STUDY OF CHROMIUM SORPTION FROM AQUEOUS SOLUTION ONTO SOILS

L.V. PAVEL[1], **D. BULGARIU**[2],
Laura BULGARIU[1], **Maria GAVRILESCU**[1]

[1]"Gheorghe Asachi" Technical University of Iaşi,
Department of Environmental Engineering and
Management; email: *pvlpavel@yahoo.com*

[2]"Alexandru Ioan Cuza" University of Iasi,
Faculty of Geography and Geology, Department of
Geology and Geochemistry

The chromium (VI) sorption to the natural soils samples was investigated by batch and column tests. Soil samples were previously analyzed and characterized. The influence of physico-chemical key parameters such as the initial concentration of chromium in solution, soil quantity, pH and the temperature of the solution has been considered in batch tests. The adsorption data are tested for a number of kinetic and isotherm equations. In order to understand the adsorption mechanism, the kinetic parameters of adsorption of chromium (VI) onto the natural soils were determined. An evaluation of thermodynamic parameters on Cr (VI) adsorption onto soil was made. The value of activation energy (Ea) suggests that the rise of the solution temperature favors sorption of chromium (VI) onto the soil, and the sorption process might be by chemical adsorption. The results are used further to determine chromium bioavailability and the need for soil remediation, based on risk assessment, since Cr (VI) is a powerful epithelial irritant, and a confirmed human carcinogen.

***Key words**: chromium, sorption, soil, heavy metals*

Heavy metals are natural compounds in soil and they can not be destroyed. As essential elements, some heavy metals (cooper, selenium, zinc) are vital for human metabolism, but in high concentration they have a toxic effect [5].

Presence of chromium in soils is a result of both natural processes and human activities. Its toxicity depends on oxidation states, Cr(III) with a reduced mobility and low toxic potential (similarly with Al and Fe) and Cr(VI) very mobile and with a higher toxic potential, even at very low concentrations [1].

Breathing high levels of Cr(VI) can cause irritation to the nose, such as runny nose, nosebleeds, and ulcer and holes in the nasal septum. Ingesting large amount of Cr(VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage and even death [3,4].

Among the methods used to remove heavy metals from the environment, sorption and biosorption are studied in literature intensively in last decades [2,3].

The objective of this study was to investigate the Cr(VI) sorption and migration onto a natural soil and the maximum amount of Cr(VI) that can be loaded on this soil.

MATERIAL AND METHOD

The experiments were made using a natural soil as a sorbent. The soil samples were obtained from the metropolitan zone of Iaşi city. The soil samples were dried in air for about two weeks and afterwards at 105ºC for 6 hours. After drying the soil was sieved in order to obtain different particle size distribution (0.2 – 2 mm). Stock solution of Cr(VI) was prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) into distilled water.

Batch experiments were conducted in Erlenmeyer flasks, witch were agitated from time to time. Equilibrium studies were made using different initial concentrations of Cr(VI) between 30 and 1200 mg/L. Equilibrium sorption data were evaluated by Langmuir and Freundlich isotherm models. The soil dose was also variable between 10 and 500 g/L.

The Cr(VI) determination was performed spectrophotometrically using 1,5 diphenylcarbazide (λ=543nm). The liquid samples were filtrated with OlimPeak-Teknokroma filters (pore dimension 0.45 μm).

The experiments were conducted at room temperature (20ºC) and at non-adjusted pH solution. The results from this experiment were used to determine the uptake, q_e (mg/g), using equation (1):

$$q_e = \frac{(C_0 - C_e)\cdot V}{m} \qquad (1)$$

where: C_0 and C_e are concentration of Cr(VI) in solution (mg/L) at t=0 and $t=t_{eq}$, V – liquid volume (L), and m is soil amount (g).

The kinetic study was performed at initial concentrations of Cr(VI) between 30 and 120 mg/L.

RESULTS AND DISCUSSIONS

Soil particle size has a significant influence on pollutants sorption from aqueous solutions because of different distribution of active centres. In this study 5 fraction were used with particle dimensions of: <0.25; 0.25 – 0.4; 0.4 – 0.8; 0.8 – 2; >2 mm. In *Figure 1* it is presented the influence of particles size on Cr(VI) sorption. It can be seen that the uptake is higher on small size soil particles.

If the amount of soil is higher, then the quantity of Cr(VI) removed from aqueous solution is also higher (*Figure 2*). This is due to the fact that a different soil dose has a different number of sorption centres.

In *Figure 3* it is presented the influence of contact time on sorption process. It can be observed that in about 40 minutes the equilibrium is reached and after that, the final concentration remain constant.

In order to determine the sorption isotherm, the uptake of Cr(VI) was calculated for different initial concentration of Cr(VI) between 30 and 1200 mg/L (*Figure 4*).

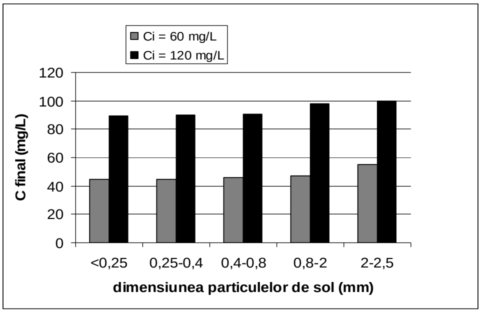

Figura 1. **The influence of soil particles size on Cr (VI) sorption onto soil**

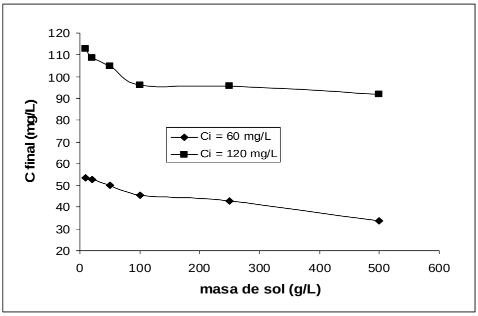

Figura 2 **The influence of soil mass on Cr (VI) sorption onto soil**

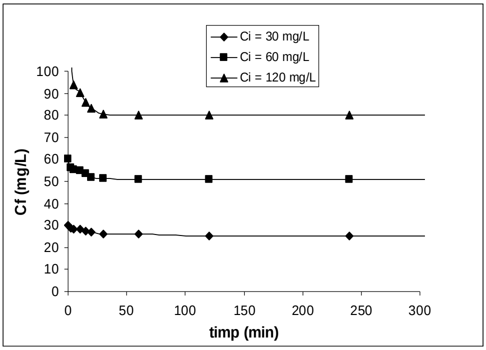

Figura 3 **The influence of contact time on Cr (VI) sorption onto soil**

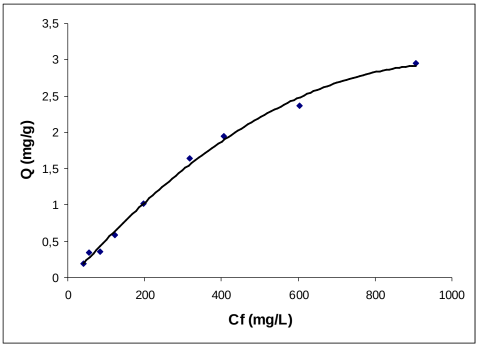

Figura 4 **The sorption isotherm of Cr (VI) on soil**

The sorption isotherm is a major tool to describe and predict the mobility of a substance in the environment. One of the most used types of isotherm is Langmuir model (equation 2):

$$\frac{q}{q_e} = \frac{K_{ads}C_e}{(1+K_{ads}C_e)} \qquad (2)$$

where: q_e – maximum chromium concentration retained on sorbent ($mg \cdot g^{-1}$), K_{ads} – Langmuir constant ($g \cdot L^{-1}$), C_e – chromium concentration at equilibrium.

Freundlich isotherm is another model used to describe the sorption phenomena (equation 3):

$$q=K_f(C)^{1/n} \qquad (3)$$

where: K_f and n are sorption parameters witch depend on temperature and the system chromium-soil.

The modeling of sorption equilibrium of Cr(VI) on soil was made using Langmuir and Freundlich equations in linear form (*Table 1*).

The Langmuir model describe better the sorption process of Cr(VI) on soil. The soil is assumed to have a limited sorption capacity q_m. All the adsorption sites are assumed to be identical, each site retains one molecule of Cr(VI) and all sites are energetically and sterically independent of the adsorbed quantity [6].

Table 1

Estimated parameters from linearization of Langmuir and Freundlich equations for sorption of Cr(VI) on soil

Isotherm	Linear Form	Estimated parameters		
Langmuir	$\frac{1}{q_e}=\frac{1}{q_m}+\frac{1}{K_L q_m}\frac{1}{C_e}$	R^2	q_m (mg g^{-1})	K_L (L mg^{-1})
		0.9920	5.750	0.00119
Freundlich	$\log q_e = \log K_F + \frac{1}{n_F}\log C_e$	R^2	n	K_F (mg $L^{1/n}$ g^{-1} $mg^{-1/n}$)
		0.9891	1.1143	0.00791

CONCLUSIONS

Sorption of Cr(VI) on soil depend on soil characteristics (particle size, soil dose) and chromium concentration in liquid phase.

From the sorption equilibrium study and the two models applied, the Langmuir isotherm describes better the retention of chromium ions on soil particles. The uptake of Cr(VI) on this soil is quite low (2mg/g), witch means that in the case of a high concentration of pollutant, this type of soil can retain only a small amount. Sorption equilibrium is reached in about 40 minutes, after that the concentration of Cr(VI) remains at the same value in liquid phase.

These results are important for bioavailability assessment of Chromium in soils, as well as for establishing the remediation strategy and technology.

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