Adsorption of heavy metals in glacial till soil

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Abstract. The charged sites on soil particles are important for the retention/adsorption of metals. Metallic counterions can neutralize the intrinsic charges on the surfaces of soil particles by forming complexes. In this study, efforts have been made to determine the effect of surface potential, pH, and ionic strength on the adsorption of four metal ions, hexavalent chromium Cr(VI), trivalent chromium Cr(III), nickel Ni(II) and cadmium Cd(II), in glacial till soil. Batch tests were performed to determine the effect of pH (2–12) and ionic strength (0.001–0.1 M KCl) on zeta potential of the glacial till soil. The point of zero charge (pH_{PZC}) of glacial till was found to be 7.0 ± 2.5. Surface charge experiments revealed the high buffering capacity of the glacial till. Batch adsorption experiments were conducted at natural pH (8.2) using various concentrations of selected metals. The adsorption data was described by the Freundlich adsorption model. Overall glacial till shows lower adsorption affinity to Cr(VI) as compared to cationic metals, Cr(III), Ni(II) and Cd(II).

Key words. adsorption, clays, electrokinetics, heavy metals, remediation, soil, zeta potential.

1. Introduction

The retention of metals by soils has been a focus of much research in recent years. 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; Al-Hamdan, 2002).

The surfaces of the fine-grained soil particles are very active chemically i.e., surface sites are negatively or positively charged or they are electrically neutral. The relative proportion of metal ions attracted to these various sites depends on the degree of acidity or alkalinity of the soil, its mineralogical composition, and its content of

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organic matter. The adsorption reactions that occur between metallic ions and the charged surfaces of the soil particles may involve either the formation of relatively weak complexes through cation exchange reactions or the formation of strongly bounded complexes through ligand exchange reactions. The actual nature of the association between the charged surface and the counterions depends on the mechanism of retention of the counterion with the surface i.e., the extent of adsorption depends on either the respective charges on the adsorbing surface and the metallic cation or on the intrinsic formation constants for the complexation reactions. Various models have been developed to predict and quantify the adsorption/ retention of metals by charged soil surfaces and are discussed in Schecher and McAvoy (1994) and Al-Hamdan (2002).

Adsorption/desorption process is one of the important physico-chemical processes affecting the transport of the heavy metals during electrokinetic remediation (e.g., Reddy and Chinthamreddy, 2003; Reddy et al., 2003). 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). The lack of data for electrostatic adsorption model parameters for soil solid 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 pore liquid. The values of zeta potential (ζ) of soils reported to range from $+50$ mV to -50 mV, and the zeta potential greater than zero 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 during electrokinetics (Eykholt and Daniel, 1994; Yeung, 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 Probstein, 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 and Daniel (1994) and Eykholt (1992) applied the pH-dependent zeta potential to the modified Helmholtz–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 electro-osmotic flow for the purposes of electrokinetic modeling is not accurate for situations where the electroosmotic contribution to contaminant mass transport is significant and the aqueous and clay properties are variable.

The objective of this study is to investigate the pH changes and the solution speciation effects on the clay surface behavior. Specifically, this study evaluates the effect of pH, ionic strength, and ionic species on the zeta potential and adsorption behavior of glacial till soil surfaces for the heavy metals Cr(VI), Cr(III), Ni(II), and Cd(II). In order to accomplish the objective, the following tasks were performed: (1) characterization of the surface charge behavior of the tested soil particles by performing potentiometric titration experiments, (2) quantification of the influence of the aqueous phase properties (i.e., pH, ionic strength and metal type and concentration) on the zeta potential of the tested soil particle by performing electrophoresis experiments, and (3) determination of the adsorption affinity of tested soil surface for Cr(VI), Cr(III), Ni(II), and Cd(II) by performing adsorption batch experiments. The results of this study can be utilized to incorporate the pH changes and solution speciation effects in the assessment and modeling of remediation processes, particularly the electrokinetic remediation of metal contaminated soils.

2. Experimental methodology

2.1. MATERIALS

Glacial till was used for this study as a representative field clayey soil. The composition and properties of this soil are given 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 ($CrCl_3.6H_2O$, certified Fisher Chemical) for Cr(III), potassium dichromate (K_2CrO_4, ACS certified) for Cr(VI), nickel chloride ($NiCl_2.6H_2O$, technical Fisher Chemical) for Ni(II), and cadmium chloride ($CdCl_2.2.5H_2O$, 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.

2.2. SURFACE CHARGE EXPERIMENTS

The pH-dependent surface charge of glacial till soil was investigated through the use of potentiometric batch tests. The batch titration of the glacial till was made using 125 ml bottles containing 10 ml of soil 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 $NaNO_3$ yields I = 0.01 M in 50 ml sample). A total of 30 samples was prepared and the pH of each sample was changed by adding varying amounts of 0.1 M HNO_3 or

Table 1.   Properties of the glacial till soil used in this study

Property	Result
Mineralogy	Quartz: 31%
	Feldspar: 13%
	Carbonate: 35%
	Illite: 15%
	Chlorite: 4–6%
	Vermiculite: 0.5%
	Smectite: trace
Particle size distribution (ASTM D422)	
Gravel	0%
Sand	20%
Silt	44%
Clay	36%
Atterberg limits (ASTM D2487)	
Liquid limit	21.7%
Plastic limit	11.7%
Plasticity index	10.0%
Specific gravity (ASTM D854)	2.71
Hydraulic conductivity (ASTM D5084)	4.1×10^{-8} cm/s
Cation exchange capacity (ASTM D9081)	13—18 meq/100 g
pH (ASTM D4972)	8.2
Organic content (ASTM D2974)	2.8%
USCS classification (ASTM D2487)	CL

0.1 M NaOH solution. The first half of batch samples contained 550, 500, 450, 400, 350, 330, 315, 305, 295, 285, 220, 160, 100, 50, and 15 ml of 0.1 M HNO_3, while the other half of batch samples contained 22, 17, 12, 8, 6, 4, 3, 2.6, 2.2, 1.2, 1, 0.9, 0.8, 0.7, and 0.6 ml of 0.1 M NaOH. One control sample was prepared without adding acid or base. The volume of acid or base added was 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, 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. Samples were tested in duplicates to ensure reproducibility.

   Glacial till showed a significant resistance to pH changes in the suspension (Figure 1). Therefore, glacial till was characterized through determination of its buffering capacity. The presence of calcium carbonate or other compounds such as magnesium carbonate contribute carbonate ions to the buffering system. The presence of free carbonates in the soil is a major reason for its buffering capacity. Quantitatively, the buffering capacity of a soil is the amount of acid, expressed in millimeters, required or added to reach a pH of 4.5. Therefore, a set of titration experiments were conducted to determine the glacial till buffering capacity using a glacial till suspension of 100 g/l and 0.1 M nitric acid as a titrant. The carbonate ions neutralize the acid in
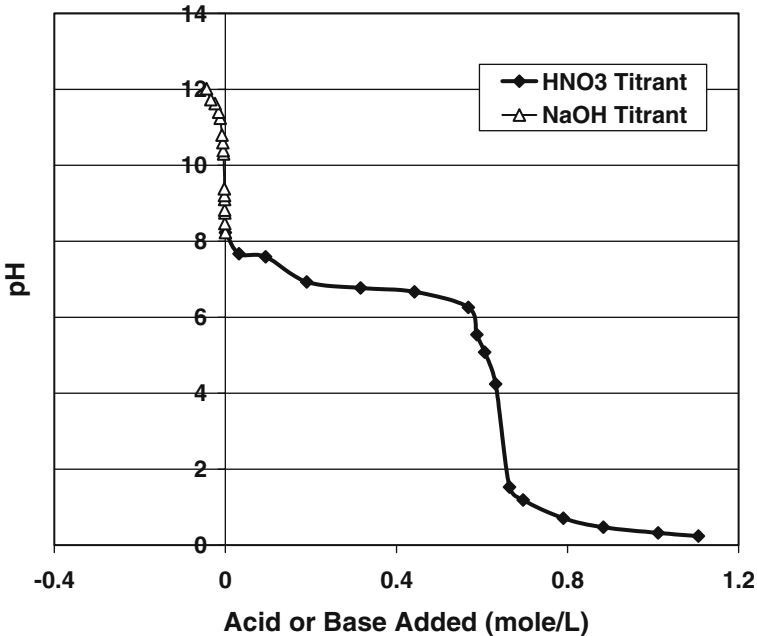
Figure 1.   Acid–base titration curve of glacial till after 24 h contact time (suspension of 0.1 g/ml).

this reaction and show the buffering capacity of the sample. From the amount of acid added to the suspension, carbonate amount was calculated. This is then expressed as mg of $CaCO_3$/l even though actually $MgCO_3$, Na_2CO_3 or K_2CO_3 may contribute to of the alkalinity.

2.3. ELECTROPHORESIS EXPERIMENTS

Electrophoresis experiments were conducted to determine zeta potential of glacial till. A total of three series of experiments was conducted on glacial till. 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 ($I_1 = 0.001$ M, $I_2 = 0.01$ M and $I_3 = 0.1$ 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 at 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 these 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

Table 2. Electrophoresis experimental program

Test series	Soil type	pH	Ionic strength	Metal concentration	Objective
I	Glacial till	(2–12)	0.001 M KCl	None	To study the effect of pH on zetal potential under different ionic strengths
	Glacial till	(2–12)	0.01 M KCl	None	
	Glacial till	(2–12)	0.1 M KCl	None	
II	Glacial till	4	0.01 M KCl	$Cr(VI) = 1, 10, 100,$ and 1000 mg/l	To study the effect of metal concentration on zeta potential
	Glacial till	4	0.01 M KCl	$Cr(III) = 1, 10, 100,$ and 1000 mg/l	
	Glacial till	4	0.01 M KCl	$Ni(II) = 1, 10, 100,$ and 1000 mg/l	
	Glacial till	4	0.01 M KCl	$Cd(II) = 1, 10, 100,$ and 1000 mg/l	
III	Glacial till	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 co-existing metals on zeta potential

measured using zeta meter, LAZER ZEE[tm] Model 500. For each test series, dupli-
cate suspensions were prepared to determine precision and repeatability of test
results.

2.4. ADSORPTION EXPERIMENTS

The EPA batch-type test procedure was followed to determine the adsorption of
heavy metals on soils (USEPA, 1992). Batch adsorption tests for glacial till 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 concen-
tration of solute (10^3 mg/l). Nickel was used as a representative solute for finding the
soil to solution ratio and the adsorption equilibrium time. The soil to solution ratio,
indicating between 10% and 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.

   With the constant soil to solution ratio of 1:10 and known equilibrium time of
24 h, batch adsorption tests were conducted with six 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)). 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
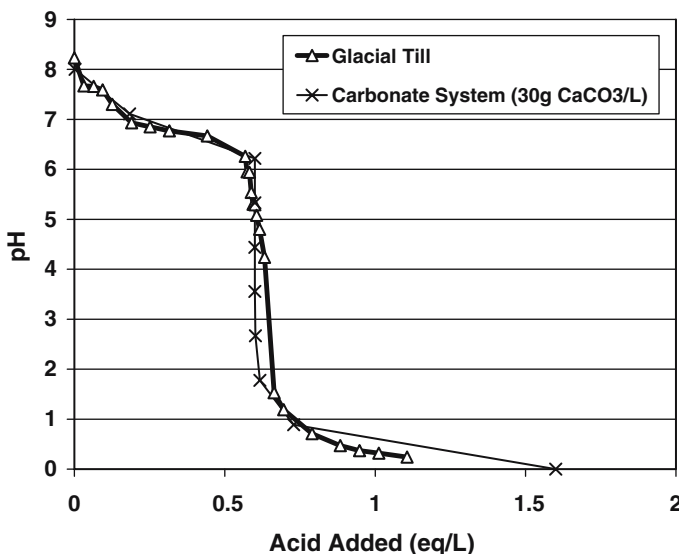using Wattman filter paper. The metal ion concentration in the supernatant was

Figure 2.   pH-acid titration curves of glacial till with suspension of 0.1 g/ml and carbonate system (30 g
CaCO$_3$/l).

determined using an Atomic Absorption Spectrophotometer (AAS). The amount of metal adsorbed per unit mass of dry soil was determined by:

$$\frac{x}{m} = \frac{C_o - C}{m} V \tag{1}$$

where: x/m = Amount of metal adsorbed per unit mass of soil, C_o = Initial metal concentration before exposure to soil, C = Metal concentration after exposure to soil at equilibrium, and V = Volume of metal solution added to the reaction container.

3. Results and Discussion

3.1. BUFFERING CAPACITY MEASUREMENTS

Figure 2 shows the pH of the glacial till suspension versus the amount of acid added to the colloid. The titration data shows that glacial till has a high resistance to pH changes. Since zero volume of titrant needed to lower the pH of the glacial till suspension to 8.3, then the predominant form of alkalinity is HCO_3^- (Snoeyink and Jenkins, 1980). The buffering capacity of glacial till was determined about 0.6 eq/l as HCO_3 or about 30 g as $CaCO_3$ per liter of suspension (i.e., 100 g of soil). In other words, about 30% of the glacial till is carbonate. For comparison purpose, the chemical equilibrium model MINEQL$^+$ (Schecher and McAvoy, 1994) was used to calculate the pH-acid titration curve of a carbonate system of 30 g $CaCO_3$/l. Figure 2 shows that glacial till suspension of 100 g/l is equivalent to a solution of 30 g $CaCO_3$/l.
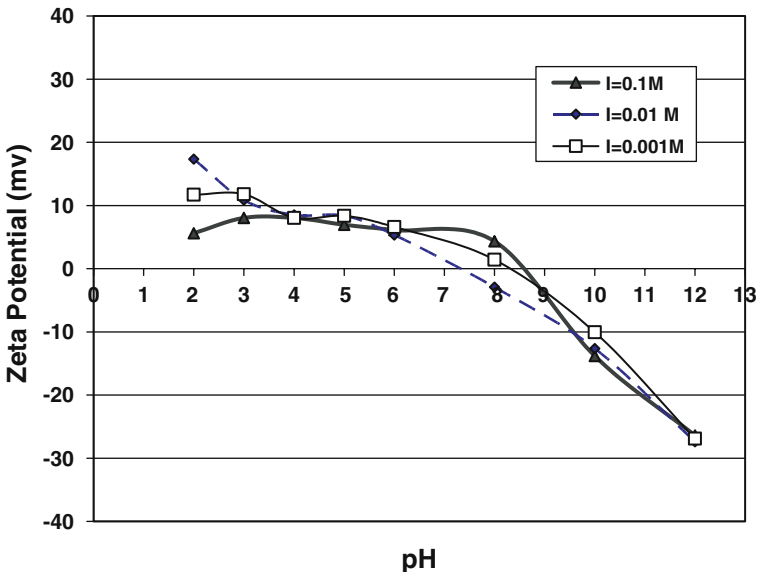

Figure 3. Effect of pH and electrolyte concentration on glacial till zeta potential at 0.1 g/l suspension and 25 °C.

3.2. ZETA POTENTIAL MEASUREMENTS

The effect of pH on zeta potential of glacial till is shown in Figure 3. The zeta potential of glacial till was found to be a function of pH, ranging at background electrolyte of 0.001 M from an average value of 11.5 mV to −26.8 mV at pH of 2 and 12, respectively. However, the effect of pH on the zeta potential of glacial till surface could be negligible since the glacial till has a very high buffering capacity. The point of zero charge (pH_{PZC}) of glacial till is found to be about 7.0 ± 2.5. The variations of glacial till pH_{PZC} could be attributed to the fact that glacial till contains many minerals such as quartz, feldspar, calcite, and illite (see Table 1), hence, glacial till was more difficult to deal with during electrophoresis experiments and in that it sometimes showed a discrepancy in the direction of particle movement toward the electrodes (i.e., at the same pH or ionic strength conditions, some particles had positive zeta potential values and others had negative values). However, Figure 3 also shows that glacial till zeta-potential is less sensitive to the background electrolyte concentration.

As seen in Figure 4, the zeta potential of glacial till is less sensitive to the presence of cationic heavy metals (Cr(III), Ni(II) or Cd(II)) at pH = 4.0. However, the zeta potential of glacial till shifts towards more negative as the concentration of Cr(VI) increases. This may be attributed to the fact that the average zero point of charge of glacial till is higher than the pH at which experiments were performed (i.e., pH = 4), leading to more sensitivity of glacial till to the negatively charged ions (CrO_4^{2-}) than to the positive ions (Ni^{2+}, Cd^{2+}, Cr^{3+}).
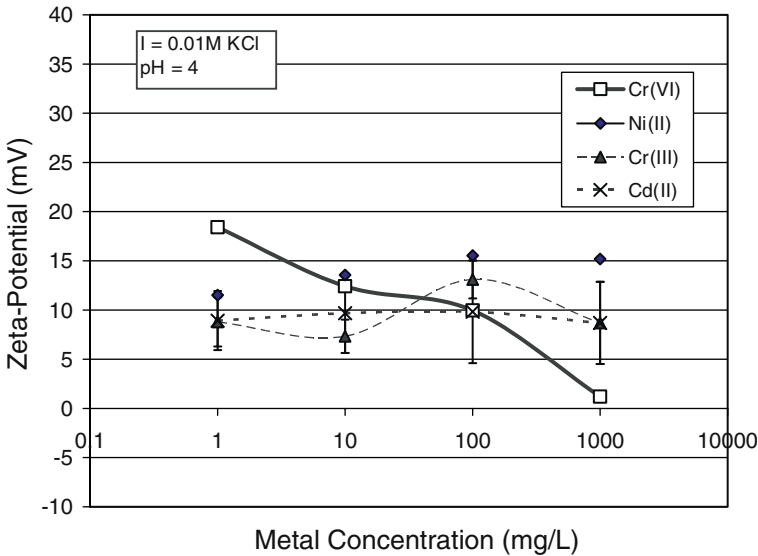

Figure 4.   Effect of metal concentration on glacial till zeta potential: all samples at pH = 4.0, 0.01 M KCl, 0.1 g/l suspension, and 22 °C.
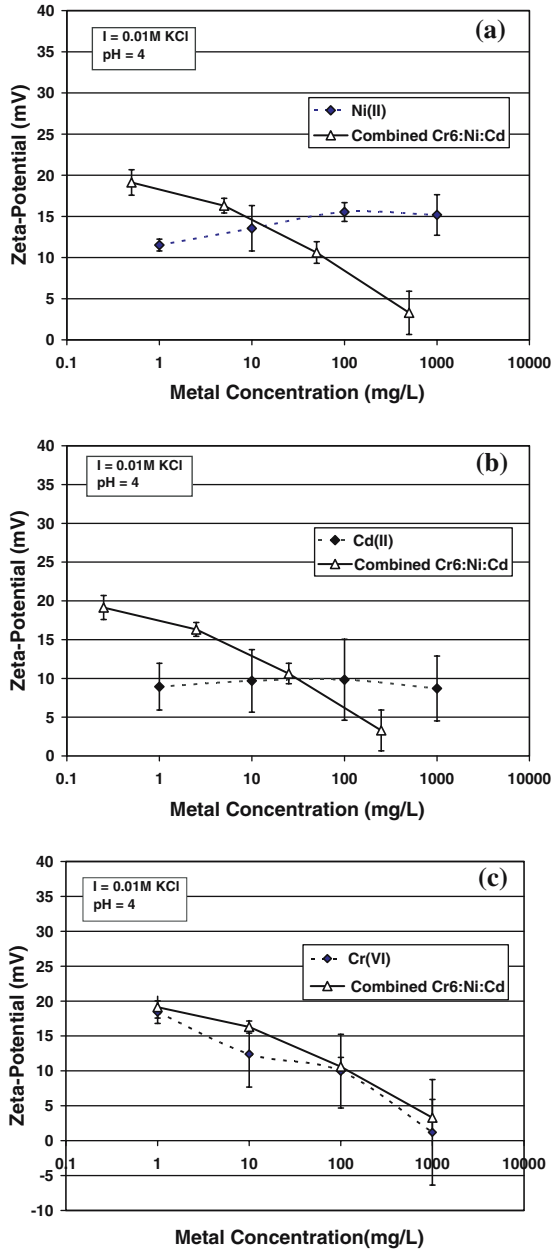
Figure 5. Effect of the presence of Ni(II), Cd(II), and Cr(VI) as a single or combined with other metals on glacial till zeta potential: all samples at pH = 4.0, 0.01 M KCl, 0.1 g/l suspension, and 25 °C, and Cr(VI):Ni(II):Cd(II) ratio of 10:5:2.5.

Figure 5 shows the effects of coexisting of Cr(VI), Ni(II) and Cd(II) on the zeta potential of glacial till as compared to the situations where individual metal (Cr(VI), Ni(II) and Cd(II)) present alone. The zeta potential of combined metal system is
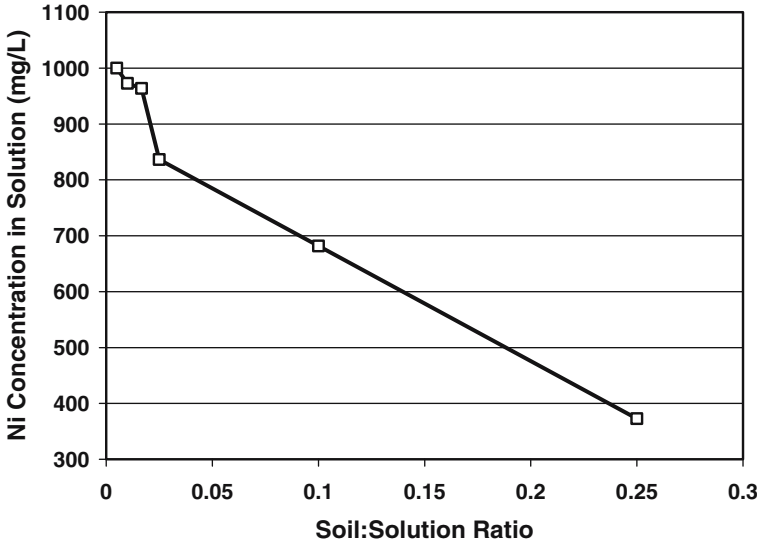
Figure 6.   Distribution of nickel concentration after 24 h of contact time with glacial till as a function of soil to solution ratio at 22 °C.

approximately the same as the zeta potential of Cr(VI) alone system, indicating that the zeta potential was not affected by the presence of Ni(II) and Cd(II). The point of zero charge of the glacial is higher than the pH = 4 of the tested systems, implying that the glacial till surfaces are positively charged and are impacted by the presence of negatively charged Cr(VI) species such as CrO_4^{2-}.
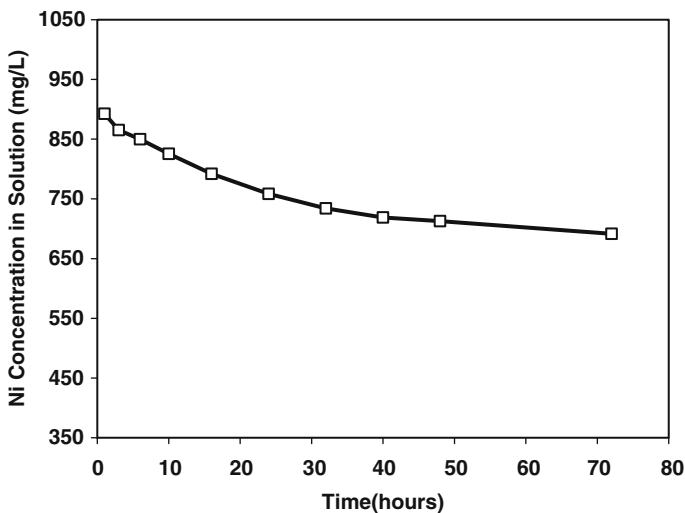

Figure 7.   Distribution of nickel concentrations in glacial till as a function of contact time at 22 °C and 1:10 soil to solution ratio.
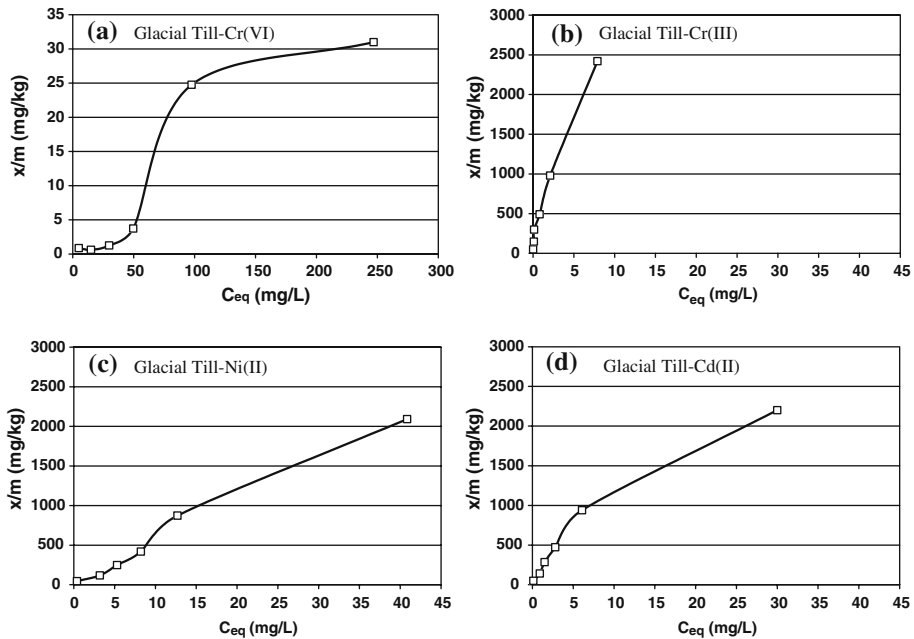
Figure 8. Adsorption isotherms of hexavalent chromium, trivalent chromium, nickel, and cadmium by glacial till at natural pH condition (pH = 8.2), 22 °C, and ionic strength of 0.1 M.

3.3. ADSORPTION MEASUREMENTS

As shown in Figure 6, as the soil to solution ratio of glacial till soil increases, the concentration of the nickel in the solution decreases, indicating that the amount of the nickel adsorbed to the soil increases. Figure 6 shows that at the soil to solution ratio of 1:10, about 16% of nickel is adsorbed by glacial till. Therefore, the soil to solution ratio used for the adsorption batch tests in this study was 1:10 (USEPA, 1992).

Figure 7 shows that as the equilibrium time increases, the concentration of the nickel in the solution decreases, indicating 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 for glacial till. Therefore, the selected equilibrium time for the adsorption batch tests for glacial till was 24 h.

Figure 8 shows the adsorption isotherms of the Cr(VI), Cr(III), Ni(II), and Cd(II) by glacial till at natural pH conditions (i.e., pH = 8.2). In general, the adsorption of cationic Cr(III), Ni(II) and Cd(II) increases with the increase in their concentration in solution. This adsorption behavior is attributed to precipitation of these heavy metals due to high pH and high acid buffering capacity of

glacial till. The adsorption behavior of Cr(VI) is significantly different than that of cationic heavy metals (Cr(III), Ni(II) and Cd(II)). Adsorption of Cr(VI) increases with the increase in Cr(VI) concentration in solution, but after reaching its adsorption capacity, most of the Cr(VI) exists in solution. Cr(VI) exists as anionic complexes such as CrO_4^{2-} and adsorbs to the positively charged surfaces of glacial till. Once, these positively charged sites are exhausted, the adsorption of Cr(VI) ceases, leading to increases in solution concentrations. The measured Cr(VI) adsorption is consistent with the measured lower surface charge of glacial till (zeta potential).

3.4. 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 depends on the shape of the resulting adsorption curves. Because of the glacial till's high buffering capacity, adsorption in glacial till was assumed to be a pH-independent process, and a regression analysis was performed to evaluate the appropriate adsorption model (Al-Hamdan, 2002). Based on this evaluation, the Freundlich model was found to best represent the adsorption isotherms for all tested metals. The mass action equation representing the Freundlich model is written as:

$$SOH + (1/n)M \leftrightarrow SOH \bullet M \tag{2}$$
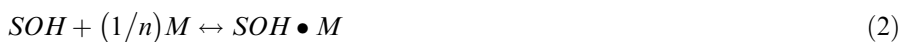
$$K_F = \frac{[SOH \bullet M]}{[M]^{1/n}[SOH]} \tag{3}$$

The adsorption model parameters n and K_F of glacial till for Cr(VI), Cr(III), Ni(II), and Cd(II) are calculated and are summarized in Table 3.

4. Conclusions

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

Table 3. Freundlich adsorption model parameters

Metal	n	$\log K_F$
Cadmium, Cd(II)	0.68 ± 0.1	-0.14 ± 0.1
Nickel, Ni(II)	0.89 ± 0.1	0.36 ± 0.2
Trivalent Chromium, Cr(III)	0.72 ± 0.2	0.69 ± 0.1
Hexavalent Chromium, Cr(VI)	1.27 ± 0.1	-1.15 ± 0.05

1. The aqueous properties, specifically pH, ionic strength and the presence of the heavy metals Cr(III), Ni(II), and Cd(II) single or combined in the system, do not significantly affect the zeta potential of a glacial till surface. However, Cr(VI) slightly affected the surface potential of glacial till. The zeta potential value for glacial till shifts to a more negative value if pH increases, however, the pH_{PZC} of glacial till is high (i.e., about 7.0 ± 2.5).
2. The glacial till possesses a very high buffering capacity (i.e., 30% as $CaCO_3$), and its pH is hardly changed by adding acid to it; hence the adsorption behavior could be assumed to be pH-independent. However, at $pH = 8.2$, glacial till possesses a lower adsorption affinity to Cr(VI) as compared to cationic metals, Cr(III), Ni(II) and Cd(II).
3. The ion-surface complexation isotherm is represented by the Freundlich model. The models parameters of Ni(II), Cd(II), Cr(III), and Cr(VI) are: $pK_{Ni(II)} = -0.36 \pm 0.2$, $n_{Ni(II)} = 0.89 \pm 0.1$, $pK_{Cd(II)} = 0.14 \pm 0.1$, $n_{Cd(II)} = 0.68 \pm 0.1$, $pK_{Cr(III)} = -0.69 \pm 0.1$, $n_{Cr(III)} = 0.72 \pm 0.2$, $pK_{Cr(VI)} = 1.15 \pm 0.05$, and $n_{Cr(VI)} = 1.27 \pm 0.1$.

Overall this study showed that glacial till possesses a high acid buffering capacity and shows lower adsorption affinity to Cr(VI) as compared to cationic metals, Cr(III), Ni(II) and Cd(II).

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