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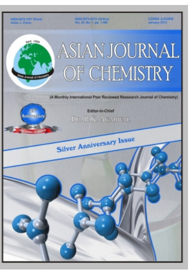

Effect of Mn and Cu on the Adsorption of Lead in Soil Sample from South of Shiraz, Iran

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Reactions of heavy metals with soils are important in determining the bioavailability and ultimate fate of these metals in the environment. To assess the competitive sorption and sequence of adsorption, we use single- and multi-solute systems consist of Pb, Cu and Mn in surface samples of calcareous soils from southern Shiraz. Heavy metals were added to soils at the rate of 300, 350, 450, 500, 600 and 750 mg kg^{-1} of Pb and 10 mg kg^{-1} of Cu and Mn. The samples were incubated for 2 h at room temperature and in pH = 8. Sorption isotherms were characterized using Linear, Freundlich and Langmuir equations. Comparison of R^2 indicated most sorption isotherms were well described by Freundlich equation. On the basis of the K_d value, the sequence of the metal adsorption is Pb > Pb - Mn > Pb - Cu, which is related to the first hydrolysis equilibrium constant.

Key Words: Single and competitive adsorption, Sorption isotherms, Heavy metals.

INTRODUCTION

Disposal of metal contaminated industrial effluent, sewage sludge, application of fertilizers, pesticides and municipal wastes in agriculture has contributed to a continuous accumulation of the heavy metals in soils[1]. In this situation, several heavy metal cations can be available at the same time in the soil.

The degree of heavy metal sorption is affected by environmental factors, soil components and properties as well as the amount of heavy metals added[2].

The total element concentration is not a reliable indicator of the bioavailability and mobile metal fraction in soils. The partitioning of metals in soils is quantified *via* partition coefficients (K_d) and adsorption isotherms. K_d is useful for comparing the sorptive capacity of soils for specific ions. A high K_d value indicates that the metal concerned is retained in the soild phase by sorption, whereas a low K_d value suggest that most of the metals remain in solution and are thus available for uptake by plants[3,4].

The Langmuir and Freundlich equations have mainly been applied to describe metal sorption in soils based on assumptions such as monometallic source terms and sorption sites of equal binding force[5].

To our best of knowledge it seems that there is no report on the combined use of batch equilibration adsorption method with atomic adsorption on competition between Pb, Cu and Mn in calcareous soil of Shiraz, Iran. Therefore, the aim of this study was to reveal the adsorption sequence in multi-solute systems by using an equilibrium adsorption method and then making the soil better for using as an adsorbent.

EXPERIMENTAL

Soil samples and characterization: Shiraz is one of the most important agricultural areas in the Iran. Samples from 0-30 cm soil horizon were collected from different agricultural areas in south of Shiraz[2]. Samples were air-dried and sieved to obtain soil samples composed of particles and aggregates < 2 mm in diameter. Then samples mixed completely chemical properties were determined[6] and are given in Table-1.

Organic carbon was determined by dichromate oxidation[2]. Soil pH were determined in a soil-solute ratio 1:5 using pH meter. HNO_3-extractable elements were determined[7] by boiling 2 g of soil with 20 mL 4 M HNO_3 solution for 12 h. Sand, silt and clay were quantitatively measured by the pipette method[8].

Preparation procedure: Batch adsorption test[9] were conducted in centrifuge tubes, using analytical-grade reagents. Optimization of the soil weight and initial concentrations were done. This soil had a lot of $CaCO_3$ and adsorbed much of the metals. The weight of soil was changed from 2 to 0.2 g. The soil adsorbed all of the amount of lead until the initial concentration 300 ppm, so the concentrations 300, 350, 450, 500, 600 and 750 ppm were chosen for single system included lead. The concentrations of 10, 20, 50, 100 ppm of copper and

TABLE-1
PHYSICAL AND CHEMICAL PROPERTIES OF STUDIED SOIL

Properties	Sand (%)	Silt (%)	Clay (%)	Texture	pH	Organic carbon (%)	Total N (%)	P (ppm)	K (ppm)	Fe (ppm)	Zn (ppm)	Cu (ppm)	Mn (ppm)	Cd (ppm)	Pb (ppm)
Amounts	51	6	43	Clay loam	8.16	0.36	0.04	0.5	132	6.4	0.44	0.8	6.56	0.5	0.26

TABLE-2
RESULTS OF ISOTHERMS

Samples	Metals in pH = 8, 2 h	Q	K_A	R^2	n	K_F	R^2	K_d	R^2
1	Mn	232.56	2.33×10^5	0.986	0.772	665.27	0.998	252.21	0.988
2	Cu	285.70	9.5×10^6	0.992	0.687	9512.60	0.994	5517.30	0.963
3	Pb	3333	3	0.997	0.697	7771	0.997	1841.1	0.986
4	Pb-Cu	2500	4	0.9634	0.871	10464	0.999	1652.9	0.979
5	Pb-Mn	2500	4	0.992	0.679	7896	0.999	1702.4	0.985

manganese were examined. 10 ppm were chosen as optimum concentration. The incubation time was 2 h^2.

The stock solution were prepared at 300:10, 350:10, 450:10, 500:10, 600:10 and 750:10 ppm of $Pb(NO_3)_2$: $Cu(NO_3)_2.3H_2O$ and $Pb(NO_3)_2$: $MnCl_2.2H_2O$. 20 mL of solutions added to 0.2 g of soil sample. For each sample, an experiment without adsorbent was performed as a blank. The suspensions were shaken for 1 h at room temperature, then the soil was separated from the solution by centrifugation at 3000 rpm for 10 min and filtered through Whatman No. 42 filter paper. The supernant liquids were analyzed and the heavy- metal cation concentrations remaining in solution were immediately ascertained by atomic adsorption spectrometer (AAS) (Varian, Spectra 220). The experiment was conducted with five replicates. The soil had pH 8.

The differences between the initial amount of metal in solution and the amount remaining in the solution after the reaction period were assumed to be adsorbed by the soil. The distribution coefficients (K_d) were calculated according to Dunn and Reddy[10], Anderson and Christensen[3] and Alloway[11]:

$$K_d = \frac{\text{Equilibrium metal concentration adsorbed}}{\text{Equilibrium metal concentration in solution}}$$

where the equilibrium metal concentration adsorbed is give per unit weight of soil and the equilibrium metal concentration in solution per unit volume of liquid.

Sorption models: The amount of lead sorbed by the soils was computed by the mass balance equation:

$$S = \frac{(C_i - C_e).V}{W} \quad (1)$$

where, S is the amount lead sorbed per unit mass of soil (mg kg^{-1}), C_i and C_e are the metal concentrations (mg dm^{-3}) in the initial and equilibrium solution, respectively, V is the volume of solution added (dm^{-3}) and W is the air-dried mass of soil (kg). The sorption data were plotted using Langmuir and Freundilch models[12].

Linearized Freundlich equation is:

$$\log S = \log K_f + n \log C_e \quad (2)$$

where, K_f and n are intercept and slope of the Freundlich isotherm, respectively. The Freundlich distribution coefficient (dm^3 kg^{-1}), K_f is the measured of a soil's ability to retain a solute and n is indicative of its affinity for the solute. n Parameter is dimensionless and informs on the heterogeneity degree of the sorption sites[13]. The amount of n is between 0 and 1. As n approaches 0, surface sites heterogeneity increases and as n approaches 1 the surface sites homogeneity increases. If n equals 1, then Freundlich equation will convert to Linear equation (3):

$$S = K_d C_e \quad (3)$$

The single-site Langmuir equation for adsorption of a single component A is linearized as (4):

$$\frac{C_A}{q_A} = \frac{1}{K_A, Q} + \frac{C_A}{Q} \quad (4)$$

where, q_A is the amount of A sorbed (meq/g), C_A is its equilibrium concentration (mol/dm^3) in solution, Q is the maximum sorption capacity and K_A is a constant related to sorption energy.

RESULTS AND DISCUSSION

The sorption isotherm parameters were determined for Pb, Cu, Mn using the Freundlich, Langmuir and linear isotherm equation for the adsorption data (Table-2). Moreover, the value of the square of the correlation coefficient was reported to indicate the goodness of the model fitness. The results indicated that the adsorption data single and competitive adsorptions were generally correlated with these models. However, the data best matched to Freundlich, because of the heterogeneity of the soil. The comparison should be done in the same concentration. But Pb adsorbed completely in 10 ppm and Cu and Mn are harmful in the used concentrations for Pb. So Pb adsorbed more than Cu.

The distribution coefficient is a useful index for comparing the sorptive capacities of different soils or materials for a particular ion under the same experimental conditions[5]. It has been calculated overall the initial concentrations of heavy metals (Table-2). A high K_d value indicates a high metal retention by the soil phase through sorption and chemical reactions, leading to a low potential bioavailability of the metal. However a low K_d value indicates a high amount of the metal remains in the solution[3,6]. Overall initial concentrations of single heavy metals, the highest K_d value were found for Pb and followed by those of Cu that shows intermediate K_d values (Table-2). However low K_d values were pronounced for Mn. This implies that Cu and specially Pb under the competitive condition are the most strongly sorbed metals by this soil, whereas Mn is the least sorbed one. Therefore the least one may pose more threats to the ground water and plants.

In competitive scenario, Pb-Mn had more K_d than Pb-Cu, because Cu sorbed more than Mn in this soil and Cu occupied the soil sites. So Cu caused the less adsorption of Pb than those of Mn.

Soil pH plays a major role in the sorption of heavy metals as it directly controls the solubility of metal hydroxides, as well as metal carbonates and phosphates[14]. In soils with high pH the predominance of the metals is in the hydrolyzed (MOH^+) form[6]. In this case, the influence of the metal hydrolysis on metal adsorption becomes more important for the more alkaline range of pH, as suggested by Brummer[15]. The order of sequence based on first hydrolysis constant is Pb > Cu > Mn.

Table-2 illustrates the adsorption isotherms for single and binary competition by the selected soil. Sorption isotherms for these metals by the soil exhibited differences in shape and in the amount retained.

An adsorption order for the trace elements was derived based on K_d and Q and the selectivity sequence. According the K_d values, the two selectivity sequences found most often were Pb > Pb-Mn > Pb-Cu for multiple competition and Pb > Cu > Mn for single competition.

The single competition sequence followed approximately the order of electronegativity of the metal cations, Cu(1.9), Pb(1.8) and Mn(1.5). According to McBride[16], electronegativity is an important factor in determining which of the trace metals chemisorb with the highest performance. The higher affinity for Cu than Mn is probably due to the existence of a greater number of active sites (mostly organic matter) with high specificity for Cu, so when it is present these sites would not be occupied by other cations. Copper exchanging sites with lead is not unusual, as indicated by the result of Fontes *et al.*[6]. The observed order for Pb and Cu is correlated with the sequence of ionic radii, which is Pb(1.20 Å) > Cu(0.72 Å)[16].

The competition scenario is related to some factors. At first, each site can be occupied with 2 metals and the competition between target metal and competitive metal depends on the selectivity of the competitive metal. Cu adsorbed by this soil more than Mn, as mentioned above. So it reduced the adsorption of Pb more than Mn.

Every process, which caused the retention of metals in the soil, is considered adsorption. This is an alkaline soil, so it has a lot of $CaCO_3$ (Table-1). There is reaction between metals and carbonate, so the metals deposit. Carbonates of these metals can be evaluated by comparing the equilibrium constants for the following reaction (5)[17]:

$$MeCO_3 + 2H^+ \rightarrow Me^{2+} + CO_2 + H_2O \qquad (5)$$

According to equilibrium constants for this reaction (5), the relative stability of metal-carbonate minerals is Pb>> Mn> Cu. So it is the reason of the high adsorption of Pb in this soil. On the other hand, hydrous ions and manganese oxides in clays are present as coating on phyllosilicates and as free gels and crystals. These metals can reduce the concentrations of tested metals in the soil solution by precipitation, specific adsorption and cation exchange. According to Backes *et al.*[18], metals cations diffuse into oxides-possibly into mineral lattice structure or into very small pores-following surface adsorption. Lead has been found to exhibit an especially high affinity for manganese oxides. In fact lead adsorption by Mn oxides has been found to be up to 40 times greater than that by Fe oxides[19].

Conclusion

Heavy metals retention in the soils is important from the perspective of plant nutrition and groundwater contamination. Calcareous soils were used to study single and competition adsorption of Cu, Mn and Pb during 2 h. Sorption isotherms were characterized using Linear, Freundlich and Langmuir equations. Comparison of R^2 indicated most sorption isotherms were well described by Freundlich equation, probably because of heterogeneity of the soil surface. Selectivity sequences for heavy metal cations, as determined by distribution coefficients (K_d), was related to electronegativity, hydrolysis properties, oxides in the soil, clay, the competitive metals and $CaCO_3$. The sequence was Pb> Pb-Mn> Pb-Cu for competition scenario and Pb> Cu> Mn for single scenario. This soil could be a great, chip and natural sorbent for adsorption of heavy metals.

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