

## SIMULTANEOUS SORPTION OF CADMIUM, ZINC AND LEAD ON MONTMORILLONITE

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Simultaneous sorption on montmorillonite of Cd, Pb and Zn ions from their binary and ternary mixed solutions was studied, by the means of batch experiments performed at  $20.0 \pm 0.1^\circ$  C, at different background electrolyte concentrations. The initial concentration of each metal cation was 0.1 mmol/L and their mole ratio was 1:1 and 1:1:1, respectively. The adsorption degree increases with the pH values and decreases with the ionic strength of the solution. Lead appeared to have the strongest affinity for adsorption on montmorillonite. The sorption affinity sequence of  $Zn < Cd < Pb$  could be explained with hard-soft acid-base (HSAB) theory. For all ions, the weakly adsorbed quantities were greater than the ones retained by strong adsorption mechanisms. The Pb amounts retained on montmorillonite by strongly adsorption mechanisms were far greater than the ones of Cd and Zn.

### INTRODUCTION

Water pollution determined by toxic metals remains an important environmental issue, due to its major impact on the public health and on the economy. It has been reported that, in terms of the quantity of water needed to dilute such wastes to drinking-water standards, the annual toxicity of all metals mobilized exceeds the combined total toxicity of the radioactive and organic wastes generated each year.<sup>1</sup> In response to these problems, there has recently been growing interest in the development of materials capable of removing low concentrations of toxic metal ions from contaminated waters.

The existing methods for the removal of heavy metals from the environment can be grouped in biotic and abiotic. Biotic methods are based on the accumulation of heavy metals by plants or microorganisms; abiotic methods include physicochemical processes such as precipitation, coprecipitation, and adsorption of the heavy metal by a suitable adsorbent.<sup>2</sup>

Among the different adsorptive materials that have conventionally been used to capture metal

ions from solution are activated charcoal,<sup>3</sup> zeolites,<sup>4-5</sup> and clays.<sup>6-8</sup>

Clays are abundant and inexpensive aluminosilicate layered minerals that present adsorbent properties. Chemical species can interact with clays either by ion exchange<sup>9</sup> or through physical adsorption,<sup>10</sup> both being reversible processes. Among the mineral clays, smectites, especially montmorillonite, deserve special attention.

Montmorillonite is a widespread mineral of weathering formation and sediment,<sup>11</sup> which possesses a large specific surface area and a high content of structural-bound mobile ions (up to 1000 meq/kg). The high surface reactivity of this mineral is a direct consequence of its lamellar and defective structure. Montmorillonite is built from layers resulted by the condensation of one central octahedral sheet and two tetrahedral sheets. Isomorphous substitution of  $Si^{4+}$  by  $Al^{3+}$  confers to montmorillonite a permanent negative structural charge, which is compensated by the cations sorption on basal planes. Divalent cations sorbed on these planes form outer-sphere (OS) surface complexes<sup>12-13</sup> and are easily exchanged with solute cations from the nearby solutions. These cation exchange properties of the montmorillonite are pH-dependent.<sup>14</sup>

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The ability of mineral clays for cation exchange has been used to treat metal contaminated waste waters<sup>15-22</sup> or for adsorbing organic<sup>23-25</sup> and inorganic pollutants.<sup>25-27</sup>

For the removal of metal species by adsorptive techniques the use of mineral clays has been investigated by many researchers, because of their high specific surface area, cation exchange capacity and adsorption capacity.

There are many types of mineral clays that have been studied for their capacity to remove heavy metals from aqueous solutions, for example: kaolinite,<sup>17,22</sup> bentonite,<sup>16</sup> montmorillonite,<sup>15,19,20,21</sup> illite,<sup>28</sup> hectorite,<sup>29</sup> sepiolite,<sup>2</sup> beidellite.<sup>28</sup>

The results of the studies showed that the sorption process of heavy metal cations from aqueous solutions depends on: type of heavy metal cation, type of mineral clay, size of mineral clay particles, solid/liquid ratio, pH of solution, solution's ionic strength, initial concentration of the metal cations, interaction time, temperature, the presence of competitive species.

In the same time it has been observed that, generally, metals adsorption isotherms have a high affinity-Langmuir character.<sup>2, 15, 16, 20, 21</sup> There were reported only few cases when adsorption data were fitted to a Freundlich isotherm.<sup>16, 21</sup>

The maximum amounts of heavy metal sorbed by clays (sorption capacity), at equilibrium, depend, especially, on the type of mineral clay and metal cation, but also on the sorption process parameters. For instance, Schlegel *et al.*<sup>29</sup> reported 27.5 · 10<sup>-3</sup> mmol Co (II)/ g hectorite, Celis *et al.*<sup>2</sup> 280 mmol Pb (II)/g montmorillonite and 170 mmol Hg (II)/ g sepiolite, Ștefan *et al.*<sup>20</sup> 370 mmol Pb (II)/ g montmorillonite and 320 mmol Cd (II)/ g montmorillonite, Bhattacharyya and Gupta<sup>21</sup> 290 mmol Cd (II)/ g montmorillonite and 484 mmol Co (II)/ g montmorillonite, Omar *et al.*<sup>22</sup> 545 mmol Pb (II)/ g kaolinite.

The reactions with reagents containing metal-chelating functionalities have been explored in an effort to enhance the heavy metal binding capacities of clay minerals and their selectivity to the type of metal.<sup>2, 30, 31</sup> For instance, covalent grafting of ligands containing the thiol (-SH) functionality has been shown to improve the loading capacities and affinities of clay minerals for Hg(II) ions.<sup>2,30</sup>

Organoclays (*i.e.*, natural clay minerals with their original inorganic exchangeable cations replaced with organic cations) have been shown to be excellent adsorbents for different kinds of organic molecules. Accordingly, they have been proposed for decontamination of soils and water

contaminated with organic pollutants.<sup>32-35</sup> In contrast, organoclays have received limited interest as adsorbents of heavy metals, primarily because the organic cations most commonly used for their synthesis have been synthetic alkylammonium-type cations, which compete with metals for adsorption sites on the clay mineral surfaces and lack organic functional groups capable of interacting with heavy metals.<sup>36</sup>

Recent studies have shown that the presence of certain functionalities (-COOH, -SH) in the alkylammonium cation can provide the resulting organoclays with affinity for heavy metal ions.<sup>2,37</sup>

Bhattacharyya and Gupta<sup>21</sup> have reported that acid activation of montmorillonite increases the adsorption capacity for the metal cations (Cd(II), Co(II), Cu(II), Ni(II), and Pb(II))

Generally, heavy metal sorption experiments have occurred in single-cation systems.

This study aims to the simultaneous sorption on montmorillonite of Cd, Pb and Zn from their binary and ternary mixed solutions.

## RESULTS AND DISCUSSION

### The influence of pH on the sorption of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> from binary and ternary systems

The Fig. 1 presents the dependence of the metal cations adsorption degree on pH for binary Cd-Pb, Cd-Zn, and Pb-Zn mixed solutions.

The removal of Zn(II), Cd(II) or Pb(II) from their mixed solutions by mineral clay was pH dependent. In the Pb-Cd and Pb-Zn system, the sorption degree of Pb on montmorillonite was greater than the ones of Cd and Zn throughout the entire pH range. In the Cd-Zn system, the percentage of adsorbed Cd was greater than the one of Zn throughout the entire pH range.

### The influence of ionic strength

For the Pb-Cd-Zn system, the experiments were performed at two ionic solution strengths, corresponding to concentrations of 0.01M and 0.1M NaNO<sub>3</sub>, respectively.

The dependence of metal cations sorption degree on pH for ternary systems is illustrated in Fig. 2. Although the cation amounts adsorbed by Na-montmorillonite varied, a common pH-dependent trend was observed. The sorption degree of Pb was greater than the ones of Cd and Zn throughout the entire pH range.

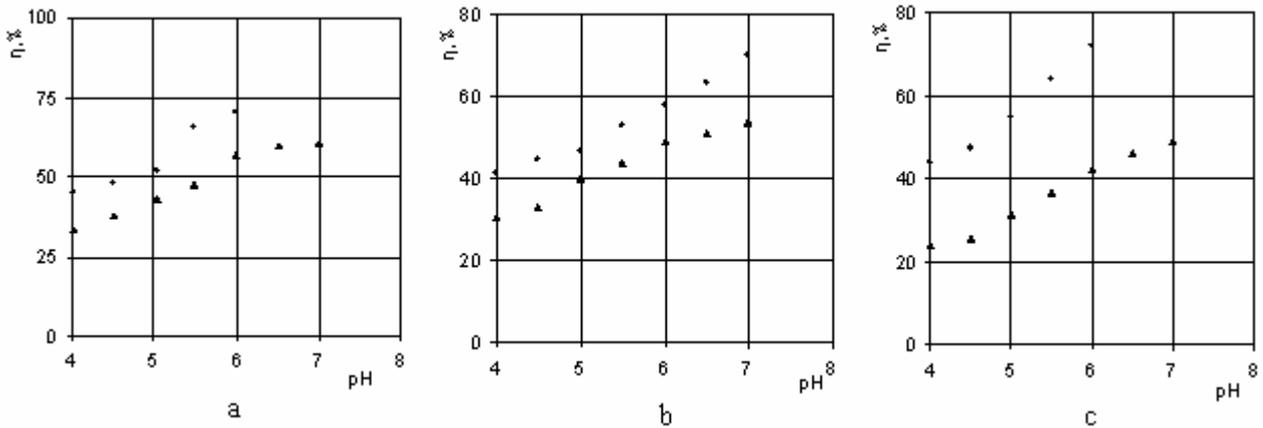


Fig. 1 – The dependence of sorption degree at equilibrium on pH in binary system;  $C_I = 0.1$  mmol/L;  $T = 20.0 \pm 0.1^\circ\text{C}$ ;  $I = 0.01\text{M NaNO}_3$ ;  $C_M = 1\text{g}\cdot\text{L}^{-1}$

a) Cd-Pb system ● Pb, ▲ Cd; b) Cd-Zn system ● Cd, ▲ Zn; c) Pb-Zn system ● Pb, ▲ Zn.

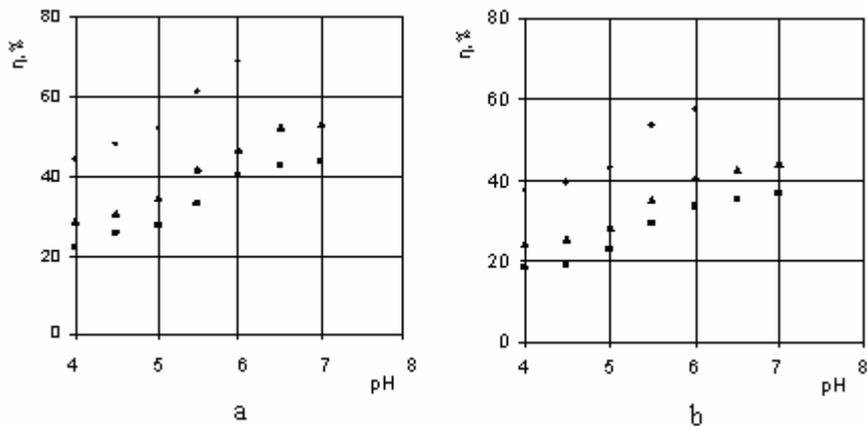


Fig. 2 – The dependence of sorption degree at equilibrium on pH in Cd-Pb-Zn system for different solution ionic strength;  $C_I = 0.1$  mmol/L;  $T = 20.0 \pm 0.1^\circ\text{C}$ ;  $C_M = 1\text{g}\cdot\text{L}^{-1}$ ; ● Pb, ▲ Cd, ■ Zn

a)  $I = 0.01\text{M NaNO}_3$ ; b)  $I = 0.1\text{M NaNO}_3$ .

In the ternary system the adsorption of total metal quantities is greater than the one corresponding to the binary systems. The amounts of Cd and Zn adsorbed on mineral clay from the ternary system are nevertheless lower than the ones retained from binary systems. The amounts of Pb sorbed by montmorillonite from binary or ternary mixed solutions were practically the same – not affected by the supplementary competing metals.

The sorption experiments in ternary systems at different background electrolyte concentrations showed that the amounts of heavy metal adsorbed on Na-montmorillonite were higher at a lower ionic strength of the solution.

### The adsorbent selectivity

The distribution ratio,  $D$ , is defined as the ratio of the fraction of added metal that is adsorbed to

the fraction of the added metal remaining into solution. A plot of  $\ln D$  versus pH is called a Kurbatov plot. The pH at which  $D=1$  – where 50% of the added metal is adsorbed and 50% is still inside the solution – is designated as  $\text{pH}_{50}$ .<sup>38</sup> The  $\text{pH}_{50}$  values are a relative measure of an adsorbent selectivity for a particular series of bivalent metal cations; the smaller the  $\text{pH}_{50}$  value, the more selective is the adsorbent towards the metal cation<sup>39</sup>.

Figs. 3 and 4 present the Kurbatov plots for all the studied systems and the obtained  $\text{pH}_{50}$  values are indicated in Table 1. A comparison of  $\text{pH}_{50}$  values of different sorption systems indicates that the selectivity of montmorillonite for metal cations increases in the order:  $\text{Zn} < \text{Cd} < \text{Pb}$ .

Puls and Bohn explained the selectivity trends by examining the metals and clays hard-soft acid base (HSAB) behaviour.<sup>40</sup> The HSAB principle states that hard Lewis acids prefer to complex or

react with hard Lewis bases and soft acids prefer to complex or react with soft bases. Mineral clays seem to behave as soft bases<sup>41</sup> while, on the basis of the Minoso softness parameter,<sup>42</sup> metal softness decreases in the order:  $Pb > Cd > Zn$ , and

montmorillonite selectivity for metal cations should follow the same sequence according to the HSAB principle. Therefore, the selectivity of montmorillonite for Zn, Cd, and Pb as observed in this study match well with the HSAB theory.

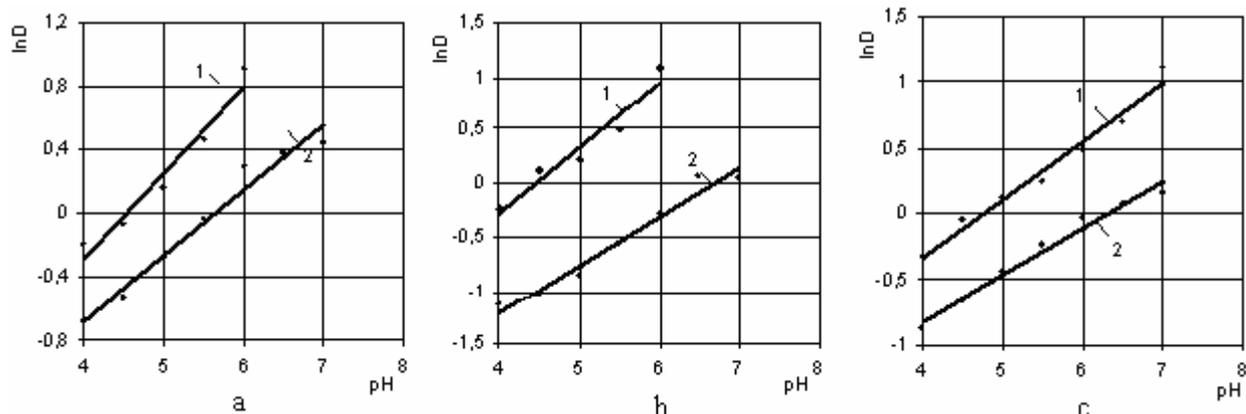


Fig. 3 – Kurbatov plots for binary systems  
a) Cd-Pb system; 1-Pb; 2-Cd; b) Pb-Zn system; 1-Pb; 2-Zn; c) Cd-Zn system; 1-Cd; 2-Zn.

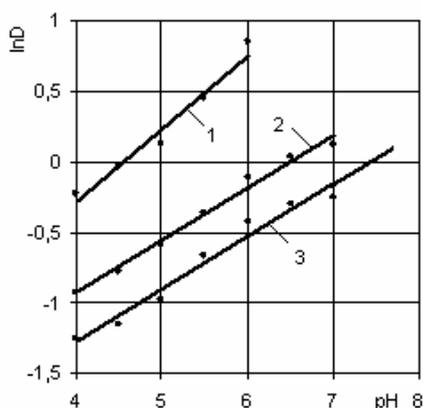


Fig. 4 – Kurbatov plots for the Zn-Cd-Pb ternary system 1-Pb; 2 Cd; 3-Zn.

Table 1

$pH_{50}$  values for the metal cations sorption on Na-montmorillonite from binary and ternary systems determined for a solution ionic strength  $I = 0.01M NaNO_3$

Cation	System	$pH_{50}$
$Zn^{2+}$	Zn-Cd-Pb	7.40
$Cd^{2+}$	Zn-Cd-Pb	6.22
$Pb^{2+}$	Zn-Cd-Pb	4.60
$Zn^{2+}$	Zn-Cd	6.31
$Cd^{2+}$	Zn-Cd	4.76
$Zn^{2+}$	Zn-Pb	6.55
<b><math>Pb^{2+}</math></b>	Zn-Pb	4.46
$Cd^{2+}$	Cd-Pb	5.65
$Pb^{2+}$	Cd-Pb	4.54

### Partitioning between strong and weak adsorption

The adsorbed heavy metals were separated into strongly and weakly bound forms as described in the experimental part. The results are presented in Fig. 5.

The totally adsorbed (TA) and strongly adsorbed (SA) amounts of Zn, Cd and Pb, as well

as the ratio SA/TA increase with the pH values for the entire range studied and depend on the metal kind.

The strong adsorption of Pb on montmorillonite is far more pronounced than that the one of Cd or Zn. This may be the reason of the selectivity differences, the weakly adsorbed quantities being about the same.

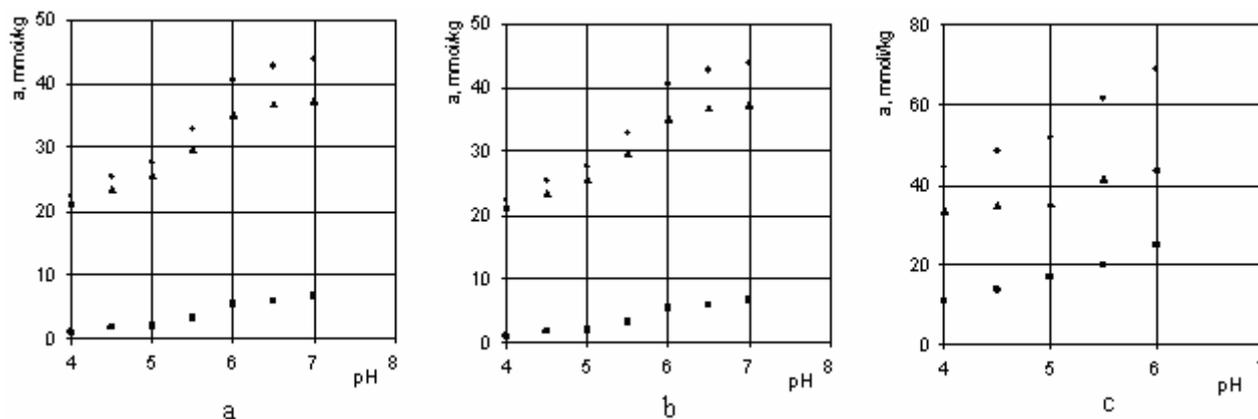


Fig. 5 – The dependence of heavy metal solid phase concentration on pH at equilibrium;  $C_i = 0.1 \text{ mmol/L}$ ;  $T = 20.0 \pm 0.1^\circ\text{C}$ ;  $I = 0.01\text{M NaNO}_3$ ;  $C_M = 1\text{g L}^{-1}$

a) ● Zn totally adsorbed; ▲ Zn weakly adsorbed; ■ Zn strongly adsorbed; b) ● Cd totally adsorbed; ▲ Cd weakly adsorbed; ■ Cd strongly adsorbed; c) ● Pb totally adsorbed; ▲ Pb weakly adsorbed; ■ Pb strongly adsorbed.

The adsorption of all three metals on mineral clay was quite significant even at low pH values. This observation along with the desorption data suggest that Cd and Zn adsorption in the low pH range could be concentrated on permanently electrically charged sites – where the protons could exert little competition. The desorption study of  $\text{Pb}^{2+}$  suggests that even at low pH, in addition to being adsorbed on the permanent charge sites, Pb might have been adsorbed on the hydroxyl groups on the of Na-montmorillonite edges.

At higher pH values, the increasing difficulties in all heavy metals desorption could result from the formation of stronger complexes and/or precipitates.

The sorption behavior of the Na-montmorillonite could be explained by a combination of cation exchange, especially at low pH, when weak adsorption occurs, and specific binding due to surface complexation (strong adsorption) at higher pH. The pH dependent charge is located at the edge sites, where the surface hydroxyl groups can be protonated or deprotonated, depending on the pH of solution. The adsorption of heavy metal cations by hydroxyl groups is governed by covalent binding and therefore is chemically specific.<sup>43-44</sup>

### EXPERIMENTAL

The adsorbent used in this study was Na-montmorillonite, with 99% of the clay particles < 10  $\mu\text{m}$  as was supplied by I.C.P.M “MINESA - S.A.” Cluj Napoca.

The cation exchange capacity of the mineral clay (CEC) measured at pH 6 by  $\text{Cs}^+$  exchange,<sup>45</sup> was equal to  $0.92 \text{ meqg}^{-1}$ . Specific surface area (SSA) of montmorillonite was obtained by  $\text{N}_2$  adsorption at 77K using a Carlo Erba Sorptomatic equipment. By applying the BET method, the calculated SSA was  $72.4\text{m}^2\text{g}^{-1}$ .

Binary and ternary mixed aqueous solutions were prepared from the nitrate salts of the metals,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$  (all p.a. – Fluka). The initial concentration of each metal cation was  $0.1\text{mmol/L}$  and the metals ratios in the binary and ternary systems were 1:1, and 1:1:1, respectively. Exact concentrations of the stock solutions were determined by flame atomic absorption spectrometry. All metal solutions were diluted to the required concentrations with redistilled water.  $\text{NaNO}_3$  has been used as background electrolyte. In all the Zn, Cd and Pb sorption experiments, the quantity of added Na-montmorillonite (the solid/liquid ratio) was  $C_M = 1\text{g L}^{-1}$ . The batch experiments were performed at  $20.0 \pm 0.1^\circ\text{C}$  using glass vessels immersed in a thermostatic water bath.

Twenty milligrams of Na- montmorillonite were mixed with 10 mL of  $2 \cdot 10^{-2} \text{ M NaNO}_3$  solution. Then, 10mL of binary or ternary metal aqueous solutions were added and the vessel content was vigorously mixed. The pH was varied from about 4 to 7 unities. The lower limit was imposed by the possible dissolution of Na-montmorillonite (at  $\text{pH} < 4$ ). The upper pH limit was imposed by the necessity to avoid the

precipitation of pure or mixed Zn, Cd or Pb carbonates or hydroxides (at pH > 6.5 for Pb<sup>2+</sup>; pH > 7.9 for Zn<sup>2+</sup>; pH > 7.5 for Cd<sup>2+</sup>).<sup>46</sup>

The pH values were adjusted by adding small volumes of 10<sup>-2</sup> M NaOH or 10<sup>-2</sup> M HNO<sub>3</sub> solutions and monitored by the means of a pH electrode (Metrohm 6.0204.100) connected to a pH meter (Metrohm 713). The electrode was calibrated with buffer solutions (Merk, titrisol). A rotating magnetic bar ensured vigorous stirring of the suspension for equilibration during interim pH adjustments.

According to a previous kinetic study a 24-h reaction period – with continuous stirring – was chosen in order to reach the equilibrium. After the equilibrium was reached, the clay was separated from solutions using a Beckman J-2-21 laboratory centrifuge at 10000 rpm for 30 minutes. The supernatant heavy metals concentration was determined by atomic absorption spectroscopy (Perkin-Elmer 1100B atomic absorption spectrometer). The amount of adsorbed metal was calculated as difference between the initial and final solution concentration.

For the experiments aiming to establish the partitioning of the adsorbed metals, after clay-solution separation, a controlled washing procedure<sup>47</sup> using 10<sup>-2</sup> M NaNO<sub>3</sub> solution was applied. First, a 10 mL aliquot of the removed supernatant solution has been replaced by 10 mL of 10<sup>-2</sup> M NaNO<sub>3</sub>. The clays resulted from the metal sorption experiments were then quickly introduced in this new solution, homogenized again and immediately centrifuged. The resulted supernatant solution was taken for the determination of the cation concentration. The amount of the metal still retained on the clay after this procedure was defined as strongly adsorbed. The weakly adsorbed (WA) metal quantity was obtained from the difference between the total adsorbed metal (TA) and the strongly adsorbed metal (SA). All measurements were run in duplicate. The reported values represent the media values.

## CONCLUSIONS

This study presents for the first time, the sorption behavior of Zn(II), Cd(II) and Pb(II) from their mixed (binary and ternary) solutions on a Romanian mineral clay (sodium montmorillonite with 99% of the clay particles < 10 μm).

The removal degree of Zn(II), Cd(II) or Pb(II) from their mixed solutions by mineral clay was pH dependent. The sorption degree of Pb was greater than the ones of Cd and Zn throughout the entire pH range. The amounts of heavy metal adsorbed on Na-montmorillonite were higher at a lower ionic strength of the solution. The pH<sub>50</sub> values determined from the Kurbatov plots indicate that the selectivity of montmorillonite for metal cations increase in the order: Zn < Cd < Pb, matching the order predicted by the HSAB theory. The weakly adsorbed quantities are greater than the ones retained by strong adsorption mechanisms, but the Pb quantities strongly adsorbed are far greater than that the ones of Cd or Zn. The influence of ionic strength on sorption process along the desorption data suggest that montmorillonite can adsorb heavy

metals via ion exchange reaction, especially at lower values of pH, and by formation of inner-sphere complexes at the clay particle edges.

Soil minerals are often negatively charged and similar effects as observed for montmorillonite are expected, meaning that a mobilizing effect should occur for Zn, Cd and Pb only in soil with high pH values.

## REFERENCES

1. J.O. Nriagu and J.M. Pacyna, *Nature*, **1988**, 333, 134-139.
2. R. Celis, M. C. Hermosin and J. Cornejo, *Environ. Sci. Technol.*, **2000**, 34, 4593-4599.
3. S.D. Faust and O.M. Ali, "Chemistry of Water Treatment", Butterworth, Boston, 1983, p. 114.
4. C.P. Huang and O.J. Hao, *Environ. Technol. Lett.*, **1989**, 10, 863-874.
5. M.J. Zamzow, B.R. Eichbaum, K.R. Sandgren and D.E. Shanks, *Sep. Sci. Technol.*, **1990**, 25, 1555-1569.
6. S. U. Aja, *Clays Clay Miner.*, **1998**, 46, 103-109.
7. T. Vengris, R. Binkienė and A. Sveikaukaitė, *Appl. Clay Sci.*, **2001**, 18, 183-190.
8. M. Cruz-Guzman, R. Celis, M. C. Hermosin, W. C. Koskinen, E. A. Nater and J. Cornejo, *Soil Sci. Soc. Am. J.*, **2006**, 70, 215-221.
9. L. Mercier and C. Detellier, *Clays Clay Miner.* **1994**, 42, 71-76.
10. T. Bandosz, J. Jagiello, B. Andersen and J. Schwartz, *Clays Clay Miner.*, **1992**, 40, 306-310.
11. M. B. McBride, "Environmental Chemistry of Soils", Oxford University Press: Oxford, 1994, p.207.
12. M. B. McBride, *Clays Clay Miner.*, **1982**, 30, 200-206.
13. F. Muller, G. Benson, A. Manceau and V.A. Dits, *J. Phys. Chem. Minerals*, **1997**, 24, 159-166.
14. L. Charlet, P. W. Schindler, L. Spadini, G. Furrer and M. Zysset, *J. Aquatic Sci.*, **1993**, 55, 291-297.
15. M. F. Brigatti., F. Corradini, G. C. Franchini, S. Mazzoni and L. Poppi, *Appl. Clay Sci.*, **1995**, 9, 383-395.
16. G. Bereket, A. Z. Aroguz and M.Z. Ozel, *J. Colloid Interface Sci.*, **1997**, 187, 338-343.
17. M. J. Angove, B. B. Johnson and J. D. Wells, *Colloids and Surfaces*, **1997**, 126, 137-147.
18. M. F. Brigatti., C. Lugli and L. Poppi, *Appl. Clay Sci.*, **2000**, 16, 45-57.
19. M.Ștefan, D. S. Ștefan and R. Popescu, *Sci. Technol. Environ. Protection*, **2004**, 11,61-70.
20. M.Ștefan, D. S. Ștefan and R. Popescu, *Sci. Technol. Environ. Protection*, **2004**, 11, 71-80.
21. K. G. Bhattacharyya and S. S. Gupta, *J. Colloid Interface Sci.*, **2007**, 310, 411-424.
22. W. Omar and H. Al-Itawi, *Appl. Sci. Am. J.*, **2007**, 4, 502-507.
23. K.Takimoto, K. Ito, T. Mukai, and M. Okada, *Environ. Sci. Technol.*, **1998**, 32, 3907-3912.
24. G. Xia, and W.P. Ball, *Environ. Sci. Technol.*, **1999**, 33, 262-269.
25. M. Ștefan, "Sorbtia poluanților pe minerale argiloase", Ed. Printech, București, 2007, p. 201.
26. B. A. Manning and S. Goldberg, *Soil Sci. Soc. Am. J.*, **1996**, 60, 121-131.

27. B. A. Manning and S. Goldberg, *Clays Clay Miner.*, **1996**, 44, 609–623.
28. E. H. Rybicka, W. Calmano and A. Breeger, *Appl. Clay Sci.*, **1995**, 9(5), 369-381.
29. M. L. Schlegel, L. Charlet and A. Manceau, *J. Colloid. Interf. Sci.*, **1999**, 220, 392-405.
30. L. Mercier and C. Detellier, *Environ. Sci. Technol.*, **1995**, 29, 1318-1323.
31. L. Mercier and L. Pinnavaia, *Environ. Sci. Technol.*, **1998**, 32, 2749-2754.
32. M. C. Hermosín and J. Cornejo, *Chemosphere*, **1992**, 24, 1493–1503.
33. Celis, R., W.C. Koskinen, A.M. Cecchi, G.A. Bresnahan, M.J. Carrizosa, M.A. Ulibarri, I. Pavlovic and M.C. Hermosín, *J. Environ. Sci. Health*, **1999**, B 34, 929–941.
34. Carrizosa, M.J., W.C. Koskinen, M.C. Hermosín and J. Cornejo. *Appl. Clay Sci.* **2001**, 18, 223–231.
35. M. S. Andrades, M.S. Rodríguez-Cruz, M.J. Sánchez-Martín and M. Sánchez-Camazano, *Intern. J. Environ. Anal. Chem.*, **2004**, 84, 133–141.
36. J. J. Lee, J. Choi and J.W. Park, *Chemosphere*, **2002**, 49,1309–1315.
37. G. Sheng, S.H. Xu and S.A. Boyd, *Soil Sci. Soc. Am. J.*, **1999**, 63, 73–78.
38. U. K. Saha, S. Taniguchi and K. Sakurai, *Soil Sci. Soc. Am. J.*, **2001**, 65, 694-703.
39. A.M.L. Kraepel, K. Keller and F. M.M. Morel, *J. Coll. Interf. Sci.*, **1999**, 210, 43-54.
40. W.R. Puls and H.L. Bohn, *Soil Sci. Soc. Am. J.*, **1988**, 52, 1289-1292.
41. P. J. Sullivan, *Soil Sci. J.*, **1977**, 124, 117-121.
42. M. Minoso, E. Ochiai, I. Sayto and Y. Yoneda, *J. Inorg. Nucl. Chem*, **1967**, 29, 2685-2691.
43. R. Van Bladel, H. Halen and P. Cloos, *Clay Miner.*, **1993**, 28, 33-38.
44. J. M. Zachara, S.C. Smith, Ch. T. Resch and Ch. E. Cowan, *Soil Sci. Soc. Am. J.*, **1992**, 56, 1074-1084.
45. S.J. Anderson and G. Sposito, *Soil Sci. Soc. Am. J.* **1991**, 55, 1569-1576.
46. R. E. Smith and A.E Martell, “Critical Stability Constants”, Vol.6: 2<sup>nd</sup> supplement, Plenum Press, New York, 1989, p.125.
47. K.G. Tiller, J. Gerth and G. Bruemmer, *Geoderma*, **1984**, 34, 1-13.

