

An Adsorption Model for Nickel in Smelter Impacted Soils

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Abstract

To be able to predict the behaviour of metals in contaminated soils, it is necessary to understand both the soluble forms of the metals in solution and the solid phases with which the metal is associated. This information will aid in predicting the bio-availability of the metal and also its fate in terrestrial and aquatic ecosystems.

Over the past number of years, surface complexation modeling has become an important tool in understanding how metals react with various soils and sediments. A number of these models are commonly used in environmental studies. These include MINEQL+, MINTEQA2, PHREEQ and HYDRAQL. Most of these models have developed from and use the algorithms found in MICROQL. These models differ in the level of sophistication in how they handle adsorption of metals to mineral and humic surfaces. Because of the limitations of many of the commercially available models, it was decided to write a model which utilized the structure and sub routines given in the computer program MICROQL (Westall, 1986). The original version of MICROQL was written in Basic but has been rewritten into Microsoft Visual Basic for the model presented here.

Four types of soils common to the Port Colborne area were used in the study. These are two kinds of Clay soils, an Organic soil (Quarry muck soil) and a Sand soil (sandy loam). Soil evaluations indicated that most Clay soils in the Port Colborne area could be grouped into two main categories: Welland Clay soils (Lacustrine soils with > 40% clay contents) and Clay Till soils (30 – 40% clay content). Clay soils indicative of these two soil groupings were used.

Determining Input Parameters

Aqueous Speciation

The formation constants for $\text{Ni}(\text{OH})^+$, $\text{Ni}(\text{OH})_2^0$, NiCO_3^0 , NiCl^+ and NiSO_4^0 were taken from Turner et al. (1981). The formation constant for nickel with dissolved organic carbon, NiL^0 , was estimated using the procedure of Gunneriusson and Sjöberg (1999). The complexation constant was calculated using the data compiled for Cd

and the assumption made that the formation constant of other metals differ from their complexation constants with oxalic acid by a constant value ($\log K_{\text{CdL}} - \log K_{\text{MeOx}}$).

Iron and Manganese Oxide Surfaces

The intrinsic acidity constants, the complexation constant for nickel, the number of sites and the specific surface for adsorption to hydrous ferric oxide were taken from Dzombak and Morel (1990).

Clay Surfaces

A clay fraction was separated from the surface horizon of a Clay Till Soil (the Jeddo Series) from the Port Colborne area. The nickel complexation constant for the Jeddo clay was determined through batch adsorption experiments. A montmorillonite clay was used as a reference. Free nickel in solution was analysed by Flame Atomic Adsorption Spectrometry (Varian SpectrAA 220) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS). The adsorbed nickel was calculated by subtracting the free nickel measured in solution from the total nickel originally added. The results of the batch adsorption experiments are shown in Figure 1. The adsorption pattern for the montmorillonite clay was very similar to that reported by Kraepiel et al. (1999).

Complexation constants were determined through the use of the least squares fitting program FITEQL (Herbelin and Westall, 1994), where estimates for the concentration of sites and the surface complexes were taken from Kraepiel et al., (1999). The nickel-clay complexation constant along with the intrinsic acidity constants were determined through the optimization procedure in FITEQL.

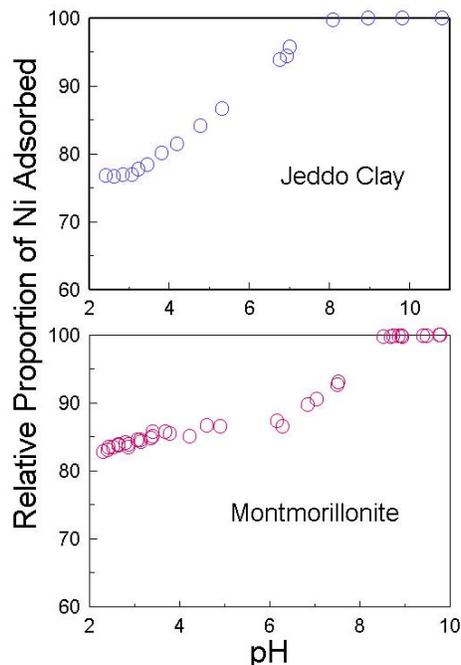


Figure 1. Nickel adsorption onto a Jeddo and a Montmorillonite clay.

The log K value for the binding of nickel to the edges of the Jeddo clay was determined to be -0.841 and the two intrinsic acidity constants were found to be 5.6 and -8.10.

Humic Surfaces

To determine the nickel complexation constants with the organic ligands present in the organic soil, the least squares fitting program, FITEQL was again employed. The data used in this process were taken from the batch adsorption experiments that were conducted on the Organic soil. The results from the batch Ni adsorption data (Figure 2) were used to find the “best fitting” complexation constants.

The dissociation constants for the humic acid were ascertained through the process of splitting the data at a pH of 6.5 and fitting each side with a monodentate complex from the diprotic acids, H_2A and H_2B respectively. It was through this process of modeling each half of the data, and then combining the two, that the dissociation complexes for HA^- , A^{2-} , HB^- and B^{2-} were found. Once these values were known, the data was modeled against six cases (Table 1), where it was discovered that Case 1, the formation of two monodentate complexes from two diprotic acids had the best fit. The log K values for the nickel humic acid complexes were -1.23 and -2.53 (Table 2), while the dissociation constants for the two diprotic acids were found to be -4.136 and -9.447 for H_2A and -6.706 and -13.238 for H_2B .

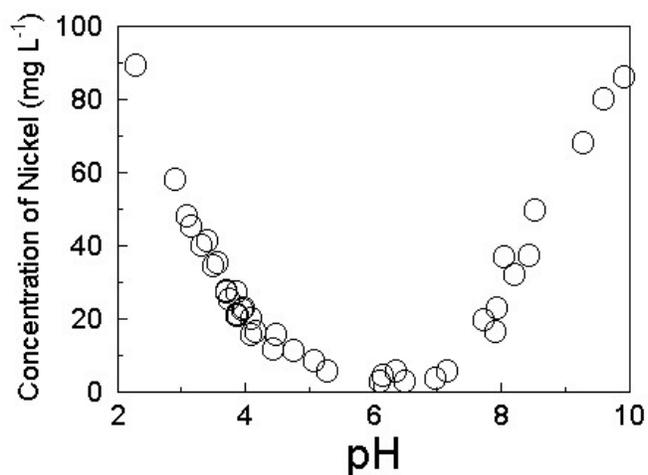


Figure 2. Batch adsorption data for the Organic soil.

Table 1. Metal-humic complexation cases investigated	
Case 1:	$\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeHA}^+ + \text{H}^+$ $\text{H}_2\text{B} + \text{Me}^{2+} \rightleftharpoons \text{MeHB}^+ + \text{H}^+$
Case 2:	$\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeHA}^+ + \text{H}^+$ $\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeA}^0 + 2\text{H}^+$ $\text{H}_2\text{B} + \text{Me}^{2+} \rightleftharpoons \text{MeHB}^+ + \text{H}^+$
Case 3:	$\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeHA}^+ + \text{H}^+$ $\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeA}^0 + 2\text{H}^+$ $\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeH}_{-1}\text{A}^- + 3\text{H}^+$ $\text{H}_2\text{B} + \text{Me}^{2+} \rightleftharpoons \text{MeHB}^+ + \text{H}^+$
Case 4:	$\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeHA}^+ + \text{H}^+$ $\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeA}^0 + 2\text{H}^+$ $\text{H}_2\text{B} + \text{Me}^{2+} \rightleftharpoons \text{MeHB}^+ + \text{H}^+$ $\text{H}_2\text{B} + \text{Me}^{2+} \rightleftharpoons \text{MeB}^0 + 2\text{H}^+$
Case 5:	$\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeHA}^+ + \text{H}^+$ $\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeA}^0 + 2\text{H}^+$ $\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeH}_{-1}\text{A}^- + 3\text{H}^+$ $\text{H}_2\text{B} + \text{Me}^{2+} \rightleftharpoons \text{MeHB}^+ + \text{H}^+$ $\text{H}_2\text{B} + \text{Me}^{2+} \rightleftharpoons \text{MeB}^0 + 2\text{H}^+$
Case 6:	$\text{H}_2\text{A} + \text{Me}^{2+} \rightleftharpoons \text{MeHA}^+ + \text{H}^+$ $\text{H}_2\text{B} + \text{Me}^{2+} \rightleftharpoons \text{MeHB}^+ + \text{H}^+$ $\text{H}_2\text{B} + \text{Me}^{2+} \rightleftharpoons \text{MeB}^0 + 2\text{H}^+$

Table 2. Results from FITEQL for the Organic Soil			
		logK	V _v
Case 1	$H_2A + Ni^{2+} \rightleftharpoons NiHA^+ + H^+$	-1.23	78.78
	$H_2B + Ni^{2+} \rightleftharpoons NiHB^+ + H^+$	-2.53	
Case 2	$H_2A + Ni^{2+} \rightleftharpoons NiHA^+ + H^+$	-1.10	858
	$H_2A + Ni^{2+} \rightleftharpoons NiA^0 + 2H^+$	-5.37	
	$H_2B + Ni^{2+} \rightleftharpoons NiHB^+ + H^+$	-8.76	
Case 3	$H_2A + Ni^{2+} \rightleftharpoons NiHA^+ + H^+$	-0.76	526
	$H_2B + Ni^{2+} \rightleftharpoons NiHB^+ + H^+$	-6.78	
	$H_2B + Ni^{2+} \rightleftharpoons NiB^0 + 2H^+$	-10.63	

Validation of the model

Batch Adsorption Experiments

The model results for the batch adsorption experiments for the Welland Clay, Till Clay and Organic Soil are shown in Figure 3. The sand

data were not modeled due to their high calcium carbonate content. From the results shown in Figure 3, it can be seen that there was a reasonably good modeled fit to the experimental data.

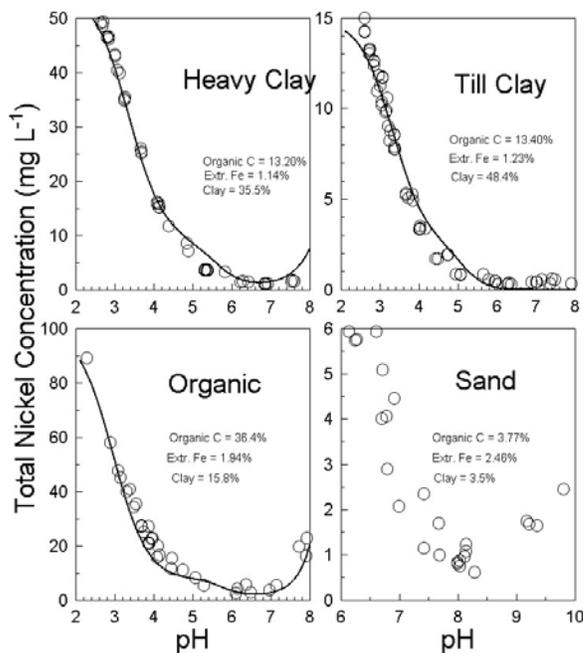


Figure 3. Modeled batch adsorption data for the Welland Clay, Till Clay and Organic soil.

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