The Adsorption 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 the 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 adsorption process. The adsorption isotherms, Langmuir and Freundlich, have been used to describe the adsorption equilibrium. The experimental data put in evidence that the adsorption capacity of heavy metals increases in order Ni²⁺ (about 110 µmol/L), Pb²⁺ (about 150 µmol/L), Cr³⁺ (about 300 µmol/L) and Cu²⁺ (about 350 µmol/L). In all cases, the Langmuir isotherms reflect more exactly the adsorption process, being recommended for thermodynamic parameters determination.

Keywords: industrial waste waters, agricultural argilaceous soils, heavy metal adsorption

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, Pb²⁺ has been reported to cause various diseases such as brain damage and anemia. Hg²⁺, Pb²⁺ and Cr³⁺ 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 pH of the soil solution influences the mobility of soil solution and therefore the soil adsorbability. Increasing the pH, the mobility of soil solution decreases and therefore the adsorption capacity of soil increases.

In the case of Pb²⁺ ions the influence of pH is strong related with soil organic matter (SOM). In the neutral pH range a high SOM increases the dissolved organic matter (DOM) thereby promoting the formation of organo Pb complexes, so increasing the Pb²⁺ 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 increase 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 pH is responsible for dissolution of Cu²⁺ and Pb²⁺ ions in soil [17].

The solubility of heavy metals in soil at alkaline pH was attributed to enhanced formation of organic metal complexes after ionization of weak acid groups. In this pH range most dissolved heavy metals are present as metal soluble organic ligand complexes [17]. For Cu²⁺ ions the dissolved organic matter can affect its solubility [18].

The role of organic acids in metal mobilisation is especially important [16]. Metal-ligand complex stability generally decreases with pH reduction, reflecting the role of RCOO⁻ 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 strength like in the case of Cu²⁺ and Ni²⁺ ions [19].

The cation and anion index is strongly related with the ionic strength. The anions can contribute in reducing heavy metal adsorption by formation of negatively charged or neutral species like MCl₂, MeCl₃ and MeCl₄⁻. In particular Cd²⁺ is known to form relatively stable Cl⁻ complexes, which influences the mobility of metals in soil. Also Cr³⁺ ions were released when the Cl⁻ solution was used as leaching electrolyte [20].

Also Cl⁻ ion could be an important factor enhancing Pb²⁺ and Ni²⁺ mobility in soil [21, 22].

The presence of Na⁺, K⁺ and Ca²⁺ as cations and Cl⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻ as anions, could be regarded to play a role in mobility of Pb²⁺ and Ni²⁺ ions [23, 24] and also of Cd²⁺ ions. The last could be explained by CdCl₂ formation.

In conclusion 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 shaken. The equilibrium being attained (after 24 h) the solid phase was filtered and the concentration before and after contact with the adsorbent. A measured volume (V ≈ 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 µmol/L for nickel, chrome and copper respectively, and between 50 and 500 µmol/L for lead. The bottles were placed in a mechanical stirrer and maintained at a constant temperature.

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

$$a = \frac{a_m b C_e}{1 + b C_e}$$  \hspace{1cm} (1)

or in the linear form:

$$\frac{1}{a} = \frac{1}{b C_m a_m} + \frac{1}{a_m}$$  \hspace{1cm} (2)

Table 1

<table>
<thead>
<tr>
<th>IONIC CONTENT OF CAMBIC CHERNOZEM [1]</th>
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<tbody>
<tr>
<td><strong>Humus, %</strong></td>
<td>2.9</td>
</tr>
<tr>
<td><strong>N total, %</strong></td>
<td>0.18</td>
</tr>
<tr>
<td><strong>P total, %</strong></td>
<td>0.09</td>
</tr>
<tr>
<td><strong>K total, ppm</strong></td>
<td>98</td>
</tr>
<tr>
<td><strong>Zn, ppm</strong></td>
<td>3.7</td>
</tr>
<tr>
<td><strong>Cu, ppm</strong></td>
<td>3.1</td>
</tr>
<tr>
<td><strong>Fe, ppm</strong></td>
<td>40.5</td>
</tr>
<tr>
<td><strong>Al, ppm</strong></td>
<td>170</td>
</tr>
<tr>
<td><strong>Mn, ppm</strong></td>
<td>4.5</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>5.4-5.6</td>
</tr>
<tr>
<td><strong>Volumetric weight, g/cm$^3$</strong></td>
<td>1.25</td>
</tr>
</tbody>
</table>

Fig. 1 The dependence of Pb$^{2+}$ concentration in solid phase, on concentration in liquid phase, $C_e$, at equilibrium

Fig. 2 The dependence of Cu$^{2+}$ concentration in solid phase, on concentration in liquid phase, $C_e$, at equilibrium

Fig. 3 The dependence of Cr$^{3+}$ concentration in solid phase, on concentration in liquid phase, $C_e$, at equilibrium

Fig. 4 The dependence of Ni$^{2+}$ concentration in solid phase, on concentration in liquid phase, $C_e$, at equilibrium
Table 2

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Langmuir</th>
<th>Freundlich</th>
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<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$a$</td>
</tr>
<tr>
<td>Plumb</td>
<td>0.9856</td>
<td>0.8684</td>
</tr>
<tr>
<td>Cupru</td>
<td>0.9997</td>
<td>0.316384</td>
</tr>
<tr>
<td>Crom</td>
<td>0.992214</td>
<td>1.144804</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.9832</td>
<td>2.646896</td>
</tr>
</tbody>
</table>

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

$$a = KC^{1/n}$$  (4)

where $K$ represents the equilibrium constant

$C$ – the concentration of adsorbate in liquid phase, $\mu$mol/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 $R^2$ (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 $\text{Pb}^{2+}$, $\text{Cu}^{2+}$, $\text{Cr}^{3+}$ and $\text{Ni}^{2+}$ was also studied. The studied pH interval was 4-7. For pH correction 0.01 M HNO₃ 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 increases with increasing pH. 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 $\text{Pb}^{2+}$, $\text{Cu}^{2+}$, $\text{Cr}^{3+}$ and $\text{Ni}^{2+}$ are found also in exchangeable form, suggesting that these metals are very mobile. So, the pH has an essential role in the adsorption process of the studied ions in argilaceous soil.

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 $a$, $b$, $K$ and $n$ respectively. The shapes of the adsorption curves and the values of $R^2$ put in evidence that the Langmuir isotherm characterises more exactly the adsorption process. The study of the influence of pH 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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Manuscript received: 21.07.2016