The Adsorption of Cadmium and Zinc Ions from Waste Waters in Agricultural Argilaceous Soils

IRINA PINCOVSCHI[1], NICOLETA NEACSU[2], CRISTINA MODROGAN[3]*, MIRCEA STEFAN[2]

[1] University Politehnica of Bucharest, Department of Hydraulics, Hydraulic Machinery and Environmental Engineering, 1-7 Polizu Str., 011061, Bucharest, Romania

[2] University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Str., 011061, Bucharest, Romania

[3] University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Str., 011061, Bucharest, Romania

The adsorption of cadmium and zinc ions from waste waters in agricultural argilaceaus soils have been studied, using a thermodynamic method in order to put in evidence the influence of adsorption conditions on adsorption degree. The adsorption isotherms, Langmuir and Freundlich, have been used to describe the adsorption equilibrium. The experimental data put in evidence that Cd^{2+} ions are more adsorbable (about 300 μmol/g) than Zn^{2+} ones (about 200 μmol/g). The Langmuir isotherms reflect more exactly the adsorption process of both Cd^{2+} and Zn^{2+} ions, being recommended for thermodynamic parameters determination.

Keywords: industrial waste waters, Cd^{2+} and Zn^{2+} adsorption, agricultural argillaceous soils

The heavy metals are undestroyable elements, the most of them having toxic effects on living organisms when exceeding a certain concentration. Some heavy metals (like cadmium and zinc) may pose a risk to human health when transferred to the food chain.

The sources of heavy metals in soil are different. In the case of cadmium and zinc ions, soil contamination occurs by the addition of phosphate fertilizers, sewage sludge and especially metallurgical activities. [1-5]

Once in soil some of the metals would be persistent because of their immobile nature. Other metals however would be more mobile. This mobility must be taken into account when the food chain is concerned.

Pollution problem arise when heavy metals are mobilized into the soil solution and taken by plants.

The main factors influencing the adsorption of heavy metals in soils are the following: the *p*H, the soil organic matter (SOM) content, the ionic strength, the cation and anion index, the soil texture, the pore structure, the residual time and the temperature.

In general, sorption increases with increasing *p*H. The lower the *p*H value the more metal can be found in solution as a result of the increased proton concentration.

The Cd^{2+} and Zn^{2+} ions are found in exchangeable form, suggesting that these metals are relatively very mobile.

The soil organic matter (SOM) is very important for the retention of metals by soil solids, because of the humic acid (HA) presence; the complexation of HA at higher pH is responsible for dissolution of some metals from soil [6].

Naidu and Harter [7] reported that the role of organic acids in Cd^{2+} mobilization is especially important. Complexation of metals by organic ligands play an important role in controlling metal solubility. Metal-ligand complex stability generally decreases with pH reduction, reflecting the role of $RCOO^-$ in metal complexation. The ligands include low molecular weight organic acids like citric, oxalic, formic, acetic, succinic, malonic. Highest amount of Cd^{2+} was released by acetat and malate ones. To separate the *p*H effect from ligand ion effect it was found that at high *p*H values Cd^{2+}- ligand ion complexation was essential for the solubilisation of Cd^{2+}.

The amount of metals adsorbed decreases with increasing ionic strength [8]. It was underlined that, there was an increase of Zn^{2+} adsorption with *p*H elevation and a reduction of ionic strength of background electrolyte. Results showed that the metal ion was more strongly adsorbed at lower ionic strengths, while any increases in electrolyte concentration produce a decrease in metal adsorption. Thus, soils with higher ionic strength may have more risk of metal leaching from sevage sludge disposal than soil with lower ionic strength [9, 10].

The soil texture plays an important role in mobility of metal in soil. Texture reflects the particle size distribution of the soil and thus the content of fine particles like oxide and clay. The clay soil retains high amount of metal when compared to sandy soil.

The cation and anion index has a big importance in metal adsorption in soil. The anions can contribute in reducing heavy metal adsorption by the possible formation of negatively charged or neutral species like: MCl_2, MCl_3^-, MCl_4^-.

Cd^{2+} is known to form relatively stable Cl^- complexes, which greatly influence the mobility of metals in soils. The ability of Cl^- to maintain relatively high concentration of heavy metals in soil solution may produce favorable conditions for faster leaching of metals.

The mobility of Cd^{2+} in soil increases at higher Cl^- concentration. The effect of Cl^- on Cd^{2+} uptake could be explained by the presence of $CdCl_n^{2-n}$ species.

The presence of hydrous iron oxides and hydrous manganese oxides has an immobilizing affect of Cd^{2+} in soil [11, 12].Competing ions can have a marked effect on ion sorption by soils [13-15] the presence of Pb^{2+}can determine a decreasing of Cd^{2+} adsorption [17, 18]. Also, the effect of Cd^{2+} on plant metabolism could be reversed by Mn^{2+} presence in soil [19, 20].

* *email: c_modrogan@yahoo.com*

Humus, %	2.9	STAS 7184/21-82
N total, %	0.18	SR ISO 11261:2000
P total, %	0.09	STAS 7184/14-79
K total, ppm	98	STAS 7184/18-80
Zn, ppm	3.7	SR ISO 11047:1999
Cu, ppm	3.1	
Fe, ppm	40.5	
Al, ppm	170	
Mn, ppm	4.5	
pH	5.4-5.6	SR ISO 1039:1999
Volumetric weight, g/cm^3	1.25	SR ISO 11272:2000

Table 1
IONIC CONTENT OF CAMBIC CHERNOZEM [16]

Experimental part

The adsorption 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 attained (after 24 h) the solid phase was filtered and the concentration was measured.

A measured volume (V = 50mL) 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 Cd^{2+} and 50-5000 μmol/L for Zn^{2+}. The bottles were placed in a mechanical stirrer and maintained at a constant temperature.

In order to measure the cation concentration in liquid phase an Atomic Absorption Spectrometer, Zenit 700 Analytik 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 (cambic).

The main characteristics of cambic soil are presented in table 1.

Results and discussions

The sorption capacity of argilaceous soil concerning the Cd^{2+} and Zn^{2+} cations was studied. The results have been presented determining the equilibrium curves in coordinates *a*-C_e, *a* being the concentration, at equilibrium, of adsorbate in solid phase, in mmol/g and C_e – the concentration of adsorbate in liquid phase, in mmol/L (fig. 1 and 2).

The adsorption process of Cd^{2+} and Zn^{2+} in cambic soil could be theoretically characterized using an appropriate equation. The shape of two groups of isotherms 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 the adsorbed compound covalent bounds are developed and between the molecules of adsorbed compounds there are no interactions.

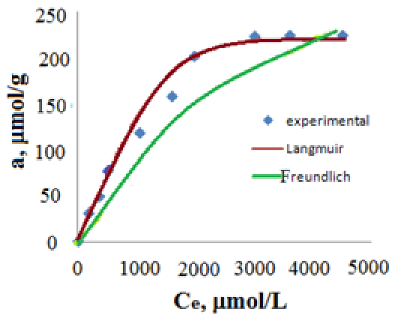

Fig. 1 The dependence of Zn^{2+} concentration in solid phase, **a** on concentration in liquid phase $\mathbf{C_e}$ at equilibrium

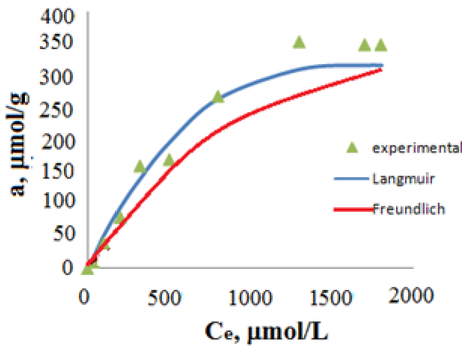

Fig. 2 The dependence of Cd^{2+} concentration in solid phase **a** on concentration in liquid phase $\mathbf{C_e}$ at equilibrium

The model is described by the following equation:

$$a = a_m \frac{bC}{1 + bC} \quad (1)$$

or in the linear form:

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

where:

a represents the concentration of adsorbate in solid phase at equilibrium, μmol/g.

a_m - the maximum adsorption capacity of adsorbate adsorbed in monolayer, μmol/g

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

b – the equilibrium constant.

Table 2
THE THERMODYNAMIC PARAMETERS a_m AND b, K AND n CARACTERISING THE ADSORPTION PROCESS Of Cd^{2+} AND Zn^{2+} IONS IN CAMBIC SOIL

Parameters	Langmuir			Freundlich		
	R^2	a	b	R^2	K	n
Zn^{2+}	0.9993	5.4710	0.0022	0.8848	1.8700	0.5920
Cd^{2+}	0.9973	1.8606149	0.0013904	0.9342	1.103986	0.789411

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

$$y = Ax + B \quad (3)$$

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

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

where:

K represents the equilibrium constant

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

n – empirical coefficient

The Langmuir and Freundlich equations have been used for modeling the adsorption process of metal ions in agricultural soils and for determination of equilibrium parameters a_m, b, K and n (table 2).

The experimental results presented in the figures 1 and 2 confirm that the Langmuir equation is more appropriate for modeling the adsorption process of metal cations in cambic soil.

The influence of *p*H on adsorption degree of Cd^{2+} and Zn^{2+} was also studied. The studied *p*H interval was 4-7. For *p*H correction 0.01 M HNO_3 and NaOH solutions were used. The results have been represented in coordinates *a*-*p*H, in equilibrium conditions, using the same technique (fig. 3 and 4).

From figures 3-4 results that sorption increases with increasing *p*H. The explanation is the following: the lower the *p*H the more metal ions are found in solution as a result of the increased proton concentration. Besides, Cd^{2+} and Zn^{2+} ions 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 both metals in cambic soil.

Conclusions

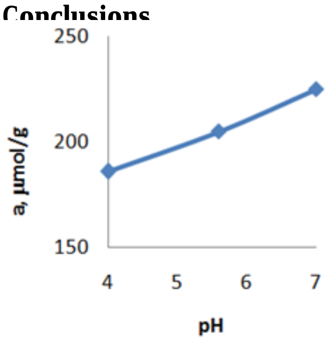

Fig. 3 The dependence of Zn^{2+} concentration in solid phase on *p*H (at equilibrium)

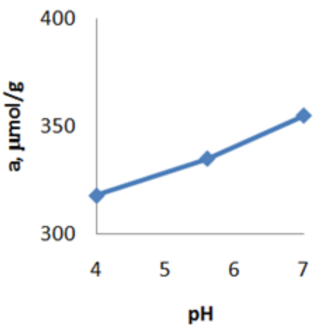

Fig. 4 The dependence of Cd^{2+} concentration in solid phase on *p*H (at equilibrium)

In this paper the adsorption of cadmium and zinc ions from waste waters in agricultural argillaceous soils have been studied. The adsorption isotherms Langmuir and Freundlich have been used to describe the adsorption process by calculating the adsorption parameters a_m and b. The shapes of the adsorption curves and the values of R^2 put in evidence that the Langmuir isotherm characterizes 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 *p*H. The explanation resides in the fact that the lower the *p*H more metal ions are found in solution as a result of the increased proton concentration.

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