Effect of Ionic Strength on Mercury Adsorption on Contaminated Soil

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Abstract—Mercury adsorption on soil was investigated at different ionic strengths using $Ca(NO_3)_2$ as a background electrolyte. Results fitted the Langmuir equation and the adsorption isotherms reached a plateau at higher equilibrium concentrations. Increasing ionic strength decreased the sorption of mercury, due to the competition of Ca ions for the sorption sites in the soils. The influence of ionic strength was related to the mechanisms of heavy metal sorption by the soil. These results can be of practical importance both in the agriculture and contaminated soils since the solubility of mercury in soils are strictly dependent on the adsorption and release process.

Keywords—Heavy metals, bioavailability, remediation, competitive sorption.

I. INTRODUCTION

HEAVY metal pollution has become a global problem in all industrialized countries. From the industrial revolution, a continuous release of heavy metals has lead to a severe contamination of soil. All metals are naturally present in soil, many are essential for living organisms (e.g, Zn, Cu), at low concentrations, but may become toxic at high concentrations with potential negative effects on human health. Mercury is a special highly toxic non-essential element and is considered a global environmental pollutant due to its ability to undergo long distance transportation in the atmosphere [1], [2]. The chemistry of mercury in soil is characterized by various reactions that involve adsorption and release from solid phases [3]. Adsorption processes which greatly influence the metal mobility and bioavailability are of paramount importance in soil since they regulate the metal transfer to the food chain and their leaching to surface and deep waters [4]-[6]

Information on the mercury adsorption process in contaminated soil especially in the presence of competing cations which may change the ionic strength condition is scarce. The ionic strength conditions can greatly influence the clean-up technology efficiency if "in situ" procedure (electrokinetic remediation or phytoremediation) is used. The purpose of this study was to investigate the adsorption of Hg on soil at various ionic strength using $Ca(NO_3)_2$ as a background electrolyte.

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II. MATERIALS AND METHODS

A. Soil

The soil used in this study was located in site contaminated with mercury derived from different industrial activities, such as the chlor-alkali and metallurgic industries. Soil samples were air dried and ground to pass through a 2 mm sieve before laboratory analysis. Soil pH was determined using a glass electrode at a soil/water ratio of 1:2.5 [7], cation exchange capacity (CEC) was determined using barium chloride (pH = 8.1) [8], texture (sand silt and clay) by the pipette method [9] and organic matter by wet combustion [10].

The main characteristics of the soils used in this study are reported in Table I.

TABLE I
MAIN SOIL CHARACTERISTICS

pH (H_2O)	7.1
sand (%)	58.4
Silt (%)	19.1
Clay (%)	22.5
Organic matter (%)	1.1
CEC (*cmol*(+) kg^{-1})	17.3
Hg (mg kg^{-1})	25.6

B. Adsorption Experiments

Sorption experiments were carried out by adding 10 mL of heavy metal solution from 0.1 to 1.5 μmol/mL to 2 g of soil at concentrations of $Ca(NO_3)_2$ ranging from 0.005 to 0.05 M. Suspensions were shaken for 24 h at 20±0.5 °C. Preliminary experiments of sorption, showed no significant variation in Hg concentration for periods longer than 24h. This time was considered adequate to obtain a metal distribution near the equilibrium.

After equilibration, the suspensions were centrifuged at 7000xg to separate the solution phase from the suspensions, and Hg concentration in the supernatants were determined. The amount of mercury adsorbed per mass of dry soil was calculated by the difference between the quantity added and that recovered in the equilibrium solution, according to the equation:

$$\frac{x}{m} = \frac{V\,(C_i - C_e)}{m}$$

where x/m is the amount of metal adsorbed per unit mass of soil, Ci is the initial metal concentration, Ce is the metal concentration at equilibrium, and V is the volume of the metal solution added. The effect of ionic strength on mercury adsorption was studied at the pH of the soil, and no modification of this parameter was necessary.

C .Mercury Analysis

Hg concentration was determined by atomic absorption spectrophotometry with an Automatic Mercury Analyzer (AMA 254, FKV, Bergamo). The analysis was performed without any further sample preparation, placing a known amount of sample into a nickel boat that was automatically introduced into the instrument. The analysis is based on mercury vapor produced during combustion and decomposition phases. All processes (thermal decomposition, amalgamation, and atomic absorption spectrophotometry) were performed under oxygen flux, using the official method SW-846 Method 7473 [11].

Quality assurance and quality control were performed by testing a standard solution every 10 samples. Certified reference material (CRM 024 – 050) was used to control the quality of the analytical system. The detection limit for Hg was 2 μg L^{-1}. The recovery of spiked samples ranged from 94 to 101% with a RSD of 1.91 of the mean.

III. RESULTS AND DISCUSSION

Results were examined by using the adsorption isotherms. According to Giles classification [12], the isotherms can be classified as "L type". The adsorption of Hg on soil proceeds until a monolayer is established, with the absence of formation of more than one layer, this can be ascribed to the electrostatic repulsion between adsorbed ions and those in solution.

The pattern of isotherms is indicative of high affinity between the soil surfaces and the mercury ions. At low initial concentrations, the metal filled all possible sites; while at higher concentrations the isotherms reach a plateau indicating that the maximum capacity of adsorption of soil was reached.

The correlation of the experimental adsorption data with Langmuir and Freundlich equilibrium isotherm was undertaken to evaluate the adsorption behavior.

The Langmuir equation can be written as:

$$\frac{x}{m} = \frac{bKC}{1 + KC}$$

where x/m is the amount of metal sorbed per unity of mass of soil (μg/g), C is the equilibrium metal concentration in solution (μg/mL), b is the amount of mercury adsorbed at complete monolayer coverage, i.e. the sorption maximum (μg/g), and K the Langmuir binding energy coefficient (mL/μg), that is related to the heat of adsorption.

The Freundlich model can be described as:

$$Q = KC^{l/n}$$

where Q is the amount of metal sorbed per unit of weight of soil (μg/g), C is the equilibrium concentration of Hg in solution (μg/mL), and K and 1/n are regression parameters characteristic of the soil and linked to sorption capacity and intensity respectively.

The equations parameters and correlation coefficients (R^2) are reported in Table II and Table III.

TABLE II
EFFECT OF INCREASING Ca(NO$_3$)$_2$ CONCENTRATION ON LANGMUIR PARAMETERS

Ca (M/L)	b (μg/g)	K (mL/μg)	R^2
0.005	3.22	1.21	0.998**
0.010	3.07	1.05	0.996**
0.025	2.07	1.00	0.997**
0.050	1.72	1.01	0.998**

The correlation of Hg adsorption data with the Langmuir isotherm was high, with R values of 0.998, 0.997 and 0.996.

K represents the equilibrium adsorption constant, therefore higher values of K were indicative of a favorable adsorption process. By comparing the values of K, it can be concluded that adsorption of mercury by soil was less favorable at increasing ionic strength.

Lower correlations were found for the Freundlich equation compared to the Langmuir model with values of R^2 ranging from 0.867 to 0,754.

TABLE III
EFFECT OF INCREASING Ca(NO$_3$)$_2$ CONCENTRATION ON FREUNDLICH PARAMETERS

Ca (M/L)	K	n	R^2
0.005	0.201	0.89	0.879**
0.010	0.115	0.80	0.890**
0.025	0.043	0.56	0.899**
0.050	0.035	0.55	0.896**

The n values of this equation were less than unity, which confirmed the favorable adsorption of the mercury over the entire concentration range used in this study. Furthermore, the soil surfaces are known to be highly heterogeneous and the energies of active sites are highly variable, which would also tend to make the values of n less than unity.

Results showed that even though small amounts of Hg competed with large quantities of Ca for the adsorption sites in the soil, a very appreciable amount of Hg was adsorbed. This can be explained by the existence of high energy sites which adsorb the metal on a very selective basis in addition to exchange reactions. The ionic strength influence on metal sorption can be considered as dependent on the predominant sorption mechanism. The specific adsorption is poorly influenced by variation in ionic strength, while the non specific adsorption can be greatly reduced by the increase in electrolyte concentration, because of the competition between ions with the same positive charge.

The increase of ionic strength can greatly influence mercury adsorption based on outer-sphere complexation because the electrolyte ion present in very high concentrations can compete with the non-specific adsorption ion for available

binding sites at the soil surfaces. The activity of the adsorbing Hg ions can be affected by the change of the interfacial potential due to the variation of electrolytes activity, since the outer-sphere complexes are located at the same plane in the generalized triple layer model with the competing Ca ions [13], [14].

The effect of increasing ionic strength did not exclude the possible formation of inner-sphere complexes among Hg ions and soil surfaces, even if inner-sphere complexation, occurs closer to the surfaces compared to the plane where the electrolyte ions are located. Strong effects of ionic strength can be ascribed to non specific outer sphere complexation mechanism, while in the presence of specific inner sphere complexation the dependence of metal sorption by ionic strength is weaker.

The effect of ionic strength on the adsorption of mercury can be described by the combined effect of two processes: the cation exchange and the specific sorption [15]. The cation exchange reactions are represented by:

$$CaX + Hg^{2+} \leftrightarrow HgX_2 + Ca^{2+}$$

The activity of the adsorbed species can be considered as corresponding to the charge equivalent fraction Y_{Hg}:

$$Y_{Hg} = \frac{Z_{Hg}Q_{Hg}}{CEC}$$

where Z_{Hg} and Q_{Hg} are the charge and the amount of Hg sorbed respectively, and CEC is the cation exchange capacity of the soil which can be expressed as:

$$CEC = 2Q_{HgX_2} + 2Q_{CaX_2}$$

The exchange coefficient, as defined [16] by the Gaines Thomas equation:

$$K_{HgCa} = \frac{Y_{Hg}a_{Ca}}{Y_{Ca}a_{Hg}}$$

where a is the activity of free metal ion in solution and Y_{Ca} the charge equivalent fraction of Ca.

From the charge balance and the mass law equation the competitive sorption isotherms can be described, according to Voegelin, by:

$$Q_{HgX_2} = \frac{1}{2}CEC \frac{K_{Hg/Ca} \, a_{Hg}}{K_{Hg/Ca} \, a_{Hg} + \, a_{Ca}}$$

Taking into account also the high specific sorption process typical of heavy metal in soils, a set of competitive reactions for the available sites L with charge -1 have to be considered:

$$Hg^{2+} + L^- \leftrightarrow HgL^+$$

$$Ca^{2+} + L^- \leftrightarrow CaL^+$$
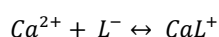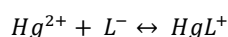
where HgL^+ represent the sites occupied by the metal.

The mass law equations correspond to:

$$K_{Hg} = \frac{(Q_{HgL^+}/Q_r)}{a_{Hg^{2+}} \, (Q_{L^-}/Q_r)}$$

and

$$K_{Ca} = \frac{(Q_{CaL^+}/Q_r)}{a_{Ca^{2+}} \, (Q_{L^-}/Q_r)}$$

where Q_{HgL}^+, Q_{CaL}^+ are the sorbed species in mol/kg and Q_r is the reference unit of 1 mol/kg .

The total site concentration is:

$$L_t = (Q_{L}-Q_{HgL^+}) + \, Q_{CaL^+}$$

Solving these equations for Q_{HgL}^+ provide the contribution of high affinity sites to the competitive sorption isotherms.

$$Q_{HgL^+} = \, L_t \frac{K_{Hg}a_{Hg}}{1 + K_{Ca}a_{Ca} + K_{Hg}a_{Hg}}$$

Total amount of mercury sorbed is the sum of the quantities sorbed in both processes cation exchange and specific adsorption:

$$Q_{Hg} = Q_{HgX_2} + Q_{HgL^+}$$

A multisite approach, although strictly empirical, is thermodynamically consistent and account for the chemical heterogeneity of soil surfaces. The results obtained in the reported sorption experiments well correspond to these mechanisms which affect mercury sorption by soil in the presence of competing alkaline ions.

Theoretically, when the electrostatic forces between the adsorbent surface and adsorbate ions were attractive, as in this system, an increase in ionic strength will decrease the adsorption capacity [17], [18]. The experimental data from this study did follow this hypothesis.

The effect of ionic strength on mercury adsorption in this contaminated soil showed that an increase in electrolytes concentration lead to a reduced sorption capacity of the soil.

Considering the chemical characteristics of mercury, the decrease in Hg adsorption with increasing ionic strength, can be reasonably ascribed to the competition between Ca^{2+} and Hg^{2+} for the same adsorption sites rather than to the formation of complexes between Hg and the NO_3 anion [19], [20].

IV. CONCLUSIONS

The results from this study can be of practical importance both in the agriculture and contaminated soils.

The solubility and mobility of mercury in soils are strictly dependent on the adsorption and release process in soil solution. In agricultural soils a reduction in the adsorption capacity of soils related to an increase in ionic strength, due as an example to the use of biosolids, can promote an increase in Hg bioavailability with potential negative effects on the food

chain.

At contaminated sites, the knowledge of the mercury partitioning between solid and liquid phases of soil is critical for selecting the most appropriate remediation strategy. The presence of high concentration of electrolytes reduces the adsorption on the soil solid phase increasing the amounts of metal in the pore water. This phenomenon, which is very dangerous in agricultural soils can be positively used in contaminated sites if in situ technologies are used. In fact technologies such as electrokinetic and phytoremediation [21], [22] are more efficient if higher amounts of contaminants are in the soil solution, and can be more easily removed from soil.

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