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ADSORPTION SELECTIVITY SEQUENCE OF HEAVY METAL CATIONS BY SOME SOILS OF EGYPT

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ABSTRACT

Heavy-metal adsorption reactions, in a competitive system, are important to determine heavy metal availability to plants and their mobility throughout the soil. Therefore, this study was conducted to estimate the competitive adsorption of several heavy metal cations in some soils of Egypt with different chemical and physical characteristics.

Distribution coefficients (k_d) were obtained for each soil and heavy metal. On the basis of these k_d, the selectivity sequence was evaluated. The most common sequences were Cr > Pb > Cu > Cd > Ni > Zn and Pb > Cr > Cu > Cd > Zn > Ni. Chromium, Cu and Pb were the heavy metal cations most strongly adsorbed by all the studied soils, whereas, Cd, Ni and Zn were the least adsorbed, in the competitive adsorption situation. Selectivity sequences related to valence for the trivalent Cr. For cations of the same valence, sequences did not follow the order of electronegativity.

Statistical analysis showed that distribution coefficient was significantly correlated to cation exchange capacity (CEC) and organic matter (O.M) for Cr; $CaCO_3$ and pH for Cd; organic matter and clay for Cu; pH and O.M for Ni; CEC, clay for Pb; CEC and clay for Zn.

Keywords: Adsorption selectivity, Sequence, Heavy metal cations, Distribution coefficient, Soil of Egypt

INTRODUCTION

Heavy metals can be introduced into agricultural soils by application of fertilizers, sewage sludge, composts, and other industrial and urban waste materials (Adriano, 1986; Alloway, 1995b). In this situation, several heavy-metal cations can be available at the same time in the soils and, therefore, their selective retention and competitive adsorption by the soil becomes of major importance in determining their availability to plants and their movement throughout the soil (Gomes et al**.,** 2001**)**.

Distribution coefficients (k_d), which represent the sorption affinity of metals for the solid phase, indicate the capability of a soil to retain a solute and also the extent of its movement in a solution phase (Reddy and Dunn, 1986). The mobility and fate of metals in the soil environment are directly related to their partitioning between soil and soil solution (Evans, 1989) and, therefore, are directly related to their distribution coefficients. Distribution coefficient is a useful parameter for comparing the sorptive capacities of different soils or materials for any particular ion, when measured under the same experimental conditions (Alloway, 1995a). Distribution coefficients had been used in studies of mobility and retention of heavy metals as related to their competition (Anderson and Christensen, 1988; Gao et al., 1997). They also had been used in soil adsorption and mobility experiments for Cd (Sanchez-Martin and Sanchez-Camazano, 1993 and Lee et al., 1996) and they had been used to study mobility and solubility of trace metals (McBride et al., 1997; Romkens and Salomons, 1998) and long-term leaching of trace elements in a sludge-amended soil (McBride et al., 1999).

Selectivity sequence of heavy-metal cation adsorption has been found for goethite in the order Cu > Pb > Zn > Cd > Co > Ni > Mn, while hematite gave the same sequence except for an exchange in positions of Cu and Pb (Schwertmann and Taylor, 1989). Aluminum hydroxides have the order Cu > Pb > Zn > Ni > Co > Cd according to Hsu (1989). Three sequences found for calcareous soil, Cu > Zn > Cd > Ni > Mn, Cu > Ni > Zn > Cd > Mn and Cu > Cd > Zn > Ni > Mn (Jalali and Moharami, 2007). For humic substances, Schnitzer (1969) reported the order Cu > Pb > Ni > Co > Zn. Abd-Elfattah and Wada (1981) report that most of the observed sequences are not correlated neither with the sequence of ionic radii, which is Pb (1.20) > Cd (0.97) >Cr (0.75) >Zn (0.74) > Cu (0.72) > Ni (0.69) A^0, nor with the sequence of electronegativity given by Cu (1.9) > Pb (1.8) = Ni (1.8) > Cd (1.7) > Zn (1.6). There is, however, an interaction between the adsorption sequence and the hydrolysis properties of the heavy-metal cations, as pointed out by several investigators (Forbes et al., 1976; Elliott et al., 1986; Schwertmann and Taylor, 1989). The objectives of this study were to evaluate the selectivity sequence of several heavy metal cations in some soils of Egypt by means of distribution coefficients, and to investigate the relationship between distribution coefficients of some heavy metal cations and some soil characteristics.

MATERIALS AND METHODS

Seven surface (0-30 cm) soil samples were collected from different locations to represent different types of soil of Egypt (alluvial, desertic calcareous and sandy noncalcareous soils). The samples were air-dried, crushed and sieved to obtain fine soil particles (<2 mm). Chemical and physical properties were determined according to Page et al. (1982). The general characteristics of the selected soils are listed in Table 1.

Table1: Some characteristics of the selected soils.

Locations	Soil type	pH_e	CEC $Cmol_c kg^{-1}$	$CaCO_3$ %	Clay %	O.M gkg^{-1}
Giza	Alluvial	7.6	32.5	2.5	27.6	22.7
Menufia	Alluvial	7.7	39.8	3.4	29.5	21.9
Sharkia	Alluvial	7.4	36.4	2.1	31.8	31.3
Fayoum	Alluvial	7.8	23.4	4.1	20.5	20.4
Noubaria	Calcareous	8.3	28.4	28.1	25.4	8.5
Ganakleis	Calcareous	8.0	18.5	11.2	12.4	9.0
Ismailia	Noncalcareous	8.2	5.5	4.6	3.5	6.6

Adsorption of Cd, Cr, Cu, Ni, Pb, and Zn was measured, in triplicates, by adding 20 ml of solutions containing concentrations of 5, 10, 20, 40, and 50 mg l^{-1} for each heavy metal cation to 2 g of soil sample. The metal cations were applied in the forms $CdCl_2$, $CrCl_3 \cdot 6H_2O$, $CuCl_2 \cdot H_2O$, $NiCl_2 \cdot 6H_2O$, $Pb(NO_3)_2$, and $Zn(NO_3)_2 \cdot 4H_2O$ diluted in distilled water. A preliminary study was conducted to select the concentrations of metals in the solution. The suspensions were shaken for 2 h at 25 C°±2 (Gomes et al**.,** 2001**)**, then, the soil was separated from the solution by centrifugation. The heavy-metal cation concentrations remaining in solution were determined by atomic absorption spectrophotometer. The adsorbed amount by the soil was calculated from the difference between the initial amount of metal in solution and the amount remaining in solution after the reaction period. The distribution coefficients (k_d) were calculated according to Alloway (1995a) as follow:

k_d = equilibrium metal concentration adsorbed / equilibrium metal concentration in solution

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

A correlation analysis was performed by using the SAS program (SAS, Institute Inc., 1988) between k_d values of the heavy metal cations and some soil characteristics.

RESULTS AND DISCUSSION

Distribution coefficients (k_d) represent the adsorption affinity of the metal cations in solution for the soil solid phase. It also indicates the capability of a soil to retain a solute and also the extent of its movement in a solution phase. According to Anderson and Christensen (1988), high values of k_d indicate that the metal has been strongly retained by the solid phase through sorption reactions, while low values of k_d indicate that a large fraction of the metal remains in solution. From Table 2 it can be seen that Cr, Cu and Pb presented the highest k_d values, showing that they were the most retained cations. The calculated k_d values showed that, in general, Cr and Pb were more strongly retained than Cu for the most studied soils. The metal cations with the lowest k_d values were Cd, Ni and Zn. This result indicated that, these heavy metal cations when they are in competition, they are easily exchanged and substituted by Cr, Cu, and Pb. The results for Pb and Cu compared with Cd and Zn are in line with the higher adsorption presented by the first two elements compared with the latter ones in a competitive experiment in three highly weathered Brazilian soils (Fontes et al., 2000), and also with the lower mobility of Pb and Cu compared with Cd and Zn in a Brazilian Oxisol (de Matos et al., 1996).

In order to compare the different metal cations in each different soil, k_d at a concentration of 50 mg l^{-1} (k_{d50}) was utilized to give one comparable coefficient for each metal and soil. From the k_{d50} values, an adsorption orders for the heavy metal cations were derived and a selectivity sequence is shown in Table 3. The two adsorption sequences most found were Cr > Pb > Cu > Cd > Ni > Zn and Pb > Cr > Cu > Cd > Zn > Ni. For the same valance, the sequences did not follow the order of the electronegativity of the metal cations, which are, according to Evans (1966), Cu (1.9), Pb (1.8), Ni (1.8), Cd (1.7) and Zn (1.6). The presence of Cr as one of the most retained cations, in spite of its lower electronegativity value (1.6), seems to be related to the fact that this metal was applied in its trivalent form, which is predominantly in soils (Smith and McGrath, 1990). McBride et al. (1997), using k_d values to indicate the potential for leaching losses of some elements, found Cr^{3+}, with a very high k_d value, to be the least mobile element. The positions of Pb and Cu in the sequence were in agreement with the results reported by Sposito (1989). In the most soils, Cd was adsorbed to a larger extent than Zn, which is in line with results of de Matos et al. (1996) for the retention of these two heavy metals in a Brazilian Oxisol. Nickel and Zn were the least adsorbed metals in all soils except Menufia and Ganaklies. Zinc was more retained than Cd in only one soil **(**Menufia), and was the least retained in most of the other soils. Also, Ni was more retained than Cu in soil of Ganaklies.

Table 2: Distribution coefficients (K_d) calculated for each added metal concentration for some soils of Egypt.

Metal	**Initial conc. (mgl^{-1})**	**Soil locations**						
		Giza	**Menufia**	**Sharkia**	**Fayoum**	**Noubaria**	**Ganakleis**	**Ismailia**
		k_d (lg^{-1})						
Cd	5	1.67	1.40	2.57	4.10	18.66	4.42	3.38
	10	0.40	0.51	1.31	0.88	7.36	1.73	1.03
	20	0.18	0.34	0.56	0.67	1.60	1.19	0.59
	40	0.09	0.18	0.25	0.18	0.68	1.12	0.45
	50	*0.04*	*0.12*	*0.09*	*0.12*	*0.16*	*0.77*	*0.23*
Cr	5	84.34	86.21	243.34	56.47	46.62	8.92	6.19
	10	43.67	71.34	117.21	19.74	8.24	3.12	1.64
	20	35.81	60.43	63.33	14.76	3.97	1.17	1.08
	40	30.00	26.98	21.92	4.16	1.67	0.88	0.88
	50	*17.81*	*5.19*	*11.02*	*2.79*	*1.67*	*0.57*	*0.53*
Cu	5	14.92	29.30	41.01	24.32	6.99	2.04	3.02
	10	2.48	7.02	10.14	4.39	2.49	0.79	1.01
	20	1.81	2.81	5.88	3.14	0.58	0.61	0.58
	40	1.44	1.79	1.71	0.73	0.19	0.40	0.25
	50	*1.14*	*1.07*	*0.98*	*0.46*	*0.07*	*0.29*	*0.11*
Ni	5	0.29	1.12	0.34	2.53	4.43	2.96	1.88
	10	0.08	0.47	0.13	0.75	0.95	1.36	0.41
	20	0.04	0.32	0.05	0.42	0.46	0.78	0.35
	40	0.02	0.18	0.01	0.18	0.27	0.59	0.20
	50	*0.01*	*0.10*	*0.01*	*0.02*	*0.17*	*0.23*	*0.07*
Pb	5	65.67	287.32	249.32	45.72	49.42	6.01	3.33
	10	52.56	170.41	122.54	13.62	17.04	2.48	1.22
	20	31.30	141.25	64.18	3.88	12.33	0.64	1.07
	40	17.82	57.38	19.98	2.81	4.53	0.41	0.31
	50	*8.70*	*39.65*	*11.37*	*1.55*	*3.42*	*0.27*	*0.19*
Zn	5	1.63	13.36	1.70	0.93	0.87	0.43	0.43
	10	0.20	1.46	0.49	0.16	0.38	0.13	0.22
	20	0.13	0.48	0.29	0.10	0.15	0.07	0.08
	40	0.02	0.15	0.08	0.05	0.03	0.03	0.06
	50	*0.01*	*0.13*	*0.07*	*0.02*	*0.01*	*0.01*	*0.01*

In order to assess the relative capacity of each soil to adsorb heavy metal cations, Fig 1 shows the sum of the amounts of adsorbed metals for each soil. The order of relative metal cations adsorption by the different soils was Menufia > Sharkia > Giza > Fayoum > Noubaria > Ganakleis > Ismailia.

The alluvial soil samples from Menufia, Sharkia and Giza with higher values of clay, CEC and organic compared with the other soils in this study (Table 1), were among the ones with highest relative capacity to adsorb metal cations. Noubaria, which has the highest pH, CEC, $CaCO_3$ and clay of all of the desertic soils, showed highest adsorption values compared to Ganakleis and Ismailia desert soil

Table 3. Adsorption sequence by soils according to the distribution coefficients (K_d values).

Soil locations	Sequence					
Giza	Cr >	Pb >	Cu >	Cd >	Zn >	Ni
Menufia	Pb >	Cr >	Cu >	Zn >	Cd >	Ni
Sharkia	Pb >	Cr >	Cu >	Cd >	Zn >	Ni
Fayoum	Cr >	Pb >	Cu >	Cd >	Ni >	Zn
Noubaria	Pb >	Cr >	Cd >	Cu >	Ni >	Zn
Ganakleis	Cr >	Pb >	Cd >	Ni >	Cu >	Zn
Ismailia	Cr >	Cd >	Pb >	Cu >	Ni >	Zn

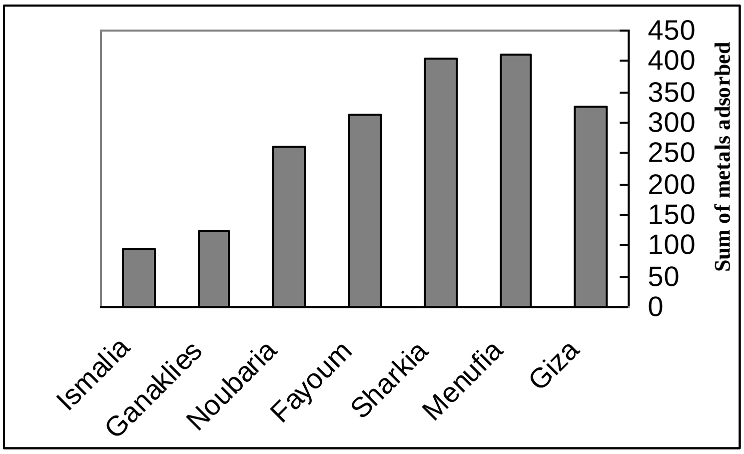

Fig 1: The sum of the amounts (mg kg^{-1}) of adsorbed metals for each soil.

Correlation Analysis

The evaluation of the influence of soil characteristics on the heavy metal cations adsorption was examined by correlation analysis. The adsorption affinity of Cr was influenced mainly by CEC and organic matter, as shown by the highly significant simple linear correlation coefficient between these variables (r = 0.931** and 0.922**). Calcium carbonate content and pH of the soil samples affected Cd adsorption presenting significant correlation coefficients (r = 0.742* and 0.674*). Alloway et al. (1985) have shown that soils containing $CaCO_3$ can adsorb Cd and reduce its bioavailability. The correlation coefficients (r = 0.684* and 0.625*) showed that Cu adsorption was related to the amounts of organic matter, clay. These results indicate the high affinity of Cu complexation by organic matter compounds and specific adsorption by clay.

The adsorption of Ni was related to pH as shown by the highly significant correlation coefficient between this variable and the k_d values for this element (r = 0.897**). Organic matter was also correlated to Ni adsorption (r =0.778). These results suggest that the hydrolyzed form, which is affected by the pH, may be important in Ni adsorption. Cation exchange capacity and clay were the variables that most strongly correlated to Pb adsorption (r = 0.776* and 0.675*). Also, it can be concluded that pH may have influenced Pb adsorption as shown by the correlation coefficient (r = 0.576*). Lead was most strongly adsorbed in higher pH soils. Lee et al. (1992) reported that, the amount of Pb adsorbed onto major type of New Jersey soil decreased as the pH decreased. Zinc adsorption was related to CEC and clay as shown by significant correlation between its k_d values and these variables (r = 0.632* and 0.588*).

CONCUSION

Selectivity sequence of heavy metal cations, as determined by distribution coefficients (K_d), was related to valence for the trivalent Cr, but for the same valence they did not follow the order of electronegativity of the metal cations. The most common sequences were Cr > Pb > Cu > Cd > Ni > Zn and Pb > Cr > Cu > Cd > Zn > Ni. The order of decreasing total amount of heavy metal cations adsorbed by soil was Menufia > Sharkia > Giza > Fayoum > Noubaria > Ganakleis > Ismailia.

Correlation analysis showed that soil characteristics that may have affected the heavy metal cations adsorption, represented by the distribution coefficients, were cation-exchange capacity (CEC) and organic matter (O.M) for Cr; $CaCO_3$ and pH for Cd; organic matter and clay for Cu; pH and O.M for Ni; CEC, clay and may pH for Pb; CEC and clay for Zn.

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اختيارية ادمصاص كاتيونات الفلزات الثقيلة بواسطة بعض الاراضى فى مصر

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تعتبر تفاعلات ادمصاص الفلزات الثقيلة, فى النظام التنافسي, مهمة لمعرفة تيسر الفلزات الثقيلة للنبات وحركتها فى التربة. لذلك فقد اجري هذا البحث لدراسة الادمصاص التنافسي للعديد من كاتيونات الفلزات الثقيلة بواسطة بعض الاراضى المصرية ذات الخواص الكيماوية والفيزيائية المختلفة.

تم الحصول على معاملات التوزيع (k_d) لكل تربة وفلز ثقيل وبالاعتماد على هذا المعامل تم ترتيب هذه الفلزات حسب اختيارية ادمصاصها وكان الترتيب التالى هو الشائع: الكروميوم > رصاص > نحاس > كادميوم > نبكل > زنك وايضا رصاص > الكروميوم > نحاس > كادميوم > زنك > نبكل. وكان الكروميوم والنحاس والرصاص اكثر العناصر ادمصاص بينما كان الكادميوم والنيكل والزنك اقلهم. ارتبط التسلسل السابق بالشحنة فى حالة كاتيون الكروميوم الثلاثى التكافؤ بينما الكاتيونات الثنائية فلم يرتبط بالسالبية الكهربية.

أظهرت نتائج التحليل الاحصائى أن معامل التوزيع يرتبط معنويا مع السعة التبادلية الكاتيونية والمادة العضوية بالنسبة للكروميوم اما فى حالة عنصر الكادميوم يرتبط مع كربونات الكالسيوم ورقم الحموضة, ومع المادة العضوية والطين فى حالة النحاس, ورقم الحموضة والمادة العضوية لعنصر النيكل, والطين ورقم الحموضة للرصاص , السعة التبادلية الكاتيونية والطين فى حالة الزنك.