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The Analysis of Heavy Metals Adsorption and Desorption Processes from Polluted Soils

Corneliu Bogatu[*], Adina Negrea[**], Giannin Mosoarca[**], Lavinia Lupa[**], Mihaela Ciopec[**]

[*] National R & D Institute for Industrial Ecology – ECOIND, Timisoara, P-ta Victoriei nr.2, phone/fax : 0256 2202369, e-mail: boggatu@yahoo.com , Romania

[**] Faculty of Industrial Chemistry and Environmental Engineering, University "Politehnica" Timişoara, Victoriei Square no.2, 300006, Romania, e-mail: giannin.mosoarca@chim.upt.ro

Abstract: Heavy metals adsorption in soils is a process which takes place in few hours, but their desorption is a difficult process. Adsorption efficiency depends on metallic cation, its concentration and humus content of soil. Maximum yields were determined for soil samples with higher content of organic matter, except that of Cr^{6+} : Cu^{2+} = 92 – 99.2 %, Zn^{2+} = 89.4 – 98.5 %, Cr^{3+} = 88 – 98 %, Ni^{2+} = 70.5 – 77.2 %; Cr^{6+} = 25.4 – 47.6 %. Mobilization yields of metallic ions depends on solid:liquid ratio and pH. Maximum yields were determined for the ratio 0.1 g/100 ml calcium chloride solution (0.1 M), 31.5 – 72.8 %, at pH = 4 and 19.3 – 51 %, at pH =6.

Keywords: heavy metals, adsorption, desorption, soil

1. Introduction

If natural functions of soil like those of buffer, filtration and transformation systems are used in extensive way, a number of phenomenon takes place: water pollution, soil pollution, pollutants accumulation in plants, especially of heavy metals. Geochemical processes which influence metals exchange at water-soil interface are adsorption and precipitation [1, 2, 3].

Heavy metals adsorption in soil is a process which takes place in few hours. When equilibrium is reached, the process is characterized by distribution coefficient, K_d , which is the ratio between metal concentrations from soild and liquid phases. Depending on specific conditions, K_d values ranged between 57 - 53000 mL/g [4, 5, 6].

The dependence of metals solubilization by their concentration in suspension, has important consequences. By decreasing of solid:liquid ratio, adsorption equilibrium of metals from soils and sediments may be turned to metal solubilization [7, 8, 9]. In this paper there are studied adsorption and desorption processes of Ni^{2+}, Cu^{2+}, Zn^{2+}, Cr^{3+} and Cr^{6+} in soil - water systems.

2. Materials and Methods

For the analysis of adsorption processes of Ni^{2+}, Cu^{2+}, Zn^{2+} (chlorides), Cr^{3+} (nitrate) and Cr^{6+} in soil-water systems (chromate), were used solutions with concentrations: 500 mg/L (1), 250 mg/L (2), 25 mg/L (3) and two samples of soil. Soil samples were characterized by the indicators: pH = 6.0, dried substance = 62 %, humus = 5.4 %, carbonate = 0.8 %, total chrome = 0.6 mg/Kg d.s., nickel = 2.7 mg/Kg d.s., copper = 16.5 mg/Kg d.s., zinc = 14.5 mg/Kg d.s., chernozem soil, sample A; pH = 6.3, dried substance = 71 %, humus = 2.1 %, carbonate = 3.5 %, total chrome = 0.5 mg/Kg d.s., nickel = 3.2 mg/Kg d.s., copper = 18 mg/Kg d.s., zinc = 19.2 mg/Kg d.s., carbonaceous soil, sample B.

Samples of dried soil, 20 g, were dissolved in 50 ml solution containing metallic ions under slow stirring, four hours, after which, equilibrium was reached. Water was separated by filtration, and soil samples were dried at 105^0 C, weighted and mineralized with aqua regia, for analysis of metallic ions by atomic absorption spectrophotometry. By taking into account concentrations of metallic ions from solutions when adsorption process was finishing, and those of initial solutions, adsorption yields were determined. Repartition coefficients, named also distribution constants, Kd, were determined by computing the ratios between concentrations of metallic ions adsorbed into soil samples and those remaining in solutions.

For analysis of metallic ions desorption from soil samples, were used samples in which ions were adsorbed as above, from solutions with 500 mg/L. The following solid-liquid ratios were used, 0.1 g : 100 mL, 0.5 g : 100 mL, 1 g : 100 mL; solutions of calcium chloride 0.1 M, at pH 4 and 6. Soil samples were introduced in calcium chloride solutions under stirring, for 6 hours. After solutions filtration, metal concentrations were determined; these were used for computing of yields of desorption process.

3. Results and Discussion

The obtained results, showed that the adsorption proces takes place in two steps: rapid step, in 30 minutes and slow step, in about 3 hours. In case of Cr^{3+} ion, 45 % from the initial quantity in solution (25 mg) was adsorbed in 30 minutes, for soil type A. In the next three hours, process is more slowly, and 43 % of initial quantity is adsorbed, fig. 1. Process is at equilibrium after 3.5 hours, when adsorption yield is 87.5 %. When solution concentration put in contact with 20 g soil is 25 mg/L, an improving of adsorption yield in rapid step took place, up to 61 %, and global yield was 98 %. In case of the other soil type (B) with a smaller content of humus, the following yields were determined for Cr^{3+}: 84.3 % (solution 1), 89 % (solution 2), and 91.5 % (solution 3).

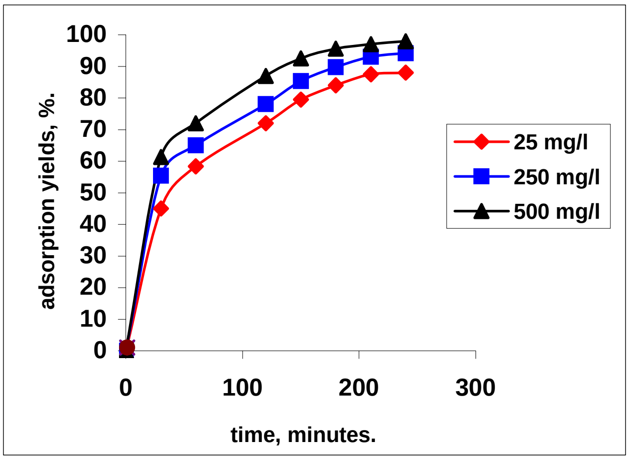

Figure 1. Dependence of adsorption yields versus contact time and concentration of chrome III solutions, for soil A

Adsorption process had smaller yields in case of Cr^6, for both soils: 25.4 % (1), 39 % (2) and 47.6 % (3), soil A, fig.2. For soil sample B, were determined the efficiencies: 34.8 % (1), 46.2 % (2) and 65.6 % (3), after 4 hours when equilibrium was established.

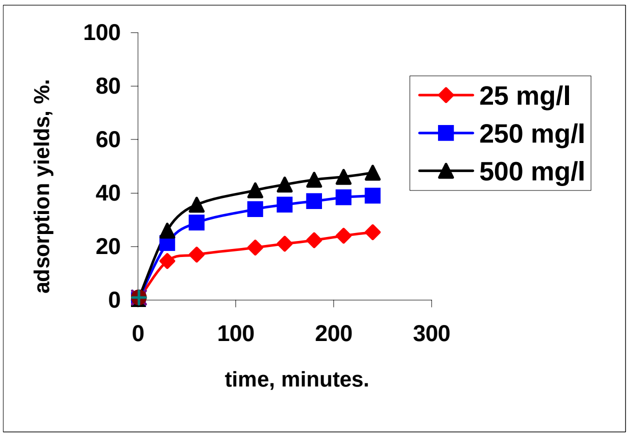

Figure 2. Dependence of adsorption yields versus contact time and concentration of chrome VI solutions, for soil A

Efficiencies of Cu^{2+} adsorption onto soil sample with a greater content of humus after four hours, are different for the two soil samples: 92 % (1), 96.4 % (2) and 99.2 % (3), soil A, fig.3 and 76.2 % (1), 81% (2) and 85.6 % (3), soil B, fig.4.

Zinc ions at equilibrium presented greater adsorption yields for soil with more organic content (A), 89.4 % (1), 92.5 % (2) and 98.5% (3), fig. 5, than soil with more carbonate, 72.5 % (1), 76.8% (2) and 82.4 % (3). The values are closed to those determined for copper. Process is similar for nickel**:** 70.5 %(1), 74 % (2), 77.2 % (3), soil A, fig. 5, and 51.8 % (1), 57.4 % (2), 65 %(3), soil B, fig. 6.

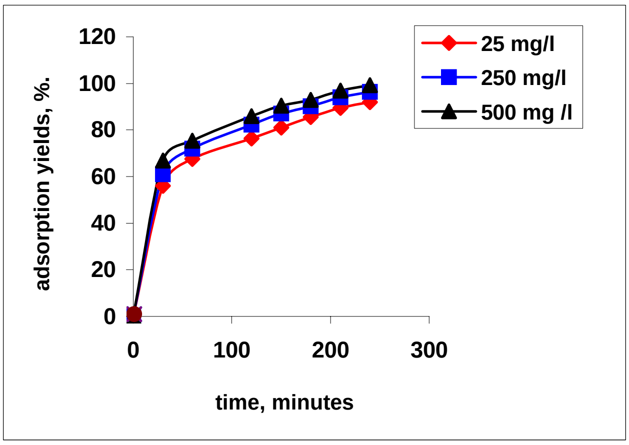

Figure 3. Dependence of adsorption yields versus contact time and concentration of Cu solutions, for soil A

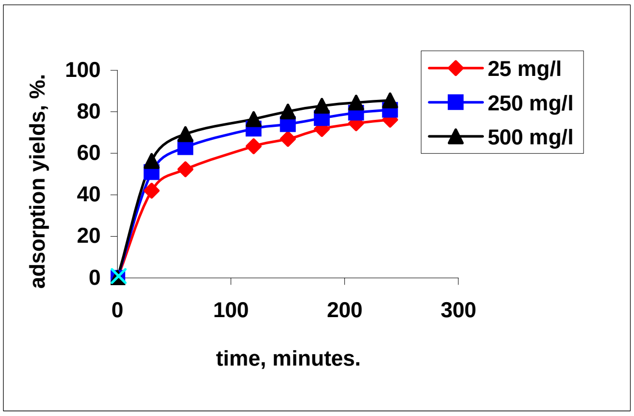

Figure 4. Dependence of adsorption yields versus contact time and concentration of Cu solutions, for soil B

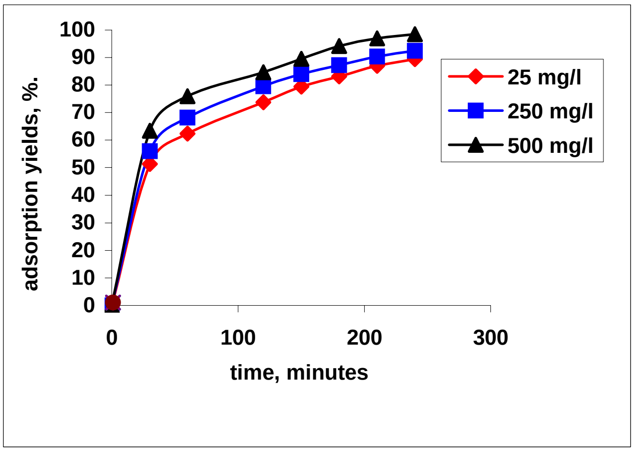

Figure 5. Dependence of adsorption yields versus contact time and concentration of Zn solutions, for soil A

The values of distribution coefficients, K_d, determined for the above mentioned soil - water systems, are presented in table 1. Their evolution versus operating conditions shows that adsorption process is more intense in case of diluted solutions.

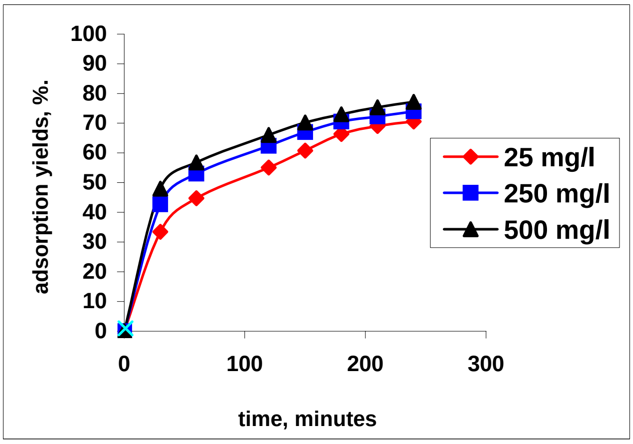

Figure 6. Dependence of adsorption yields versus contact time and concentration of Zn solutions, for soil B

The yields for metallic ions mobilization form soils, after their adsorption, depend on solid: liquid ratio, and pH. Thus, for ratio 0.1g /100 mL calcium chloride, were determined maximum yields for metallic ions desorption:

a) Zn = 72.8 %, Cu = 62 %, Cr (III) = 48.7 %, Ni = 34.5 % and Cr (VI) = 31.5 %, at pH = 4;

b) Zn = 51 %, Cu = 45 %; Cr (III) = 32.7 %; Ni = 22.6 %; Cr (VI) = 19.3 %, at pH = 6.

By decreasing of solid : liquid ratio, desorption efficiency decreased to both pH values; e.g., for ratio 1g soil/100 mL solution, the following yields were recorded:

a) Zn = 27.2 % ; Cu = 14 %; Cr (III) = 16.5 %; Ni = 11.6 % and Cr (VI) = 19 %, at pH = 4;

b) Zn = 8.2 %; Cu = 5.5 %; Cr (III) = 6.1 %; Ni = 6.8 %; Cr (VI) = 5.3 %, at pH = 6.

Maximum efficiencies were determined for solid : liquid ratio 0.1 g/100 mL, at pH 4.

TABLE 1. Evolution of repartition coefficients K_d (mL/g), versus metallic cation, soil type and solution concentration.

Cation	500 mg/L soil A	500 mg/L soil B	250 mg/L soil A	250 mg/L soil B	25 mg/L soil A	25 mg/L soil B
Cr^{3+}	7.2	5.3	16.2	8.5	48.5	11.3
Cr^{6+}	0.33	0.52	0.63	0.85	1.08	1.8
Cu^{2+}	11.3	3.1	26.4	4.1	122.7	5.8
Zn^{2+}	8.3	2.5	12.2	3.2	67.7	4.5
Ni^{2+}	2.3	1.06	2.8	1.2	3.3	1.8

TABLE 2. Dependence of desorption yields for Cu^{2+}, Ni^{2+}, Zn^{2+}, Cr^{3+} and Cr^{6+} versus solid : liquid ratio, by using calcium chloride solution 0.1 M, at pH 4 and 6.

solid:liquid ratio, g/mL	Cu^{2+}, η %		Zn^{2+}, η %		Ni^{2+}, η %		Cr^{3+}, η %		Cr^{6+}, η %	
	pH = 4	pH = 6	pH = 4	pH = 6	pH = 4	pH = 6	pH = 4	pH = 6	pH = 4	pH = 6
0.1:100	62	45	72.8	51	34.5	22.6	48.7	32.7	31.5	18.3
0.5:100	46,5	23.5	55	33.6	27	15	22	19.2	24	12
1:100	14	5.5	27.2	8.2	11.6	6.8	16.5	6.1	19	5.3

4. Conclusions

1. Adsorption process of metallic ions onto soil samples takes place in two steps:

- rapid step, in first 30 minutes of soil contact with solutions containing metallic ions;
- slow step, which takes place in 3 - 4 hours.

2. Process efficiency depends on metallic cation, its concentration and humus content of soil. Maximum yields were determined for soil samples with higher content of organic matter, except of Cr^{6+}, Cu^{2+} = 92 – 99.2 %, Zn^{2+} = 89.4 – 98.5 %, Cr^{3+} = 88 – 98 %, Ni^{2+} = 70.5 –77.2 %; Cr^{6+} = 25.4 – 47.6 %.

3. Mobilization yields of metallic ions depends on solid:liquid ratio and pH. Maximum yields were determined for the ratio 0.1 g/100 mL calcium chloride solution (0.1 M), 31.5 –72.8 % at pH = 4 and 19.3 – 51 %, at pH =6.

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