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Adsorption of Heavy Metals on Na-Montmorillonite. Effect of Ph and Organic Substances

Khadjibayev Diyor Asadullaevich
Associate Professor of Jizzakh Polytechnic Institute

Umarov Shavkat Isomiddinnovich
Associate Professor of Jizzakh Polytechnic Institute

Abstract:

Clays (especially montmorillonite and bentonite) are widely used as barriers in landfills to prevent contamination of subsoil and groundwater by leachates containing heavy metals. For this reason it is important to study the adsorption of metals by these clays. The sorption of seven metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) on Na-montmorillonite was studied as a function of pH and in the presence of ligands, forming complexes of different stabilities with the metals of interest. The continuous column method was used as it better simulates natural conditions. The total capacity of Na-montmorillonite towards these metals was determined. The pH variations influence to a higher extent the concentrations of Cu, Pb and Cd in the effluent. Moreover the results suggest that complex formation hinders the sorption of the metals on the clay, with an increasing influence in the order: Mn p Pb p Cd p Zn o Ni o Cu o Cr. The evaluation of the total capacity of Na-montmorillonite shows that this clay is a good sorbent towards all examined metals.

Keywords: Na-montmorillonite; Heavy metals; Adsorption; Metal complexes; Breakthrough.

Introduction.

The concentration and the mobility of heavy metals in soils and sediments have been widely studied in the last decades [1,2]. Although many heavy metals are neces- sary in small amounts for the normal development of the biological cycles, most of them become toxic at high concentrations. Heavy metals are introduced into the environment through natural phenomena and human activities, such as agricultural practices, transport, industrial activities and waste disposal [3].

Clay linings have been used as barriers in landfills to prevent contamination of groundwater and subsoil by leachates containing metals. Generally, these linings are constituted of bentonite and, in particular, montmor illonite. These clays are chosen to avoid pollutant release into the environment owing to their high specific surface areas, low cost and ubiquitous presence in most soils [4]. Montmorillonite can adsorb heavy metals via two different mechanisms: (1) cation exchange in the interlayers resulting from the interactions between ions and negative permanent charge and (2) formation of inner-sphere complexes through Si–O and Al-O groups at the clay particle edges [5–7]. Both mechanisms are pH dependent because in acid conditions (pH **o** 4) most silanol and aluminol groups are protonated; therefore, in particular for the latter, an acidification can lead to an increase in mobility of metals bound to soil [8]. For this reason, it is necessary to improve the knowledge of the effect of pH on the sorption capacity of montmorillonite in soil–solution system.

The continuous column method, instead of a conven- tional batch technique, was used to understand the effect of pH and of the presence of ligands able to originate metal complexes on the sorption capability of mon- tmorillonite. Batch technique, in fact, is very useful to study the reaction mechanisms happening at the soil/ water interface but has the following limitations: solubilisation of soil components due to soil sample agitation and soil/solution ratios very different from those existing in natural systems [9]. The used technique, not having these disadvantages, better simulates the real natural conditions. With this method, the total capacity of montmorillonite towards the considered heavy metals has been determined under the considered conditions [10].

Materials, reagents and instruments.

The sodium form of montmorillonite was supplied as montmorillonite KSF by Aldrich. The element composi- tion of the clay was determined by ICP-AES (Induc- tively Coupled Plasma Atomic Emission Spectrometry) after solubilisation by acid digestion in microwave oven and is reported in Table 1. The percentages of SiO_2 and Al_2O_3, principal constituents of montmorillonite, are

48.57 and 34.95, respectively. In order to respect the natural characteristics of montmorillonite and to eval- uate the retention behaviour in landfill liners, the clay was not treated. The surface area is 20–40 mg and the cation exchange capacity (CEC) is B30 meq/100 g, therefore, they are lower than those generally reported for montmorillonites [11], but this is probably due to the lack of treatment. In fact, it is possible that, in this way, N_2 molecules (employed to calculate the specific surface area by BET method) and cations can be introduced less easily in the interlayer regions as indicated by Barbier et al. [12].

All the reagents used were of analytical grade.[1] All metal solutions were prepared from concentrated stock solutions (Merck Titrisol). High-purity water (HPW) produced with a Millipore Milli-Q system was used throughout. A Delta 320 Mettler Toledo pH meter provided with incorporated thermal probe was used for pH measure- ments; two standard buffer solutions at pH 4.0 and 7.0 were employed for calibration. Metal determinations were performed with a Varian Liberty 100 model Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). The instrument is provided with a Czerny-Turner monochromator, a Sturman-Masters spray chamber, a V-groove nebuliser and a radio frequency (RF) generator at 40.68 MHz. The instrumental conditions were: plasma power 1.0 kW; nebuliser pressure 150 kPa; sample aspiration rate 15 rpm (B2 ml /min$^{—1}$); argon auxiliary flow 1.5/ min. A Gilson Minipuls 2 multichannel peristaltic pump was used to drive the sample solutions into the columns with a constant and reproducible flow rate (0.5 cm^3 min^{-1}) This pump was connected to the columns by polypropylene low-pressure fittings and PVC tubes (i.d. 1.29 mm). The polypropylene columns (Bio-Rad), 4 cm high and 5 mm i.d., were packed with 1 g of Na-montmorillonite. A Milestone MLS-1200 Mega microwave laboratory unit was used for the dissolution of the clay.

The continuous column method was used to study the adsorption of heavy metals on Na-montmorillonite. The apparatus for continuous ion exchange is schematised in Fig. 1. At the bottom of the column, on the porous polymer bed support, a 0.45 mm cellulose acetate filter (Millipore) was placed. The slurry packing technique was used to obtain a homogenous bed in the column. Before each experiment the clay packed in the column was conditioned at the working pH with a buffer solution. Solutions were driven through the columns with the aid of a peristaltic pump. Six replicates of each experiment were performed. Blanks were simultaneously run in order to take account of possible contaminations and eventual releases of the investigated metals from the clay. In the study of pH and ligand effect, 25 ml of the eluate was collected. The Cd, Cu, Cr, Mn, Ni, Pb and Zn concentrations in the influent and effluent solutions were determined using an atomic emission spectrophotometer (ICP-AES). The amount of every metal adsorbed on to the clay was calculated by the difference between the content of metal in influent solution and that one in effluent solution, corrected with the blank, and it was expressed in percentage.

The pH range studied was 2.5–8.0. The NaAcetate/ Acetic Acid buffer was used in the pH interval between

2.5 and 5.5, while the HEPES-Na [4-(2-hydroxyethyl).

Table 1 Element composition of the Na-montmorillonite determined by ICP-AES

Element	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Ti	Zn	Zr
g/kg	0.01	0.03	0.01	32.5	9.71	12.64	0.18	1.93	0.03	0.07	1.78	0.01	0.12

Results and discussion. The influence of pH on the adsorption of bivalent and trivalent metal ions (Cd, Cr, Cu, Mn, Ni and Pb) on Na- montmorillonite was studied. The results obtained are represented in Fig. 2. As expected, the adsorption of metals decreases with decreasing pH because the aluminol and silanol groups are more protonated and, hence, they are less available to retain the investigated metals. This effect is strongly evident for Cu, Pb and Cd, and less pronounced for the others. The reason of this behaviour is that the surface complexation reactions are influenced also by the electrostatic attraction between the surface charge and the dissolved ions. In fact, since cadmium and lead have larger ionic radius (0.97 and1.20 A respectively), they have lower charge density and, therefore, are more affected by the protonation of the surface groups that determine a reduction of the adsorption sites on clay. The Cu(II) behaviour, instead, is probably due to the structure of its aquaion. In fact, $[Cu(H_2O)_6]^{2+}$ has a tetragonal distortion due to the Jahn–Teller effect in which the octahedral structure has been contracted along the x^- and *y* axes [13]. There fore, the binding of ligands along the x^- and y^- axis is supported whereas the ligands along the *z* axis are shielded from the Cu^{2+} ion by an extra electron. This contraction along the x^- and y^- axis results in a structure having four shorter bonds and two longer bonds and this hinders in part the binding of the copper (II) aquaion with the clay surface groups. This effect is more evident when these groups are more protonated because the binding is supported only along particular directions (x^- and y^- axis) For these reasons, hence, the adsorption of Cu, Pb and Cd is hindered by cation exchange mechanism whereas this mechanism domi nates the adsorption of Cr, Mn, Ni and Zn ions. These.

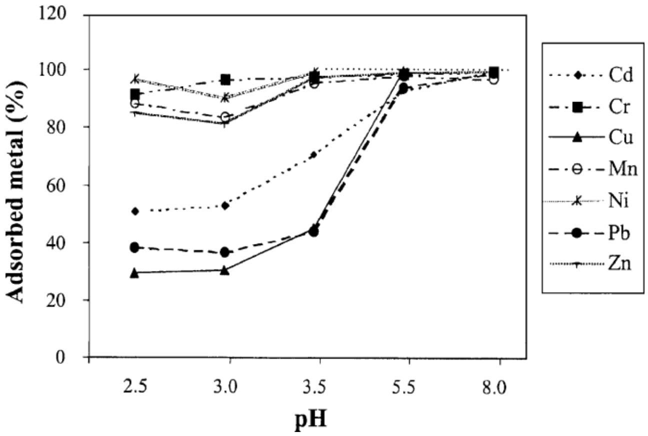

Fig. 2. Adsorption of Cd, Cr, Cu, Mn, Ni, Pb and Zn on Na- montmorillonite as a function of pH (initial concentration of metals 1.0 × $10^{—4}$

References

1. Alloway BJ. In: Heavy metals in soils. Glasgow, London: Blackie, Wiley, 1990. p. 7–40, 100–219, 261–77.
2. Aller AJ, Deban L. Total and extractable contents of trace metals in agricultural soils of the Valderas area, Spain. Sci. Total Environ. 1989;79(3):253–70.
3. Hani H. The analysis of inorganic and organic pollutants in soil with special regard to their bioavailability. In. J. Environ. Anal. Chem. 1990;39(2):197–208.
4. Bailey SE, Olin TJ, Bricka RM, Adrian DD. A review of potentially low-cost sorbents for heavy metals. Water Res. 1999;33(11):2469–79.
5. Schindler PW, Fu. rst B, Dick R, Wolf P U. Ligand properties of surface silanol groups. I. Surface complex formation with Fe3+, Cu2+, Cd2+ and Pb2+. J. Colloid Interface Sci. 1976;55(2):469–75.
6. Mercier L, Detellier C. Preparation, characterization, and applications as heavy metals sorbents of covalently grafted thiol functionalities on the interlamellar surface of montmorillonite. Environ. Sci. Technol. 1995;29(5): 1318–23.
7. Kraepiel AML, Keller K. Morel FMM. A model for metal adsorption on montmorillonite. J. Colloid Interface Sci. 1999;210(1):43–54.
8. Batchelor B. Leach models for contaminants immobilized by pH-dependent mechanisms. Environ. Sci. Technol. 1998;32(11):1721–6.
9. Altin O, Ozbelge OH, Dogu T. Effect of pH, flow rate and concentration on the sorption of Pb and Cd on montmor- illonite: I. Experimental. J. Chem. Technol. Biotechnol. 1999;74(12):1131–8.
10. Minczewski J, Chwastowska J, Dtbczynski R. The column process. In: Separation and preconcentration methods in inorganic trace analysis. Chichester: Ellis Horwood Limited, 1982. p. 355–64.
11. Evangelou VP. Soil minerals and surface chemical proper- ties. In: Environmental soil and water chemistry: principles and applications. New York: Wiley, 1998. p. 100–224.
12. Barbier F, Duc G, Petit-Ramel M. Adsorption of lead and cadmium ions from aqueous

solution to the mon- tmorillonite/water interface. Colloids Surf. A 2000; 166(1–3):153–9.

13. Nicholls D. Complexes, first-row transition elements, London: Basingstoke. Macmillan. 1974. p. 56–72.