



Role of Organic Matter in the Adsorption/Desorption of Cr, Cu and Pb in Competitive Systems in Two Different Soils

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Received 1 August 2014; revised 25 September 2014; accepted 27 October 2014

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Abstract

The various methods of remediation of contaminated soils include isolation, immobilization, toxicity reduction, physical separation and extraction. In this context, a noteworthy technique is vermicomposting, which uses worms to break down recent organic matter, turning it into a chemically more stable form able to retain metal ions, rendering them unavailable to the environment. To understand the transport of these elements in the soil, it is necessary to study their dynamics in the environment. Thus, the aim of this study was to evaluate the adsorption and desorption of metal species in soils, assessing the influence of added organic matter in order to assess the risk that these elements carry to the environment and human health. The curves of adsorption of three toxic elements in the soil were determined by adding a solution of metal salts at various concentrations, leaving 24 h centrifuging and analyzing the supernatant. The concentrations of adsorbed components were taken as the difference between those added initially and those remaining after the equilibration (C_e). Desorption was carried out by adding a solution of $0.01 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2\cdot 2\text{H}_2\text{O}$ to soil samples where the metal ions were adsorbed. Following the same procedure, the concentrations of desorbed metal ions were measured.

Keywords

Vermicomposting, Sorption of Metal Species in Soils, Remediation, Contaminated Soils

Subject Areas: Analytical Chemistry, Environmental Chemistry

1. Introduction

Soils are contaminated by various elements concurrently, creating competition between them, and this has an

How to cite this paper: Mendes, L.A., Bucater, L.F.P., Landgraf, M.D. and Rezende, M.O.O. (2014) Role of Organic Matter in the Adsorption/Desorption of Cr, Cu and Pb in Competitive Systems in Two Different Soils. *Open Access Library Journal*, 1: e1022. <http://dx.doi.org/10.4236/oalib.1101022>

impact on their mobility in soils. Hence, multielement or competitive adsorption should be studied [1].

The choice of working with a multi-elemental solution came from the principle that the soil solution is not set with a single element, but rather with a mixture of them, which gives the chemical complexity present in soils.

The adsorption of metal ions under natural conditions is a competitive process between the species present in solution and the retained in the soil solid phase. The presence of such competing cations in the soil solution can increase the mobility of metals, owing to their competing for the same adsorption site with others elements present in the soil solution. This tends to reduce the degree of retention of metal ions, leading to increased availability of metal species in the environment [2].

Echeverria *et al.* [3] used isotherms to explain the competitive performance of Cd, Cu, Pb, Ni and Zn in three soils. The study concluded that Cu and Pb were adsorbed in larger quantities and through stronger bonds than Cd, Ni and Zn. The trials varied in both intensity and soil type.

Oliveira *et al.* [4] recorded competitive adsorption isotherms of Cd, Cu, Zn, Ni and Pb for two soils of different acidity. They found an increase in the metal adsorbed as the concentrations increased. In general, the relative affinity of these metal species in both soils was $Pb > Cu > Cd \sim Ni \geq Zn$.

Bradl [5] measured the adsorption of toxic metal ions in three soils. Empirical and mechanistic model approaches for heavy metal adsorption and parameter determination in such models have been reviewed.

The study showed that the concentration of Cd and Zn was greatly reduced when adsorbed by tropical soils; owing to the competitive effect of Cu with Pb, the adsorption isotherms fit a quadratic polynomial and the study also showed a less pronounced reduction in Cd and Zn adsorption.

Gomes *et al.* [6] studied the selectivity of adsorption of metal species in Brazilian soils. The commonest selectivity sequence observed in their study was $Cr > Pb > Cu > Zn > Ni$, and Cr and Zn swapped positions with Pb and Ni, respectively, for some of the soils. The authors concluded, after statistical correlation analysis, that the soil attributes that best explained the selectivity of adsorption were: acidity and cation exchange capacity (CEC) for Cd, Cr and Ni; acidity for Pb and organic carbon, clay and gibbsite for Cu. The study also noted that the amount of adsorbed Zn did not correlate significantly with chemical and mineralogical properties such as pH, CEC, organic carbon and clay contents, oxides of Fe and Al, hematite, goethite or gibbsite.

However, in some of these experiments, the concentrations of the elements were not equimolar, which made the behavior of the metallic species harder to compare [2].

Thus, the objective of this study was to investigate the adsorption and desorption of the toxic elements under study, in contact with soil/vermicompost mixtures, as well as in individual soils, and to assess the competitive effect between these elements through multielement adsorption/desorption isotherms, with the aim of elucidating the final destination when these toxic elements are present in the soil.

2. Materials and Methods

Experiments were carried out to construct four isotherms, namely: sandy soil, clay soil, sandy soil:vermicompost and clay soil:vermicompost, mixtures in the ratio of 1:1 (m/m).

The supporting electrolyte solution, $0.01 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$, was prepared by dissolving 1.10 g CaCl_2 in 1 L of ultrapure water.

The metal ion stock solution was prepared by dissolving 0.121 g $\text{Cu}(\text{NO}_3)_2$, 0.2 g $\text{Cr}(\text{NO}_3)_3$, and 0.166 g $\text{Pb}(\text{NO}_3)_2$ in 500 mL of the electrolyte solution. Working solutions were obtained by diluting this solution, in CaCl_2 electrolyte solution in the following proportions: 0.01, 0.05, 0.1, 0.5 and $0.1 \text{ mmol}\cdot\text{L}^{-1}$.

The four adsorption isotherms were prepared by mixing 2.0 g of 1) sandy soil; 2) clay soil; 3) sand soil + vermicompost 1:1 (w/w) or 4) clay soil + vermicompost 1:1 (w/w) with 20 mL of the metal ion stock solution. The mixtures were shaken on a rotary shaker for 24 hours and then centrifuged. The supernatant was analyzed by atomic absorption. The atomic absorption technique was chosen due to the work being done entirely with multi-elemental solutions. The technique helps once the analysis was done individually for each element not having any interference of other metal species in the element in question.

Desorption was carried out after the adsorption process: the samples used were filtered and the material retained on the filter was washed with distilled water and dried in an oven, after which it was placed in a beaker with 20 mL of $0.01 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$ solution and shaken for 12 hours. Finally the samples were filtered and analyzed for Cu(II), Cr(III) and Pb(II).

The amount of each ion adsorbed per gram of soil was calculated, to construct the isotherms.

In this paper, for each adsorbent-adsorbate combination, only one adsorption model (Langmuir or Freundlich) was chosen. To find out which model best fitted the isotherm for a metal ion and soil, the coefficients of linear correlation were compared and that with greater r was taken as the model that best elucidated the sorption process in question. Correlation coefficients were obtained from the linear regression method.

3. Results and Discussion

Models of Langmuir and Freundlich were linearized, and the correlation coefficients of these models were obtained by linear regression, to achieve the best fit to the data recorded for each assay.

For mixtures of the two types of soil with vermicompost, the model that fitted the data was Freundlich. This can be seen readily by comparing the two correlation coefficients for each metal ion shown in **Table 1**.

The Freundlich model assumes that the adsorption active sites have distinct affinities for the adsorbate, or adsorption is carried out on a heterogeneous surface, and sites of greatest affinity are filled first. According to the model, the energy of adsorption decreases logarithmically as the surface becomes covered by the adsorbate. It is also assumed that the energy distribution of adsorption sites is essentially exponential, implying that the adsorption of metal species from solution increases with increasing concentration. The linearized form of the Freundlich model provides us with values of some parameters that show interesting features of the adsorption of metal species on the vermicompost, such as:

$$\left(\frac{X}{M}\right) = \text{is the amount of solute was retained on vermicompost;}$$

C_{eq} = is the concentration of the metal species in the equilibrium solution;

K_F = the Freundlich coefficient, which indicates the capacity of vermicompost to retain the metal species;

n = dimensionless parameter (range 0 - 1) associated with the slope of the isotherm, which indicates the affinity of vermicompost for the metal species.

The values of K_F and n can be seen in **Table 2**. In the case of experiments performed with soil alone, the value of n shown in **Table 2** was greater than unity, due to the fact that these matrices fit the Langmuir model better.

This might be because soils display a smaller number of adsorption sites, making them more easily saturated and suggestion that these matrices adsorb only a monolayer, as described by the Langmuir model. The study still needs to be better suited for application *in situ*. But, the Langmuir model proves it. According to SPARKS [7], one disadvantage of the Freundlich model is that it does not predict the maximum adsorption capacity (Q_m), which can be found in the Langmuir model.

Mathematically, the parameter n shown in **Table 2** can be interpreted as a measure of the heterogeneity of the adsorption sites: as n approaches zero, the heterogeneity of the surface increases, and as n tends to 1 or is greater

Table 1. Correlation coefficients (r) of the Langmuir and Freundlich adsorption isotherms for the metal species Cr^{3+} , Cu^{2+} and Pb^{2+} in competitive system in soils before and after addition of vermicompost.

Matrix	Metal species	Freundlich isotherm (r)	Langmuir isotherm (r)
Sandy soil + Vermicompost	Cr^{3+}	0.95185	-0.39428
	Cu^{2+}	0.95874	-0.49963
	Pb^{2+}	0.97101	-0.81676
Clay soil + Vermicompost	Cr^{3+}	0.99905	-0.81715
	Cu^{2+}	0.94758	-0.52377
	Pb^{2+}	0.99581	-0.82192
Sandy soil	Cr^{3+}	0.94826	0.99715
	Cu^{2+}	0.95771	0.94361
	Pb^{2+}	0.93215	0.96884
Clay soil	Cr^{3+}	0.88773	0.99741
	Cu^{2+}	0.90564	0.95895
	Pb^{2+}	0.89735	0.99364

Table 2. Parameters of adsorption isotherms of Langmuir and Freundlich obtained by linearization of the models, for the three metals in mixed solution adsorbed in soils, before and after addition of vermicompost.

Matrix	Metal ion	Freundlich model		Langmuir model	
		K_F (L·mmol ⁻¹)	n	K_L (L·mmol ⁻¹)	Q_m (mmol·g ⁻¹)
Sandy soil +	Cr ³⁺	2.77×10^4	0.60	-2.93×10^{-3}	-6.08×10^3
	Cu ²⁺	4.47×10^2	0.62	-2.86×10^{-3}	-6.04×10^3
Vermicompost +	Pb ²⁺	1.93×10^9	0.27	-2.72×10^{-4}	-1.12×10^3
	Cr ³⁺	3.88×10^{21}	0.19	-1.59×10^{-4}	-3.76×10^4
Clay soil +	Cu ²⁺	3.95×10^7	0.34	-7.20×10^{-4}	-1.70×10^3
	Pb ²⁺	2.95×10^5	0.40	-6.35×10^{-4}	-1.18×10^3
Sandy soil	Cr ³⁺	0.038	2.22	9.43×10^{-3}	459.98
	Cu ²⁺	0.015	2.41	7.54×10^{-3}	72.73
	Pb ²⁺	7.51×10^{-3}	2.14	5.02×10^{-3}	27.36
	Cr ³⁺	0.167	1.82	0.01	1.793.4
Clay soil	Cu ²⁺	0.015	2.59	8×10^{-3}	91.97
	Pb ²⁺	0.017	1.89	7.49×10^{-3}	46.38

than unity, the adsorbent surface tends to become homogeneous, fitting better the Langmuir model [8].

For the experiments done with the sandy soil or clay soil alone linear model isotherms were also generated. These matrices fitted the Langmuir model best.

The Langmuir model, in turn, describes a mechanism of homogeneous adsorption, assuming that the adsorptive surface is uniform; that is, adsorption is constant and independent of the extent of surface coverage of the adsorbent material, while the active adsorption sites are energetically identical and have a finite number. Furthermore, the Langmuir isotherm also implies that the adsorption occurs at specific sites without interaction with the other metal species and that adsorption reaches a maximum when a monomolecular layer completely covers the surface of the adsorbent. The Langmuir equation is attractive as it provides linearization parameters that quantify the maximum adsorption capacity (Q_m) and the adsorption energy, also known as Langmuir affinity constant (K_L), which can be used to compare soils, biosorbents etc., with different capacities for adsorption, as is the case in this study.

From **Table 2**, it can be seen that the clay soil has a greater adsorption capacity than the sandy soil, which may be due to its higher content of organic matter, as well as a higher CEC, and therefore a greater number of active sites capable of retaining these metals.

In both models, it can be seen that chromium was the element showing interaction with any matrix used, followed by copper and finally lead. As previously stated this is due to chromium being trivalent and copper and lead divalent. There is also a relationship with the ionic radius, and the ascending order $Cr^{3+} < Cu^{2+} < Pb^{2+}$ means that lead is the least adsorbed of the three elements.

In desorption isotherms it is observed that the amount of metal desorbed was proportional to the concentration of the mixed ion solution; these isotherms were linearized for the Langmuir and Freundlich models, again used correlation coefficients to determine which of the methods best fits the data recorded for each test.

For all desorption isotherms, sandy soil, clay soil, sand soil + vermicompost 1:1 (w/w) and clay soil + vermicompost 1:1 (w/w), the Freundlich model gave the best fit, as determined by comparing the values of correlation coefficients for each metal ion in the two methods (**Table 3**).

4. Conclusions

The proposed addition of vermicompost to the soil showed satisfactory results, since the adsorption of toxic metals was higher in the mixtures than in samples containing only the soil. On addition of vermicompost, the greater number of active sites resulted in increased interaction with metal ions.

Analysis of the adsorption isotherms confirms that the active sites adsorb chromium more readily than lead and copper ions, since they have a greater affinity for the trivalent element, whereas the other two elements are bivalent, apart from the influence of the size of the ions. Regarding the linearization of the Langmuir and Freundlich models, we saw that, for the simple sandy and clay soils, the Langmuir model gave the better fit, while for

Table 3. Correlation coefficients (r) of the Freundlich and Langmuir desorption isotherms for metal species Cr³⁺, Cu²⁺ and Pb²⁺ in soils before and after addition of vermicompost.

Matrix	Metal ion	Freundlich isotherm (r)	Langmuir isotherm (r)
Sandy soil + Vermicompost	Cr ³⁺	0.71455	0.55825
	Cu ²⁺	0.90985	-0.31051
	Pb ²⁺	0.74074	0.4568
Clay soil + Vermicompost	Cr ³⁺	0.60735	0.15695
	Cu ²⁺	0.98522	-0.30003
	Pb ²⁺	0.78245	0.58087
Sandy soil	Cr ³⁺	0.98746	0.13156
	Cu ²⁺	0.98509	-0.010194
	Pb ²⁺	0.9474	0.65443
Clay soil	Cr ³⁺	0.79966	0.14882
	Cu ²⁺	0.7613	0.70583
	Pb ²⁺	0.89691	-0.00535

the soil:vermicompost mixtures, the Freundlich model fitted best, according to the analysis of the correlation coefficients of each isotherm of each species.

Thus, it can be concluded that the relative strength of adsorption of the three cations observed in all experiments performed in this study was in the order Pb²⁺ < Cu²⁺ < Cr³⁺.

With regard to the desorption studies, linearization of the isotherms indicated that both simple and mixed soils were best fitted by the Freundlich model.

With the results obtained, it can be concluded that the addition of organic matter to the soil, improving its fertility as well as helping to control the mobility of metal species, which in high concentrations contaminates the environment and decreases crop productivity, leading to economic problems. Another important factor in the addition of organic matter is that this will serve as a filter, preventing the arrival of contaminants to groundwater, since they may become trapped in the active sites of humus.

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