



Evaluating the Behavior of Metals in soil environment

Beata Draszawka-Bołzan^{1,*}, Emil Cyraniak²

¹Department of Chemistry and Protection of the Aquatic Environment, University of Szczecin, 3C Felczaka Street, 71-412 Szczecin, Poland

²The Board of Marine Ports of Szczecin and Świnoujście S.A., Environment and Health Research Laboratory, 7 Bytomska Street, 70-603 Szczecin, Poland

*E-mail address: atkadb@o2.pl

ABSTRACT

Metals added to soil will normally be retained at the soil surface. Movement of metals into other environmental compartments, i.e., ground water, surface water, or the atmosphere, should be minimal as long as the retention capacity of the soil is not exceeded. The extent of movement of a metal in the soil system is intimately related to the solution and surface chemistry of the soil and to the specific properties of the metal and associated waste matrix. The retention mechanisms for metals added to soil include adsorption of the metal by the soil solid surfaces and precipitation. The retention of cationic metals by soil has been correlated with such soil properties as pH, redox potential, surface area, cation exchange capacity, organic matter content, clay content, iron and manganese oxide content and carbonate content. Anion retention has been correlated with pH, iron and manganese oxide content and redox potential. In addition to soil properties, consideration must be given to the type of metal and its concentration and to the presence of competing ions, complexing ligands, and the pH and redox potential of the soil-waste matrix.

Keywords: Heavy metal, Soil sorption, sorption study

1. SORPTION STUDIES

Soil sorption studies are commonly performed to evaluate the extent of metal retention by a soil or soil constituent. Sorption studies are often used in an attempt to generate the

equilibrium distribution coefficient (K_d), the ratio of metal sorbed to metal in solution at equilibrium, which may be utilized in transport models. Sorption studies are also used for comparison of the relative retention of several metals by a soil or the relative retention of a metal by several soils, and are used extensively in correlation studies to determine the relative importance of a soil's chemical and physical properties for metal retention. Sorption studies also can be used to evaluate the effect that changing a soil solution parameter, e.g., adjustment of pH, ionic strength, addition of competing cations, or addition of inorganic or organic ligands, has on metal retention by a soil.

In a sorption study, the soil is reacted with solutions containing varying quantities of the metal(s) of interest for a specified time period using either batch or column techniques. The concentration range used in the study should overlap the concentration of environmental concern. A background electrolyte solution also should be used to simulate normal soil's solution chemistry or the waste matrix and to equalize the ionic strength across all soils. The reaction time should approach thermodynamic equilibrium, usually determined by a preliminary kinetics experiment. After the specified time period the soil and solution are separated by centrifugation and/or filtration. The soil and/or solution phases are then analyzed by atomic absorption spectrophotometry or inductively coupled plasma emission spectrometry. With these techniques it is not possible to distinguish between true adsorption and precipitation reactions. For that reason the term sorption will be used.

Two techniques, batch and column studies, may be used to generate sorption isotherms. The batch technique involves placing the soil and the solutions containing the various concentrations of the metals into a vessel and mixing the samples for a prescribed time period. This is the most commonly used technique because of its ease of laboratory operation and ease of data handling. The disadvantages of the technique are 1) results are sensitive to the soil:solution ratio used, 2) soil:solution ratios in actual soil systems cannot be done in batch studies, so scaling of data from batch studies to soils systems is uncertain, 3) results are sensitive to the mixing rate used, 4) separation techniques may affect results, and 5) many investigators have found that batch generated sorption coefficients are not adequate to describe the behavior of metals in flow through systems.

The column method consists of packing a glass or plastic column with soil. The solutions containing various concentrations of the metals of interest are pumped through the columns and the effluents are collected and analyzed by AA or ICP. Breakthrough occurs when the effluent concentration equals the influent concentration. The advantages of this technique are 1) low soil:solution ratios can be used, 2) separation of the soil and solution phase is not required, 3) mechanical mixing is not required and 4) column studies more closely simulate field conditions than batch methods. The disadvantages are 1) results depend on flow rates used, 2) columns are difficult to set-up and maintain, 3) uniform packing of the column is difficult often leading to channel flow, and 4) fewer columns can be operated at one time compared with the number of batch reactors.

Equilibrium sorption is described by a sorption isotherm. A sorption isotherm is the relationship between the amount of metal sorbed and the equilibrium concentration of the metal or, more correctly, the activity of the free metal in the soil solution. A typical sorption isotherm is shown in Figure 1. If the relationship is linear over the concentration range studied then the sorption process can be described by a single coefficient, the distribution coefficient, K_d . For metals, however, the relationship is seldom linear and other equations with two or more coefficients must be used to describe the data.

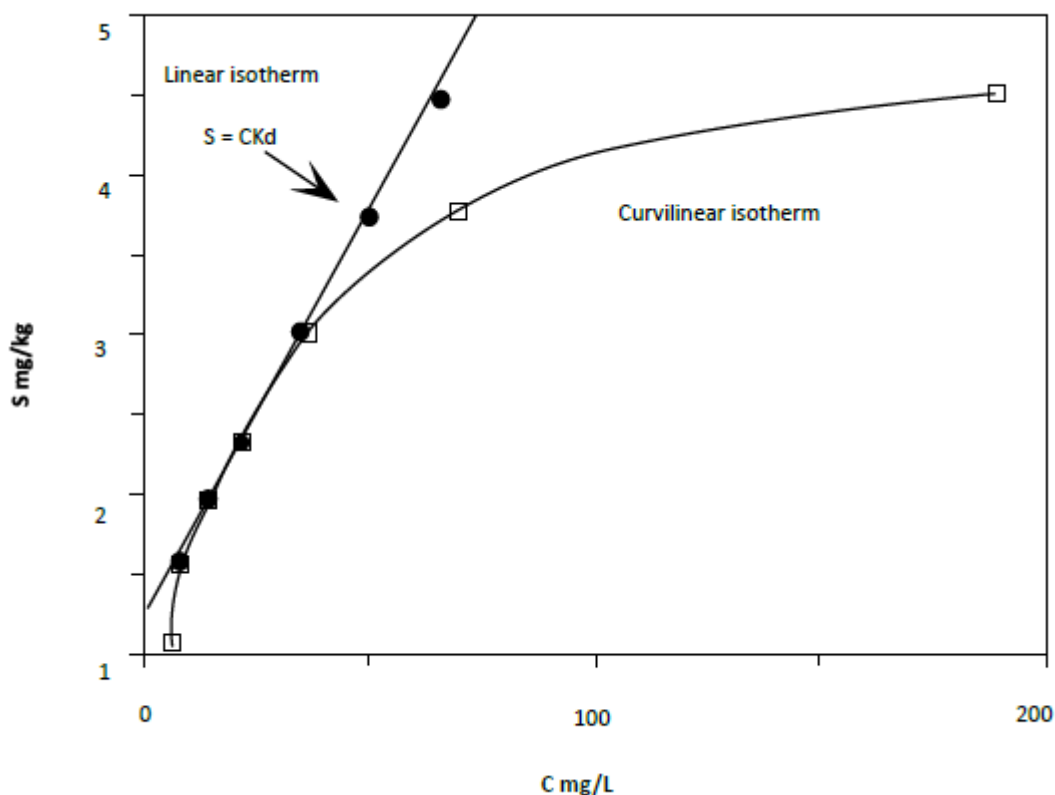


Figure 1. Sorption isotherms.

Equations most frequently used, because of their relative simplicity, to describe the curvilinear sorption behavior of metals in soil are the Langmuir and the Freundlich equations. The Langmuir equation was developed to model gas adsorption on solid surfaces.

The derivation of the equation was based on the assumption that adsorption is independent of surface coverage, that there is no interaction between adsorbed ions, and that only a monolayer of adsorption occurs on the surface. These conditions are not typically met with metals sorption on soils.

The linearized form of the Langmuir equation is:

$$\frac{C}{S} = \frac{C}{M} + \frac{1}{Mb} \quad (1)$$

where: C is the concentration or activity of the free metal in solution, S is the quantity of the metal ion sorbed by the soil (i.e., mg metal sorbed/Kg soil), M is the maximum sorption capacity of the soil, and b is the coefficient related to bonding energy. When C/S is plotted as a function of C, the slope is the reciprocal of the sorption capacity, M, and the intercept is 1/Mb.

The Freundlich expression is an empirically derived equation to describe the logarithmic decrease in adsorption energy with increasing surface coverage. The linearized form of the Freundlich equation is:

$$\log S = (N)\log C + \log K \quad (2)$$

where S and C have the same definition as above and N and K are constants fitted from the experimental data. When the slope, N, equals 1, the equation simplifies to:

$$S = CK_d \quad \text{or} \quad K_d = \frac{S}{C}$$

where: K_d is the distribution coefficient. In most studies reported in the literature for metal sorption, the slope of the Freundlich isotherm is seldom equal to 1 and the simplified expression and its single term, K_d , are not appropriate to describe the data.

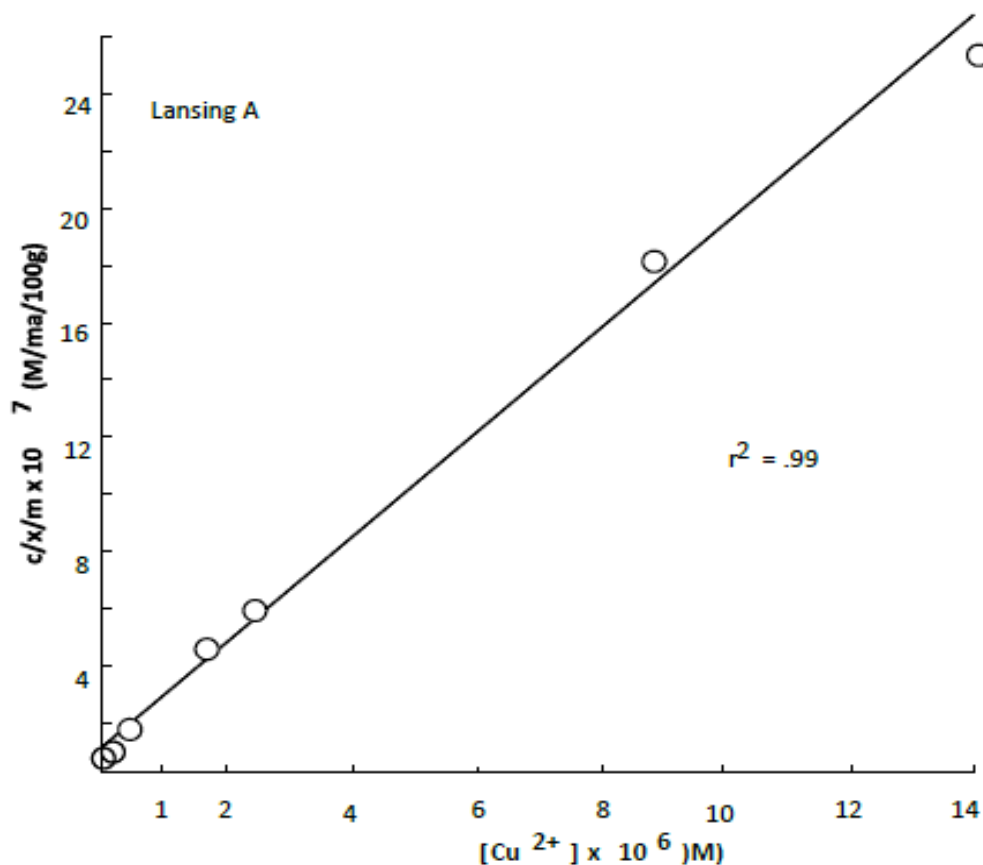


Figure 2. Langmuir adsorption isotherm for Cu²⁺ adsorption on the Lansing A soil (Cavallaro and McBride 1978).

Figure 2 illustrates the use of the Langmuir expression to describe Cu sorption by a soil (Cavallaro and McBride, 1978). The equation describes the behavior of Cu over all concentrations used in this study. Often, however, nonlinear behavior over the concentration range studied is observed with the use of either the Langmuir or Freundlich equations. In Figure 3, the Langmuir expression was used to describe the sorption behavior of Cd and Zn by hydrous manganese oxide (Zasoski and Burau, 1988). This non-linear behavior when using the Langmuir equation has been noted by numerous researchers using various metals and soils and soil constituents (Benjamin and Leckie, 1981; Shuman, 1975; Loganathan and Burau, 1973). Non-linearity of metal sorption using the Freundlich equation has also been noted by Zasoski and Burau (1988) Benjamin and Leckie (1981), Catts and Langmuir (1986), O'Connor et al. (1984), O'Connor et al. (1983), and Elrashdi and O'Connor (1982). This non-linear behavior has been interpreted to indicate multiple sites of sorption that have different energies of retention. The mechanisms at low concentrations have been attributed to specific adsorption, whereas the mechanisms at higher concentrations have been considered to be exchange reactions or precipitation. These results illustrate the importance of generating sorption data over the concentration range of interest for a particular application. Large error in predicting sorptive behavior may result from using data generated in one system and applied to a system with higher or lower metal concentration.

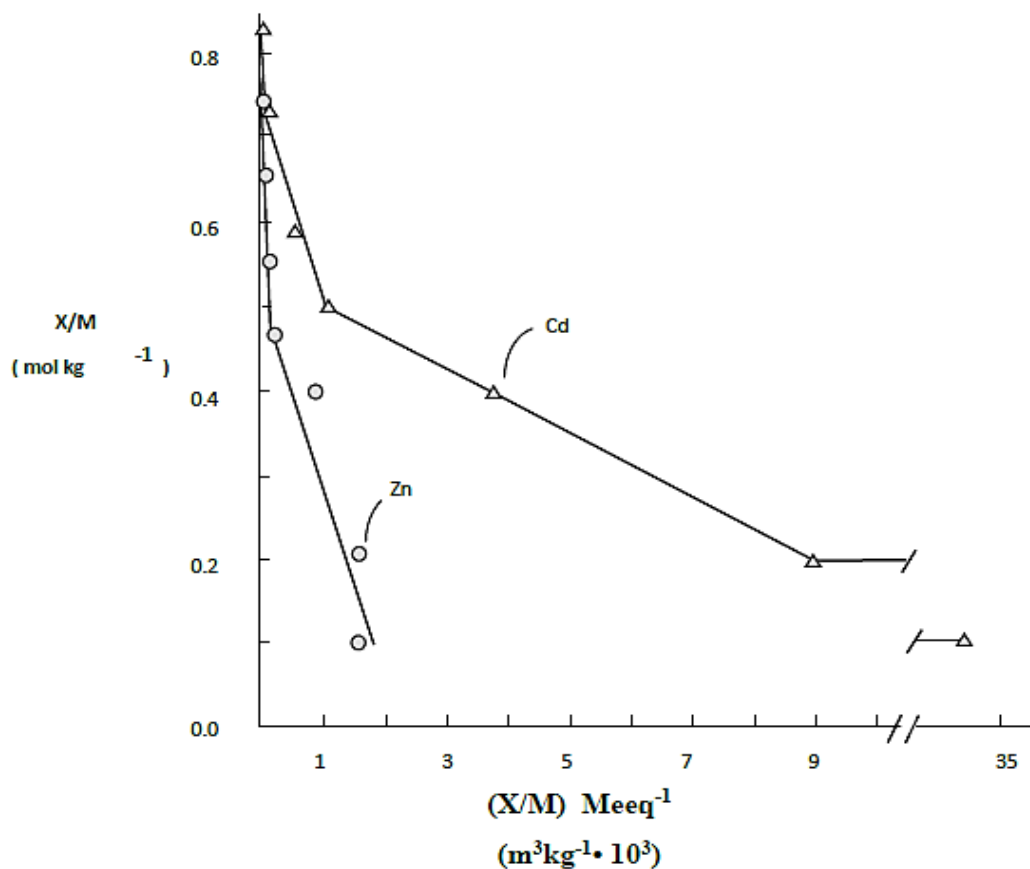


Figure 3. Langmuir plots of Cd and Zn sorbed on δ^- MnO₂ for the noncompetitive pH 4 data (Zasoski and Burau, 1988).

Several researchers have, however, suggested that other equations, for example the two-surface Langmuir equation (Sposito, 1982; Travis and Etnier, 1981) or the competitive Langmuir equation (Griffin and Au, 1977; Travis and Etnier, 1981), be used to describe the non-linear behavior encountered with the Langmuir equation (Sposito, 1982).

The Langmuir and Freundlich isotherm expressions have proven valuable in interpreting metal behavior in soils. The adsorption isotherm equations were, however, developed for modeling gas adsorption on solids. The sorption of metals by soils violates many of the assumptions associated with these equations. Also, the mechanism described by these equations is adsorption, but it is impossible in a soil system to distinguish between adsorption and precipitation reactions.

Adsorption isotherm equations should not be used to indicate adsorption mechanisms without collaborative evidence, but they can be used for an empirical description of the data. Harter (1984) warned against over interpreting the sorption maximum and "bonding energy" determined using the Langmuir equation. The applicability of adsorption isotherm equations to the interpretation of soil chemical phenomena is a subject of controversy. For further discussion of this controversy see Elprince and Sposito (1981), Griffin and Au (1977), Veith and Sposito (1977), Sposito (1979), Harter and Baker (1977), and Harter (1984).

2. CONCLUSIONS

Metals added to soil will normally be retained at the soil surface. Movement of metals into other environmental compartments, i.e., ground water, surface water, or the atmosphere, should be minimal as long as the retention capacity of the soil is not exceeded. The extent of movement of a metal in the soil system is intimately related to the solution and surface chemistry of the soil and to the specific properties of the metal and associated waste matrix.

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1. facilitated transport caused by metal association with mobile colloidal size particles,
2. formation of metal organic and inorganic complexes that do not sorb to soil solid surfaces,
3. competition with other constituents of waste, both organic and inorganic, for sorption sites, and
4. decreased availability of surface sites caused by the presence of a complex waste matrix.

Because of the wide range of soil characteristics and various forms by which metals can be added to soil, evaluating the extent of metal retention by a soil is site/soil/waste specific. Changes in the soil environment over time, such as the degradation of the organic waste

matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes also may enhance metal mobility. The extent of vertical contamination is intimately related to the soil solution and surface chemistry of the soil matrix with reference to the metal and waste matrix.

Laboratory methods for evaluating the behavior of metals in soils are available in the literature. Thermodynamic equilibrium computer models are also available to assist with this evaluation. The advantages and disadvantages of some of the available procedures have been presented in this document.

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