

Applications of Bentonite to Soil Decontamination

MARIN RUSANESCU¹, CARMEN OTILIA RUSANESCU^{2*}, GHEORGHE VOICU^{2*}, MIHAELA BEGEA²

¹ Valplast Industrie Bucharest, 9 Preciziei Blvd., 062202, Bucharest, Romania

² Politehnica University of Bucharest, Faculty of Biotechnical Systems Engineering Bucharest, 313 Splaiul Independentei, 060042, Bucharest, Romania

A calcium bentonite from Orasu Nou deposit (Satu Mare Romania) was used as raw material. We have conducted laboratory experiments to determine the influence of bentonite on the degree of heavy metal retention. It has been observed that the rate of retention increases as the heavy metal concentration decreases. Experimental studies have been carried out on metal retention (Zn) in bentonite. In this paper, we realized laboratory experiments for determining the influence of metal (Zn) on the growth and development of two types of plants (Pelargonium domesticum and Kalanchoe) and the effect of bentonite on the absorption of pollutants. These flowers were planted in unpolluted soil, in heavy metal polluted soil and in heavy metal polluted soil to which bentonite was added to observe the positive effect of bentonite. It has been noticed that the flowers planted in unpolluted soil and polluted with heavy metals to which bentonite has been added, the flowers have flourished, the leaves are still green and the plants whose soils have been polluted with heavy metals began to dry after 6 days, three weeks have yellowish leaves and flowers have dried. Experiments have demonstrated the essential role of bentonite for the removal of heavy metals polluted soil.

Keywords: bentonite, soil pollution, metal, montmorillonite

Bentonite is an aluminium phyllosilicate, being natural clay containing a high percentage of montmorillonite, an acid silicate where several Al and Si atoms were replaced with Fe and Mg atoms.

Montmorillonite has the following chemical formula: $(\text{Na}, \text{Ca})_{0.3}(\text{Al}, \text{Mg})_2[\text{Si}_4\text{O}_{10}(\text{OH})_2]_n \times n\text{H}_2\text{O}$ [19].

Montmorillonite was formed by alteration of basic rocks and pyroclastic materials (glasses, ashes, volcanic tuffs, etc.) in aqueous media with alkaline pH ($\text{pH} > 8$) that was weakly levigated by circulating waters with a high concentration of Mg and Ca and also having a K deficit [4].

They inherit the physical and chemical properties of the primary materials but also display new properties as a result of sedimentary and hydrothermal petrogenesis.

Concerns about exploring of natural materials as sources of low-cost products have resulted in research in order to valorization of natural zeolites and clay minerals. Thus clays such as sepiolite, kaolinite, montmorillonite and bentonite are used for the absorption of organic dyes in wastewater [9].

Bentonite is a good adsorbent for non-polar organic pollutants, with diverse applications in the domain of industrial wastewater purification [6, 9].

This paper describes the influence of heavy metals of two types of plants (pelargonium and kalanchoe), analyzes the efficiency of bentonite as an adsorbent for removing hydrocarbons and heavy metals from the soil.

Zeolites are a group of hydrated aluminosilicates of alkali or alkaline earth metals. Zeolites were used as ion exchangers [18], adsorbents for separation of various chemical species or catalysts [5, 8, 21].

Bentonites are selected for each industrial need on the basis of type and quality. This selection is based principally on physical properties, and chemistry of the bentonite becomes involved only to the extent that it influences the physical properties [7].

The clays and clay minerals, either in its natural state or after modification, will be recognized as the materials of the 21st century due to their abundance, low cost and environment friendly. Clays and minerals in clay are less

than 2 micrometers in size and are lamellar or semi-laminated silicates [9].

The origin of bentonite is attributed to the alteration of volcanic ash, or glass, but common use of the term is extended to include material of primarily a montmorillonite composition which may have formed in another manner [23].

After mining, the bentonite is stockpiled, dried, separated with respect to particle size or ground to a powder, bagged, and shipped [12].

In Romania, the pearls from New Town (Satu Mare County) were formed at the end of Badenian. Over the upper Badenian formations are the products of the first cycle of eruption (riolite and pyroclastes). During the volcanic eruptions, suddenly underwater and underwater cooling of the riolytic lava gave rise to a volcanic bottle around the cooling centers forming aggregates with concreting appearance. Sometimes, these centers, due to a beginning of crystallization, form a spherulitic or spheroidal structure. The pearl deposit is open about 1.5 km west of New Town, in Black Hill. Peperies of pearls also appear in Ciap Hill, Nucilor Hill and Mujdeni Hill, with thicknesses of 20-30m.

Given the soil pollution due to the mining activity (transport and selective smelting of non-ferrous metals), the effect of bentonite on soil degradation is important [16].

In heavy metal contamination, the most common elements are Cd, Cr, Cu, Hg, Pb and Zn. The main anthropogenic sources of heavy metals are the various industrial activities, including mining activities, but also the mining activities, smelters and foundries, and diffuse sources of car traffic, burning of products, etc. [22]. Heavy metals can reach soil or plants because they are found in fertilizers, amendments or pesticides used in the production process, or they can come from atmospheric gases from various industries and combustion. Powders and gases are carried by air streams and eventually stored on plants, on the soil or in surface waters [17]. The persistence of contaminants in the soil is much higher than in other compartments of the biosphere, and soil pollution

* email: ghvoicu_2005@yahoo.com; 0724715585
rusanescuotilia@gmail.com; 0723259702

with heavy metals appears to be virtually permanent in soils, soil decontamination is a concern of many researchers [1, 25-32]. The period of existence of metals in soil in temperate climatic conditions can be estimated for the following elements, as follows: - Cd between 75 and 380 years; - Hg between 500 and 1000 years; - and between 1000 and 3000 years for Ag, Cu, Ni, Pb, Se and Zn [14].

In Romania, soil pollution through *up to date* mining exploitations for the extraction of coal (lignite) is the most serious because the fertile soil layer is lost and various agricultural and forestry uses disappear. At the country level, 24,432 ha are affected, of which 23,640 ha are excessively affected. The largest areas are in Gorj County (12.093 ha), Cluj County (3.915 ha) and Mehedinti County (2.315 ha) [3].

Waste pollution from the extractive industry affects 844 ha, of which 360 ha are excessively affected. The largest affected areas are in the counties with mining activity, steel industry and non-ferrous metallurgy activities, such as Dolj County - 150 ha, Galati - 177 ha, Maramures - 103 ha and Timis - 106 ha [20].

Cadmium is a toxic heavy metal harmful to humans, animals and plants. High cadmium uptake causes kidney dysfunction. Main sources of soil contamination include fertilizers, pesticides besides industrial and municipal wastes emissions. Plating operations and disposal of cadmium-containing wastes as well are sources of cadmium contamination [24, 25]. Cadmium is highly toxic to living organisms. It can accumulate in the kidney and hinders its function. It is highly mobile in soils compared to Pb(II) and Cu(II). Lead battery manufacturing, pigment and chemical manufacturing, lead-contaminated wastes are the primary industrial sources of lead. Lead mobility in soil is restricted by adsorption, ion exchange, precipitation and complexation with sorbed organic matter. Lead has a long residence time and a low mobility in soils. It binds to Mn oxide in the soil more strongly than other metals such as copper and zinc [24, 26].

Experimental part

Materials and methods

Bentonite is a term used to designate a naturally rock, very fine grained material largely composed of the clay mineral, montmorillonite. Bentonite, in addition to montmorillonite, contains a small portion of other mineral matter, usually quartz, feldspar, volcanic glass, organic matter, gypsum, or pyrite.

Volcanic glass has been transformed (clay) by the change of chemistry and the structural change of the glass paste. Chemical transformations consisted of leaching SiO_2 and K_2O and enrichment in Na_2O , MgO and hydroxyl ions. The transformations took place under the influence of epithermal solutions related to the putting into place of the rhyolite, with indices of manifestation in two pulses, one characterized by an alkaline pH giving rise to montmorillonite and another later, with a weak acid under the influence of which Minerals such as halloysite and zeolites have been formed [15].

Bentonite has a gray, white, brick color. It's tough, sometimes soft, plastic, and brittle. From the mineralogical

point of view, bentonite has about 70% montmorillonite and subordinate to feldspar, small, quartz and opaque minerals [7]. Chemically, montmorillonite is described as a hydrous aluminum silicate containing small amounts of alkali and alkaline -earth metals, clay minerals as aluminum silicates with water constitution and with layer structure. Clay minerals are constructed of two coordinative groups: tetrahedral (T) with central Si^{4+} cations and octahedral (O) with central Al^{3+} , Fe^{3+} or Mg^{2+} cations [21]. Binding of coordinative groups from network leads to structural elements, which in the case of clay minerals, are presenting in the form of sheets and / or chains that gives them a characteristic layered and filamentous structure [9]. The 2:1 layer structure of phyllosilicates consists of an octahedral sheet which is sandwiched between two opposing tetrahedral sheets (fig. 1) [6]. The connection between layers is very weak, the external surfaces of lack of active oxygen layers being bound by residual van der Waals forces. Montmorillonite adsorbs water whenever it is available. Water adsorption occurs to the greatest extent on the basal surfaces of the clay and in this fashion pries adjacent flakes apart, resulting in an overall volume increase of the clay. Evidence of this swelling mechanism is seen as an increase in the c-axis dimension of the clay (fig. 2).

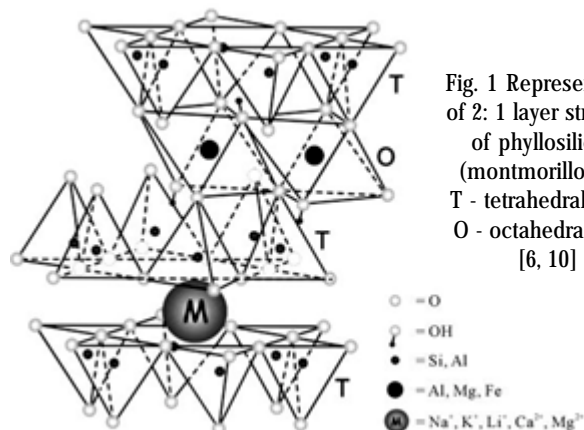


Fig. 1 Representation of 2:1 layer structure of phyllosilicate (montmorillonite): T - tetrahedral layer; O - octahedral layer [6, 10]

The water which is adsorbed primarily on the basal surfaces of the clay (frequently referred to as *bound* or *oriented* water) consists of a regular, rather than a random, arrangement of water molecules; the energy with which the water orients and is bonded to the clay flake is measured as heat of wetting [1]. In table 1 typical analysis of bentonite is shown. It is found that clay turns towards non-swelling if CaO content tends to 1% or more, or if MgO content in form of exchangeable ions is above 2.5%. General rule may be applied: if $\text{Na}_2\text{O}/\text{CaO}$ is more than 4, bentonite is regarded to be of excellent quality; if $\text{Na}_2\text{O}/\text{CaO}$ is 2-3, bentonite is of good quality, and for ratio values 1-2 bentonite is of tolerable quality requiring further processing. Chemical analysis however cannot replace physical tests for determination of the commercial quality. The content of montmorillonite is between 20-85%, depending on the rock alteration stage and can reach up to 95% [14, 15].

The high content of Al_2O_3 and low Na_2O content is noted.

Oxizi%	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Orasul	60.62-	0.15-	15.40-	0.84-	1.18-	0.54-	0-0.3	0.25-
Nou	71.46	0.36	23.55	2.34	1.86	2.05		2.16

Table 1
CHEMICAL COMPOSITION OF
SODIUM BENTONITE

Results and discussions

In this paper, we have presented the influence of bentonite on Zn polluted soil on two types of plants (Pelargonium domesticum, Kalanchoe), research was carried out over 60 days. The use of zeolite was to absorb excess free cation Zn. The chemical composition of bentonite used in the laboratory experiments is presented in table 1 [11, 12].

The soil pH represents a measure of the acidity which plays an important role in determining the solubility of important elements and processes from soils [2, 10, 13].

In this type of experiment, 400 mL polyethylene tanks were used (fig. 3). The plants were in a constantly monitored microclimate vegetation chamber. A night alternating regime (8h) / day (16h), during the night the temperature was maintained at 16°C and during the day the temperature was 22°C. The relative humidity was 40% throughout the experiment. The plants were watered daily with distilled water.

Adsorption experiments were carried out with a known amount of adsorbent (bentonite 0.5, 1.0, 2.0, 3.0, 4.0, 8.0 g dispersed in distilled water) and 100 mL of metal at fixed metal concentrations of pH = 4.5, 22 °C. It is shown that this metal (Zn) was adsorbed by bentonite after adsorption.



Fig. 2 Pelargonium on the first day of the experiment



Fig. 3a. Pelargonium in unpolluted soil b. Pelargonium in soil polluted with metal c. Added bentonite



Fig. 4 Kalanchoe before pollution



Fig. 5 a Kalanchoe in unpolluted soil, b Kalanchoe in soil polluted with metal, c Added bentonite



Fig. 6 The flowers of the 7th day from the soil



Fig. 7 Flowers at the end of the experiment

Figure 3 presents pelargonium one week after the experiment. In figure 3 a it's pelargonium in unpolluted soil, 3 b pelargonium in soil polluted with Zn. 3 c pelargonium in soil polluted with Zn that was added bentonite (20 g).

After four days of soil pollution, the leaves that have been contaminated with Zn have dried out at the base of the dried roots.

In figure 6 is seen in the flowers of the 7th day from the soil, with metal. The influence of oil on plants was determined by phenological observations at plant level.

At the end of the experiment, the plant has bloomed red water watered plant in soil polluted by metal but also containing bentonite and the continued flowering plant in soil polluted with metals was withered (fig. 7). The results presented in figure 8 indicate that the adsorbed metal concentrations increase with increasing bentonite concentration in the solution and increasing the pH.

The efficiency of the adsorption process was followed by the adsorption yield that was calculated using the relationship:

This is an example of an equation:

$$\eta = \frac{C_i - C_e}{C_i} \cdot 100 \quad (1)$$

where:

C_i is the initial solution concentration of the organic compound considered [mg/L]; C_e is the concentration in solution at the equilibrium of the calculated organic compound, expressed [mg/L]

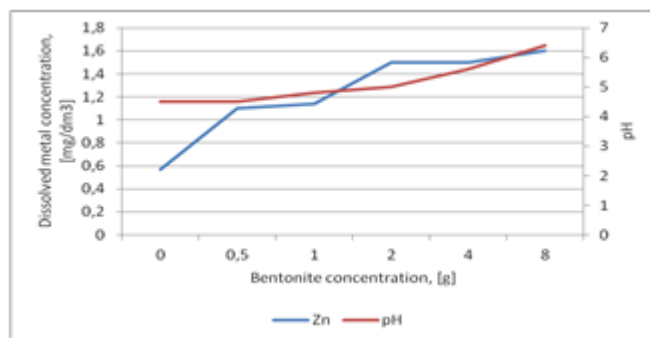


Fig. 8 Absorption of zinc concentrations with bentonite

Figure 9 shows the rate of metal absorption (Zn) by bentonite.

When the amount of bentonite in solution is doubled, there is an increase in the adsorption yield of Zn.

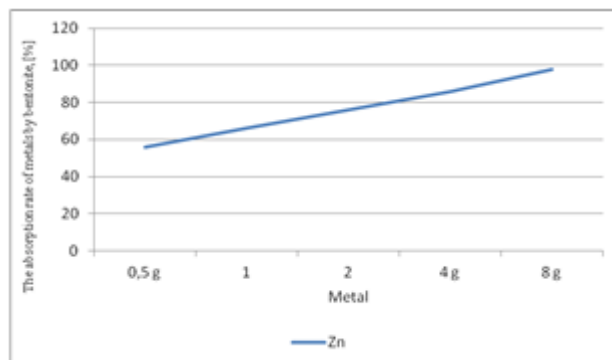


Fig. 9 The bentonite Zn absorption rate (0.5, 1.0, 1.5, 2.0, 4.0, 8.0 g bentonite in 100 mL solution)

Conclusions

In this paper the influence of bentonite in the New Town of Romania on the soil pollution with metal (Zn) was analyzed. From the experimental data, it was observed

that bentonite was a good adsorbent for isolating heavy metals in polluted soils. According to experimental data, the metal retention rate is dependent on the initial concentration of metal in the solution. The sorption coefficient for a metal decreases significantly when the concentration increases. Bentonite property for metal retention could be used to isolate metal mining waste.

Bentonite, in addition to the physical protection of artificial gaskets, minimizes the risk of dispersing contaminants into the environment, as it is a natural layer acting as a complementary barrier. Bentonite in Romania, thanks to its high content of montmorillonite, due to its high natural availability and low cost, is a good candidate for the development of materials used in environmental rehabilitation. Bentonite has contributed to the growth of flowers planted in a heavy metal polluted soil. Experiments have demonstrated the essential role of bentonite for the recovery of polluted soil. The ability of bentonite to absorb water and heavy metals has suggested the use of this natural resource in the treatment of tailings dumps to improve the degree of vegetation recovery. Existence of bentonite resources in Orasul Nou, Satu Mare can be used in polluted soils.

Bentonite exploitation through mining operations to date is simple and is in the vicinity of Maramures Mining Basin can contribute to soil decontamination.

References

1. ULMANU, M., MATSI, T., ANGER, I., GAMENT E., OLANESCU G., PREDESCU CR., SOHACIU, M., Sci.Bull, Series B: Chemistry and Materials Science, **69**, **2**, 109-116, 2007.
2. ANTONIO LOFU, PIERO MASTRORILLI, MARIA MICHELA DELL'ANNA, MATILDA MALI, RAFFAELLO SISTO, RODOLFO VIGNOLA, Archives of Environmental Protection **42**, **1**, 2016.
- 3.*** Annual Report on the State of the Environment in Romania for 2009, Chapter 5. The Soil, http://www.anpm.ro/upload/16102_5%20SOL%202009.pdf.
4. BERGAYA, F., THENG, BKG., LAGALY, G., Handbook of Clay Science, Elsevier, Amsterdam, 1-18, 2006.
5. BOMBOS, D., GANEA, R., MATEI, V., MARINESCU, C., BODNAREV, A., MIHAI, S., NATU, T., TAMAS, I., Rev. Chim. (Bucharest), **65**, no. 8, 2014, p. 976-982
6. BRANA, V., ARAMESCU, C., CALUGARU, I., Non-metallic mineral substances, Technical Publishing House, Bucharest, 44-55, 1986.
7. CALLEJA, G., MELERO, J.A., MARTINEZ, F., MOLINA, R., Water Res. **39**, 1741-1750, 2005.
8. GAVRILOAIEI, T., Rev. Chim. (Bucharest), **63**, no. 4, 2012, p. 396
9. GEORGESCU, A.M., NARDOU, FR., NISTOR, D. IL., Journal of Engineering Studies and Research, **22**, **1**, 32-37, 2016.
10. GLIGOR, D., BALAJ, F., MAICANEANU, A., GROPEANU, R., GROSU, I., MURESAN, L., POPESCU, I.C., Materials Chemistry and Physics **113**, 283-289, 2009.
11. GRIM, R. E., Clay Mineralogy New York, 384, 1953.
12. HUYUAN ZHANG BO YANG, GUANGWEI ZHANG, XUECHAO ZHANG, Archives of Environmental Protection, **42**, **2**, 2016.
13. KABATA-PENDIAS A., Trace Elements in Soils and Plants. Fourth Edition. Taylor and Francis Group, LLC, 2011.
14. KALMAR I., Studies geological, geophysical, geographic, geology series, **20**, **2**, 187-202, Bucharest, 1975.
15. LIAO GUO-LI, LIAO DA-XUE, LI QUAN-MING, Transactions of Nonferrous Metals Society of China, **18**, 207-211, 2008.
16. LIXANDRU, GH., Agrochemistry, Didactic and Pedagogic Publishing House, Bucharest, 212-240, 1990.
17. MACOVEANU, M., BILBA, D., BILBA, N., GAVRILESCU, M., SOREANU, G., Ion exchange processes in environmental protection, Matrixrom, Bucharest, 2002.
18. MARUTOIU, O. F., BRATU, I., MARUTOIU, C., HODISAN, S., LAZAR, M., PERHAITA, I., TIGAE C., Rev. Chim. (Bucharest), **66**, no. 9, 2015, p. 1455
19. MICLE, V., Ecological restoration of degraded areas. U.T. Publishing House Pres, Cluj-Napoca, 184 2009.
20. PUSINO, A., BRASCHI L., GESSA C., Clay Miner. **48**, **1**, 19-25, 2000.
21. THARI, M., BENYAICH, F., BOUNAKHLA, M., BILAL, E., GRUFFAT, J.J., MOUTTE, J., GARCIA, D., Env.Monitoring and Assesment, **102**, 405-417, 2005.
22. YANG R.T., Adsorbents, in: Fundamentals and Applications, John Wiley & Sons, Inc., NJ, p. 157, 253, 280, 2003.
23. RANDELOVIC, M., PURENOVIC, M., PURENOVIC, J. J.of En-vi-ron-men-tal Protection and Ecology, **3**, **12**, 1049-1057, 2011.
24. AMRUTHUR RAMAMURTHY1, HESHAM SCHALCHIAN, Environment Protection Engineering, Vol. 39 2013 No. 3, pp.87-99.
25. KHODADOUST A.P., REDDY K.R., MATURI K., J. Haz. Mater., **117**, **15**, 2005.
26. JINESCU, GHE., PANTURU, E., RADULESCU, R., JINESCU, C.V., MARES, M., Excellence research - a favorable premise for the development of Romanian research space, vol. I, p.L2.11 (1-10), 2006.
27. ULMANU, M., ANGER, I., GAMENT, E., OLANESCU, G., PREDESCU, CR., SOHACIU, M., Sci. Bull, Series B: Chemistry and Materials Science, **68**, **3**, 67 - 78, 2006.
28. JINESCU, GHE., PANTURU, E., RADULESCU, R., JINESCU, C.V., MARES, M., ISOPENCU, G., Conference Excellence Research-A Way to Innovation, v.I, p.57(1-6), 2008.
29. PANTURU, E., RADULESCU, R., JINESCU, C.V., ISOPENCU G., FILCENCO-OLTEANU A., JINESCU, GHE., Excellence research - a favorable premise for the development of Romanian research space 2007.
30. JINESCU, V., MANEA, S.E., JINESCU, C., Rev. Chim.(Bucharest), **68**, no. 4, 2017, p. 656
31. RUSANESCU, C. O., JINESCU, C., RUSANESCU, M., BEGEA, M., GHERMEC, O., Rev. Chim..(Bucharest), **69**, no. 1, 2018, p. 105
32. GROS, F., URSU, A.V., DJELVEH, G., JINESCU, C., NISTOR, IL. D., JINESCU, GHE., Rev. Chim. (Bucharest), **61**, no. 6, 2010, p. 590

Manuscript received: 22.01.2018