# The Adsorbtion of Lead, Copper, Chrome and Nickel Ions from Waste Waters in Agricultural Argilaceous Soils

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The aim of this work is the study of te adsorption process of some heavy metals like lead, copper, chrome and nickel in agricultural argilaceous soil in order to put in evidence the influence of adsorption conditions on adsoption process. The adsorption isotherms, Langmuir and Freundlich, have been used to describe the adsorption equilibrium. The experimental data put in evidence that the adsoption capacity of heavy metals increases in order  $Nr^+$  (about 110 µmol/L),  $Pb^{2+}$  (about 150 µmol/L),  $Cr^{3+}$  (about 300 µmol/L) and  $Cu^{2+}$  (about 350 µmol/L). In all cases, the Langmuir isotherms reflect more exactly the adsorption process, being recomendet for thermodynamic parameters determination.

Keywords: industrial waste waters, agricultural argelaceous soils, heavy metal adsortion

The industrial development has lead to increased amounts of pollution sources [1-5]. Due to the presence of different chemicals as heavy metals and poisonous materials, as well as potential capability of producing leachate they are considered the main pollutant sources of ground and surface waters [6-10].

Toxicological impacts of various heavy metals are of environmental concern [11]. For example, Pb<sup>2+</sup> has been reported to cause various diseases such as brain damage and anemia. Hg<sup>2+</sup>, Pb<sup>2+</sup> and Cr<sup>3+</sup> are classified as very poisonous sources [12].

The main factors influencing the adsorption of heavy metals in soils are the following: the pH, te ionic strength, the cation and anion index and the presence of organic matter.

Te *p*H of the soil solution influences the mobility of soil solution and therefore the soil adsorbability. Increasing the *p*H, the mobility of soil solution decreases and therefore the adsorption capacity of soil increases. In the case of  $Pb^{2+}$  ions the influence of *p*H is strong

In the case of  $Pb^{2+}$  ions the influence of *p*H is strong related with soil organic matter (SOM). In the neutral *p*H range a high SOM increases the dissolved organic matter (DOM) thereby promoting the formation of organo Pb complexes, so increasing the  $Pb^{2+}$  ions solubility [13-15].

As a rule, sorption increases with increasing pH. The lower the pH value the more metal is mobilized. When the pH decreases the ion mobility is enhanced as a result of the increased proton concentration. At pH value above 7, some heavy metals tend to form hydroxy-complexes which will inrease the metal solubility. The adsorption of chromate did not change as significantly as other metals with pH changes. This is due to its oxyanion character in oxidizing conditions [16].

Soil organic matter is very important for metal sorption. The dissolution of humic acid (HA) at higher *p*H is responsible for dissolution of  $Cu^{2+}$  and  $Pb^{2+}$  ions in soil [17]. The solubility of heavy metals in soil at alkaline *p*H was

The solubility of heavy metals in soil at alkaline *p*H was attributed to enhanced formation of organic metal complexes after ionization of weak acid groups. In this *p*H range most dissolved heavy metals are present as metal soluble organic ligand complexes [17]. For  $Cu^{2+}$  ions the disolved organic matter can affect its solubility [18].

The role of organic acids in metal mobilisation is especially important [16]. Metal-ligand complex stability generaly decreases with *p*H reduction, reflecting the role of RCOO<sup>-</sup> in metal complexation. Cd-ligand ion complexation is essential for metal solubilization.

The ionic strength is very important in metal ions solubilisation. The amount of metals adsorbed decreases with increasing ionic strenght like in the case of  $Cu^{2+}$  and  $Ni^{2+}$  ions [19].

The cation and anion index is strongly related with the ionic strenght. The anions can contribute in reducing heavy metal adsorption by formation of negatively charged or neutral species like MCl<sub>2</sub>, MeCl<sub>3</sub><sup>-</sup> and MeCl<sub>4</sub><sup>-</sup>. In particular Cd<sup>2+</sup> is known to form relatively stable Cl<sup>-</sup> complexes, which influences the mobility of metals in soil. Also Cr<sup>3+</sup> ions were released when the Cl<sup>-</sup> solution was used as leaching electrolyte [20].

Also Čl<sup>-</sup> ion could be an impotant factor enhancingPb<sup>2+</sup> and Ni<sup>2+</sup> mobility in soil [21, 22].

The presence of Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup> as cations and Cl, NO<sub>3</sub>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> as anions, could be regarded to play a role in mobility of Pb<sup>2+</sup> and Ni<sup>2+</sup> ions [23, 24] and also of Cd<sup>2+</sup> ions. The last could be explained by CdCl<sub>n</sub><sup>2-n</sup> formation.

In concusion the sorption of heavy metals in agricultural soils is a complex process, depending on many factors.

## **Experimental part**

The sorption experiments were performed using a method based on the determination of the solute concentration before and after contact with the adsorbent.

In order to ensure the uniformity, the solution-adsorbent mixture was mechanically shaked. The equilibrium being attained (after 24 h) the solid phase was filtered and the concentration was measured.

A measured volume (V  $\approx$  50 mL) of liquid phase was placed in a 500 mL vessel, containing, in all experiences the same amount of adsorbent (m = 0.1 g). The initial concentration of solution was ranged between 50 and 2000  $\mu$ mol/L for nickel, chrome and copper respectively, and between 50 and 500  $\mu$ mol/L for lead. The bottels were placed in a machanical stirrer and maintained at a constant temperature.

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Humus, %	2.9	STAS 7184/21-82
N total, %	0.18	SR ISO 11261:2000
2		0
P total, %	0.09	STAS /184/14-79
K total nom	08	STAS 7194/19 90
ix totai, ppili	50	5115 /104/10-00
Zn, ppm	3.7	
Cu, ppm	3.1	
_		GD 100 11047-1000
Fe, ppm	40.5	SK ISO 11047:1999
A1 onm	170	
лі, ррш	1/0	
Mn, ppm	4.5	
pH	5.4-5.6	SR ISO 1039:1999
Volumetric weight, g/cm <sup>3</sup>	1.25	SR ISO 11272:2000

In order to measure the cation concentration in liquid phase an Atomic Absorption Spectrometer, Zenit 700 Analytic Jena, has been used.

The experiments were performed using a soil with argillaceous texture, sampled from Teleorman area, known in agricultural practice as clay chernozem.

The main characteristics of soil are presented in table 1.

### **Results and discussions**

The sorption capacity of argilaceous soil concerning the lead, copper, chrome and nickel ions was studied. The results have been presented determining the equilibrium curves in coordinates a-C<sub>e</sub>, where a represents the concentration, of adsorbate in solid phase, at equilibrium, in  $\mu$ mol/g and C - the concentration of adsorbate in liquid phase, in  $\mu$ mol/L (figs.1-4).

The adsorption process of  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Cr^{3+}$  and  $Ni^{2+}$  in argilaceous soil could be theoretically characterised using an appropriate equation. The shape of two groups of isothermes suggests the opportunity to use the Langmuir and Freundlich equations. The Langmuir equation starts from the hypothesis to which between the adsorbent surface and the molecules of adsorbed compound,





covalent bonds are developed and between the molecules of adsorbed compounds there are no interactions.

$$a = a_{m} \frac{bC}{1 + bC}$$
(1)

or in the linear form:

$$\frac{1}{a} = \frac{1}{bCa_m} + \frac{1}{a_m}$$
(2)

where *a* represents the concentration of adsorbate in solid phase at equilibrium,  $\mu$ mol/g.

 $a_m$  - the maximum adsorption capacity of adsorbate adsorbed in monolayer,  $\mu$ mol/g

C – the concentration of adsorbate in liquid phase,  $\mu mol/L$ 

b – the equilibrium constant,  $\mu$ mol/L.

Making the variable changes 1/a = y and 1/C = x the equation of a line is obtained:

$$y = Ax + B \tag{3}$$

Table 2							
THE THERMODYNAMIC PARAMETERS a <sub>m</sub> b, K AND n CARACTERISING THE ADSORPTION PROCESS OF							
Pb <sup>2+</sup> . Cu <sup>2+</sup> . Cr <sup>3+</sup> AND Ni <sup>2+</sup> IONS IN CAMBIC SOIL							

Parameters	Langmuir			Freundlich		
	R <sup>2</sup>	a	b	R <sup>2</sup>	K	n
Plumb	0.9856	0.8684	0.0020	0.973	4.0565	0.6319
Сирги	0.9997	0.316384	0.0034829	0.8916	10.758573	0.5262621
Crom	0.992214	1.144804	0.0009553	0.9098	5.3310687	0.599191
Nichel	0.9832	2.646896	0.003682	0.9788	2.781271	0.543247

The Freundlich model is an semiempirical one, having the form:

$$= \mathbf{K}\mathbf{C}^{1/n} \tag{4}$$

а where K represents the equilibrium constant

C – the concentration of adsorbate in liquid phase, umol/L

n - empirical coefficient

The Langmuir and Freundlich equations have been used for modeling the adsorption process of metal ions adsorption in agricultural soils and for determination of the equilibrium parameters a ,, b, K and n (table 2). The experimental results presented in the figures (1-4)

and the value of  $\mathbb{R}^2$  (table 2) confirm that the Langmuir equation is more appropriate for modeling the adsorption process of studied metal cations in argilaceous soil.

The influence of pH on adsorption degree of  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Cr^{3+}$  and  $Ni^{2+}$  was also studied. The studied *p*H interval was 4-7. For pH correction 0.01 M HNO<sub>3</sub> and NaOH solutions were used. The results have been presented in coordinates a-pH, in equilibrium conditions, using the same technique (figs. 5-8).

From the figures 5-8 results that sorption increses with increasing *p*H. The explanation is the following: the lower the pH the more metal ions are found in solution, as a result of the increased proton concentration. Besides the cations  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Cr^{3+}$  and  $Ni^{2+}$  are found also in exchangeable form, suggesting that these metals are very mobile. So, the *p*H has an essential role in the adsorption process of the studied ions in argelaceous soil.





Fig. 7 The dependence of Cr<sup>3+</sup> concentration in solid phase, on pH, at equilbrium.

Fig. 8 The dependence of Cu2+ concentration in solid phase, on pH, at equilbrium

### Conclusions

In this paper the adsorption of lead, copper, chrome and nickel ions from waste waters in agricultural argilaceous soils have been studied. The adsorption isotherms Langmuir and Freundlich have been used to describe the adsorption process by calculating the adsorption parameters a and b and the empirical parameters K and n respectively. The shapes of the adsorption curves and the values of R<sup>2</sup> put in evidence that the Langmuir isotherm characterises more exactly the adsorption process. The study of the influence of *p*H on adsorption process put in evidence that, in all cases, the sorption increases with increasing pH. The explanation resides in the fact that the lower the pH, more metal ions are found in solution as a result of the increased proton concentration.

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