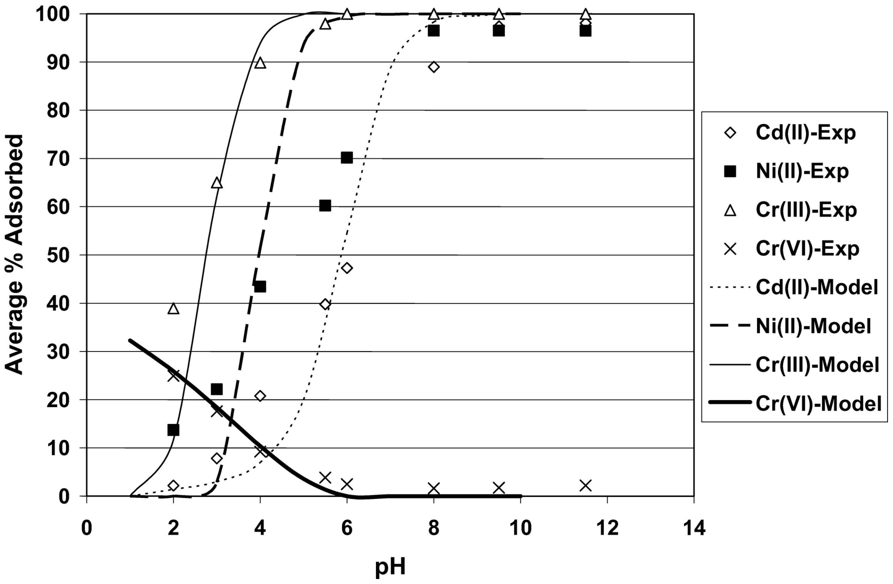

Figure 16. Electrostatic adsorption models of Cr(VI), Cr(III), Ni(II), and Cd(II) in kaolin.

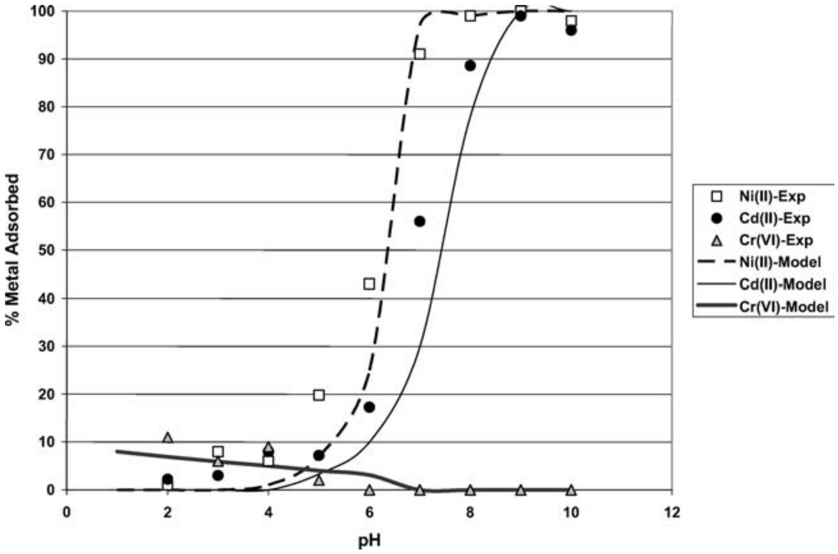

Figure 17. Experimental and model adsorption by kaolin for a combination of Cr(VI), Ni(II), and Cd(II).

complexation models are limited to one or two sets of homogenous sites so that the number of adjustable parameters is maintained at a reasonable level. Values obtained for constant capacitance model in this study are dependent on the surface site density and capacitances. In addition, constant capacitance is found to be a function of electrolyte concentration. Therefore, one must select the values of all input parameters based on the project-specific soil. Advanced models, such as diffuse-layer and triple layer models, should be considered which account for electrolyte concentration and other factors such as surface energetic heterogeneities in complex soil-contaminant conditions.

For each pH condition, the percentage amount of metal adsorbed by kaolin in the case of multiple contaminants was calculated. These results were then compared with MINEQL+ model adsorption results of multiple contaminants case and using the developed adsorption model in Table 3. Figure 17 shows that the developed adsorption model in Table 3 gives a valid adsorption results compared to the experimental results in the case of multiple metals in the system. In other words, the developed model in this study takes into consideration the synergistic effects of coexisting multiple metals on adsorption of individual metal by kaolin.

Conclusions

Based on the results of the potentiometric, electrophoresis, and adsorption batch experiments of kaolin using the following heavy metals: Cr(VI), Cr(III), Ni(II) and Cd(II), the following conclusions can be drawn:

- The aqueous properties: pH, ionic strength and the presence of the heavy metals Cr(VI), Cr(III), Ni(II), and Cd(II) single or combined in the system affect the zeta potential of a kaolin surface. The zeta potential of kaolin shifts to a more negative value if the pH increases. An increase in the ionic strength or in the metal concentration shifts the zeta potential to a more positive value.
- The amount of heavy metal adsorbed by kaolin has a pronounced sensitivity to the pH. The adsorption of trivalent chromium, nickel, and cadmium by kaolin increases as the pH increases, while adsorption of hexavalent chromium decreases as the pH increases. However, in an acidic environment (3<pH<7), the overall adsorption affinity by kaolin of Cr(III)>Ni(II)>Cd(II)>>Cr(VI).
- The constant capacitance protonation-dissociation intrinsic constants of kaolin are $pK_{+}^{int} = -3.8 \pm 0.5$ and $pK_{-}^{int} = 9.4 \pm 0.5$. The ion-kaolin surface complexation constants of Cr(VI), Cr(III), Ni(II), and Cd(II) are $pK_{Cr(VI)}^{int} = -12.5 \pm 0.5$, $pK_{Cr(III)}^{int} = -5.0 \pm 1.0$, $pK_{Ni(II)}^{int} = 2.6 \pm 0.6$, and $pK_{Cd(II)}^{int} = 3.3 \pm 1.0$, respectively. Also, the zero point of charge pH_{ZPC} of kaolin is 2.8 ± 0.5.

Overall this study showed that a complex relationship does exist between the kaolin particle zeta potential and aqueous phase properties, and adsorption behavior of heavy metals by kaolin is pH-dependent. These two aspects highlight the importance of understanding the pore fluid chemistry of kaolin during the electrokinetic remediation process because the sensitivity of kaolin particle zeta potential, and its surface charge, to the aqueous phase properties (i.e., pH, ionic strength, and metal type and concentration) translates into a sensitivity of the electroosmotic flow and the adsorption process to these properties during electrokinetic remediation. Implementing the electrostatic adsorption models in the electrokinetic remediation assessment and modeling could be a unique and innovative attempt to directly address some of the major issues related to electrokinetic soil remediation technique.

Nomenclature

η	viscosity of the solution (kg/m s)
Ψ	surface potential (V)
ζ	zeta potential of the clay surface (V)
ϕ_e	electrical potential (V)
ε	permittivity of the medium (Farad/m)
ε_o	permittivity of the vacuum (8.854×10^{-12} C/V m)
C_i	concentration of species i (mol/L)
C_o	initial metal concentration (mol/L)
F	Faraday constant (96,485 C/mol)
I	ionic strength of the suspension (mol/L)
J_w^e	electroosmotic flow rate (m/s)
K_e	electroosmotic permeability coefficient (m^2/V s)
K_+^{int}	protonation intrinsic equilibrium constant
K_-^{int}	dissociation intrinsic equilibrium constant
K_i^{int}	intrinsic equilibrium constant of component i
n	porosity of the soil (dimensionless)
N_s	surface site density of the soil (site/m^2)
R	gas constant (8.31144 J/mol°K)
S_A	surface area of the soil (m^2/g)
[SOH]	surface functional group concentration (mol/L)
T	absolute temperature (°K)
x/m	amount of metal adsorbed per unit mass of soil (mg/kg)

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