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A COMPARATIVE STUDY OF THE BENTONITES AND NATURAL ZEOLITES CAPACITIES TO REDUCE THE BIOAVAILABILITY OF HEAVY METALS IN A CONTAMINATED SOIL

Mihaela COSTEA[1, 2], Nicoleta-Olimpia VRÎNCEANU[1], Dumitru-Marian MOTELICĂ[1], Veronica TĂNASE[1], Mirela Alina SANDU[2], Costică CIONTU[2]

[1]National Research and Development Institute for Soil Science, Agrochemistry and Environment, 61 Marasti Blvd, District 1, Bucharest, Romania
[2]University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59 Marasti Blvd, District 1, Bucharest, Romania

Corresponding author email: cosmihaela96@gmail.com

Abstract

Soil contamination with heavy metals is a major environmental challenge, particularly in industrial regions such as Copșa Mică, Romania. Past industrial emissions have resulted in substantial soil pollution, with levels of lead (Pb), cadmium (Cd), and zinc (Zn) exceeding permissible limits. This study investigates the effectiveness of various bentonites and natural zeolites in reducing heavy metal mobility and bioavailability in contaminated soil. Laboratory incubation tests were conducted using six inorganic additives sourced from Romania. The additives were applied at a 3% (w/w) dosage, and their effectiveness was evaluated using single metal extraction methods with DTPA + $CaCl_2$ + TEA (pH 7.3) and 1M NH_4NO_3. The results demonstrate that all amendments significantly reduced heavy metal mobility, with variations depending on the specific metal. Activated bentonite exhibited the highest efficiency in immobilizing Pb and Zn, while zeolite proved most effective for Cd stabilization. This study highlights the potential of natural zeolites and bentonites as cost-effective and environmentally friendly solutions for soil remediation in heavily polluted areas.

Key words: *additives, contamination, immobilization, metals, soil.*

INTRODUCTION

Soil pollution with heavy metals is a global environmental issue, directly affecting ecosystems, agriculture, and human health. Heavy metals such as lead (Pb), cadmium (Cd), and zinc (Zn) are highly toxic and persistent in the environment, tending to accumulate in soils, where they reduce fertility and can be absorbed by plants, entering the food chain (Bolan et al., 2014; Buzatu & Dodocioiu, 2023). In Central and Eastern Europe, industrial regions are particularly affected by this issue, especially those with a long history of intensive industrial activities and insufficient environmental regulations in the past.

In Romania, Copșa Mică stands as a stark example, with decades of industrial emissions from SOMETRA and CARBOSIN leading to widespread heavy metal pollution. According to Vrînceanu et al. (2010), the area impacted by this pollution reached approximately 180,000 hectares by the 1990s. This contamination, exacerbated by the region's acidic soils, necessitates immediate remediation to mitigate risks to human and environmental health.

This area requires immediate interventions to reduce the mobility and bioavailability of metals. Soil in this region, which are generally acidic, favor increased mobility of heavy metals, amplifying the risks associated with their transfer into the food chain. Increasing the soil pH through inorganic amendments such as zeolites and bentonite can significantly reduce the mobility of metals, contributing to the protection of the environment and human health (Ören & Kaya, 2006).

Heavy metal contamination is increasingly becoming a significant threat to soil quality worldwide (Houben et al., 2013; Cui et al., 2016, cited by Vrînceanu et al., 2019). Furthermore, their absorption by plants represents a source of food contamination with severe effects on human health, including neurological, renal, and cardiovascular problems. Moreover, soil contamination with heavy metals is also a major environmental problem, having a profound impact on human health, groundwater quality, and agricultural productivity. The main sources of these contaminants include industrial activities, uncontrolled waste discharges, and excessive use of chemical fertilizers. Heavy metals such as lead (Pb), copper (Cu), cadmium (Cd), and zinc (Zn) are particularly dangerous due to their persistent toxicity and ability to bioaccumulate in the food chain (Alloway, 2013; Liu et al., 2022).

Remediation of soils polluted with heavy metals is a priority in the context of environmental protection and public health. Due to their persistence in the environment and toxic effects, managing these pollutants requires efficient and accessible technologies. Therefore, developing effective, ecological, and economically accessible remediation methods is essential. Conventional solutions, such as excavating and storing contaminated soils, are expensive and have a negative environmental impact.

Numerous specialized studies have highlighted the effectiveness of using inorganic additives in immobilizing heavy metals. In fact, two key properties of these materials are exploited: the alkaline reaction and/or their high cation exchange capacity.

The effects of incorporating materials with a high metal retention capacity into the soil are amplified under alkaline conditions. This is due to the increase in the number of metal retention centers, intensifying retention processes and reducing the number of competing protons for the sorption sites in the soil's adsorptive complex (Vrînceanu et al., 2010).

Heavy metal immobilization is a remediation method aimed at reducing the mobility and bioavailability of these metals, without completely removing them from the contaminated environment. This method involves using additives that stabilize heavy metals through physicochemical mechanisms such as adsorption, ion exchange, or precipitation. Among the most promising additives are bentonite, a clay with remarkable colloidal properties, and natural zeolite, an aluminosilicate material with a porous structure. The specialized literature (De Compos et al., 2010) has identified 40 natural zeolites and over 150 synthesized zeolites, according to Pant et al. (2020). The main objectives of these amendments are to sequester heavy metals through chemical, physical, and biological processes, reducing their mobility and bioavailability. A secondary objective of the amendments is to stabilize pollutants when the amendments can form stable compounds with pollutants, preventing them from spreading into the environment. A third goal would be to reduce the mobilization capacity by modifying the pH, soil structure, or organic matter content. Some researchers argue that bentonite is known for its ability to adsorb heavy metals through stable chemical bonds, while zeolites offer increased ion exchange potential due to their large surface area and high porosity.

This research aims to evaluate the capacity of natural zeolites and bentonites to immobilize heavy metals in a contaminated soil sample from the Copșa Mică area, providing a scientific basis for implementing effective remediation measures. Through a laboratory experiment, the efficiency of these materials in reducing the mobility of heavy metals in contaminated soils will be analyzed, offering sustainable solutions for their remediation.

This research contributes to understanding the mechanisms involved and the development of ecological technologies applicable in areas affected by heavy metal pollution. The need to restore the initial properties of the soil has driven us to search for new and reliable alternative soil cleaning methods.

MATERIALS AND METHODS

Study area and soil sampling

The study was conducted in the Copșa Mică area, one of the most polluted regions in Romania, located in the Transylvanian Depression. Soil pollution in this area is characterized by high concentrations of heavy metals, such as lead, cadmium, and zinc, which exceed the permissible limits for agricultural or residential uses.

For this study, the soil material used was collected from the vicinity of the former SOMETRA industrial platform, approximately 1,775 meters from the factory's exhaust stack, at a depth of 0-20 cm, corresponding to the arable layer that was affected. The collected material was dried, crushed, homogenized, and passed through a 2 mm sieve to remove roots, stones, and other impurities.

Soil characterization

The physicochemical properties of the soil were analyzed at the National Institute for Research and Development in Soil Science, Agrochemistry, and Environmental Protection (ICPA Bucharest). The results, presented in Table 1, revealed heavy metal concentrations (Cd, Cu, Pb, and Zn) exceeding the intervention thresholds for sensitive land uses as per Order 756/1997. The soil's acidic pH (4.59) and medium texture further contribute to the high mobility of these pollutants.

Table 1. Average values of the main chemical and physical properties of the soil material

Characteristic	Unit of measurement	Average value (n=3)
pH		4.59
Kjeldahl Nitrogen content	%	1.119
Organic Carbon content	%	1.06
Available Phosphorus Content (PAL)	mg/kg	16.7
Available Potassium content (KAL)	mg/kg	119
Cadmium content (Aqua Regia)	mg/kg	35.1
Copper content (Aqua Regia)	mg/kg	206
Lead content (Aqua Regia)	mg/kg	2,815
Zinc content (Aqua Regia)	mg/kg	2,630
Cadmium content (NH_4NO_3)	mg/kg	27.0
Copper content (NH_4NO_3)	mg/kg	11.88
Lead content (NH_4NO_3)	mg/kg	616
Zinc content (NH_4NO_3)	mg/kg	1,257
Textural Class	SM - Medium Texture – Medium Sandy Clay	

Inorganic additives

Comparative studies of various immobilization materials often employ a methodology that includes percolation experiments, bioaccessibility testing of metals, and examination of factors such as temperature, contact time, type of metal, and environmental pH to evaluate immobilization efficiency (Vrînceanu et al., 2010).

This study investigates the capacity of two inorganic additives, bentonite and zeolite, to immobilize heavy metals in soil. These additives have garnered significant interest in the scientific community for their potential in environmental protection. A brief characterization of these inorganic additives used in the case study, according to the technical sheet provided by the manufacturer, is presented in Figure 1.

Incubation experiment

To evaluate the effects of various additives on heavy metal immobilization, incubation tests were conducted in the Physico-Chemical Analysis Laboratory of the National Institute for Research and Development in Soil Science, Agrochemistry, and Environmental Protection (ICPA) in Bucharest. The experiment focused on a single factor: the type of additive used.

Six different treatments were evaluated in this study, each using a different additive to immobilize heavy metals:

- *Bentonite-based additives*

a1 – $B_{ha}GS$ - bentonite for animal feed (Gurasada, Hunedoara County)

a2 – $B_{nac}GS$ - non-activated ground bentonite (Gurasada, Hunedoara County)

a3 – $B_{acff}GS$ - activated bentonite ground with drilling fluids (Gurasada, Hunedoara County)

- *Zeolite-based additives*

a4 – $Zn_{(0-0.4)}ZL$ – natural zeolite (0-0.4 mm) (Zalău, Sălaj County)

a5 – $Zn_{(1-3)}ZL$ - natural zeolite (1-3 mm) (Zalău, Sălaj County)

a6 – ZnRP - natural zeolite from Rupea (Rupea, Brașov County)

Each additive was applied to the soil at a concentration of 3% of the dry soil mass. A control group with no additive was also included in the experiment.

For the incubation experiment, approximately 1 kg of dry soil material was weighed into each of the 21 boxes. After incorporating the equivalent dose of 3% of each additive into the contaminated soil material, approximately 150 ml of distilled water (free of carbon dioxide) was added to reach the maximum water-holding capacity.

Heavy metal extraction and analysis

After the 30-day incubation period, soil samples were collected from each container. Heavy metal concentrations were determined using single metal extraction methods with DTPA + $CaCl_2$ + TEA (pH 7.3) and 1M NH_4NO_3. The extracted metals were then analyzed to assess the effectiveness of each additive in reducing their mobility.

Statistical analysis

The values obtained through the analysis of soil samples collected from the incubation experiment were processed using several specific methods of mathematical statistics. The first method is analysis of variance (ANOVA), a technique for decomposing the total variance into at least two components that reflect the sources of variation induced in the experiment. By estimating the dispersion of a random variable (soil characteristic in our case), considering the influence of a factor and then removing its influence, comparing the two dispersions provides information regarding the effects of the factor on the studied random variable. If the first dispersion is greater, the factor exerts an influence (Iosifescu et al., 1985).

NATURAL ZEOLITE (0 – 0,4 mm)		NATURAL ZEOLITE (1 – 3 mm)	
GRANULATION	0 – 0,4 mm	GRANULATION	1 – 3 mm
MINERALOGICAL COMPOSITION	60-70 % clinoptilolite	MINERALOGICAL COMPOSITION	60-70 % clinoptilolite
	4-8 % feldspar		4-8 % feldspar
	1-2 % small		1-2 % small
	2-10 % quartz		2-10 % quartz
	1-3 % calcutta		1-3 % calcutta
CHEMICAL CHARACTERIZATION INDICATORS			
pH	8,99 ± 0,2	pH	9,5 ± 0,3
CONTENTS OF HEAVY METALS	Cd – 0,061 mg/kg	CONTENTS OF HEAVY METALS	Cd – 0,061 mg/kg
	Cu – 1,82 mg/kg		Cu – 1,82 mg/kg
	Pb – 3,14 mg/kg		Pb – 3,14 mg/kg
	Zn – 8,31 mg/kg		Zn – 8,31 mg/kg

BENTONITE FOR ANIMAL FEED		UNACTIVATED GROUND BENTONITE		ACTIVATED GROUND BENTONITE FOR DRILLING FLUIDS	
GRANULATION	0,63 – 1,2 mm	GRANULATION	ó0,2 mm – max 5%	GRANULATION	ó0,16 mm – max 15%
			ó0,063 mm – max 25%		ó0,063 mm – max 25%
MOISTURE	2 – 3 %	FREE SAND	max. 10 %	FREE SAND	max. 10%
CHEMICAL CHARACTERIZATION INDICATORS					
		pH	7,8 ± 0,2	pH	10,2 ± 0,2
SiO2	57 - 64 %	CONTENTS OF HEAVY METALS	Cd – 0,064 mg/kg	CONTENTS OF HEAVYMETALS	Cd – 0,073 mg/kg
Al2O2	13 - 21 %		Cu – 2,05 mg/kg		Cu – 1,15 mg/kg
CaO + MgO	5 - 12 %		Pb – 19,6 mg/kg		Pb – 28,2 mg/kg
			Zn – 20,1 mg/kg		Zn – 15,1 mg/kg

NATURAL ZEOLITE	
GRANULATION	0 – 1 mm
MINERALOGICAL COMPOSITION	90 % clinoptilolite
	2,60 % plagioclase
	2,20 % anker
	2,60 % quartz
	1,40 % calcutta
	1,20 % biotite
CHEMICAL CHARACTERIZATION INDICATORS	
pH	9,5 ± 0,3
CONTENTS OF HEAVY METALS	Cd – 0,049 mg/kg
	Cu – 1,67 mg/kg
	Pb – 9,27 mg/kg
	Zn – 6,1 mg/kg

Figure 1. Characterization of inorganic additives of the bentonite and zeolite type used in the case study

RESULTS AND DISCUSSIONS

This study focuses on two primary outcomes from the application of the additives: changes in soil pH and the reduction of heavy metal mobility. The goal is to limit the toxicity of heavy metals and their potential transfer to plants.

Incubation tests using a 3% additive dosage revealed that activated bentonite for drilling fluids ($B_{acff}GS$) from Gurasada caused the most significant increase in soil pH, raising it from 4.59 in the control group to 5.40. This increase is crucial because soil pH significantly influences the mobility of heavy metals. As the soil pH becomes more neutral, the availability of heavy metals to plants decreases. In contrast, bentonite for animal feed ($B_{ha}GS$) had a minimal effect, increasing the pH by only 0.24 units (Figure 2).

As a result of a study conducted by Vrînceanu et al., 2019, investigating the effectiveness of amendments such as activated bentonite, dolomite, natural zeolites, and manure in limiting the infiltration of heavy metals into the food chain and, implicitly, reducing health risks, an experimental field was established to examine the effects of these amendments on soils contaminated with heavy metals. The study demonstrated that their application could be an effective solution for reducing the transfer of heavy metals from soil to plants. These amendments have the ability to modify the physicochemical properties of the soil, reducing the bioavailability of heavy metals and their accumulation in plants. The main experimental results showed an increase in soil pH from 5.18 in the control sample to 7.16 in the case of activated bentonite application, as well as a significant decrease in the available concentrations of cadmium, lead, and zinc. The effectiveness of the amendments in reducing the availability of heavy metals followed this order: control > natural zeolite > manure > bentonite > dolomite. At the same time, Soca & Daza-Torres (2016) also state that after the application of zeolite, both the calcium, potassium, and magnesium content, as well as the pH value, increased significantly. An increase in pH value after the application of zeolites in the soil was also recorded by Filcheva & Tsadilas (2002), who conducted a study on the evaluation of the effect of clinoptilolite and compost.

In this case, the effectiveness of the additives in immobilizing heavy metals varied depending on the type of metal, being assessed through extraction with 1M NH_4NO_3.

Analyzing the specialized literature (Misaelides, 2011; Ören & Kaya, 2006), natural zeolites and bentonite have proven to be promising materials for immobilizing heavy metals in contaminated soils due to their unique adsorption and ion exchange properties. O'Connor et al. (2018), suggests that using these natural materials offers significant advantages due to their low cost, availability, and ability to immobilize heavy metals directly in the soil.

In a study conducted by Chen et al. (2000), regarding the evaluation of the effect of various chemical treatments applied to soils (a clayey soil and a sandy soil) contaminated with cadmium (Cd) and lead (Pb), cultivated with wheat, the researchers observed that the accumulation of cadmium and lead in wheat was reduced with the application of calcium carbonate, zeolite, and manganese oxide. Moreover, they found that chemical remediation methods using different treatments could significantly reduce the absorption of cadmium and lead to wheat shoots. The exchangeable (or available) forms of these elements in both cadmium and lead-contaminated soils could be transformed into unavailable forms after modification with 1% manganese oxide or zeolite.

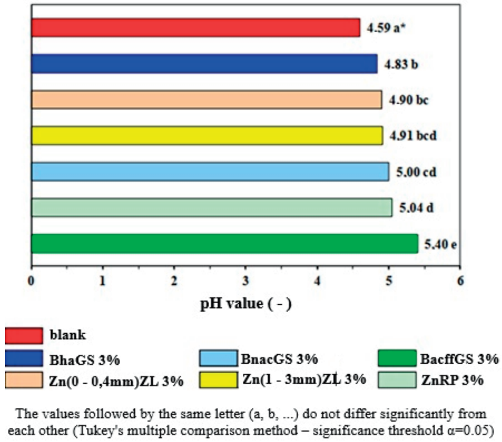

Figure 2. Effects of using bentonite and natural zeolite on the pH value of a soil material contaminated with heavy metals

These materials can neutralize soil acidity, reducing the mobility of heavy metals and transforming them into forms that are less accessible to plants. Zeolites and bentonites can also serve as secondary nutrient sources, improving the overall quality of the soil and promoting vegetation regeneration (Bolan et al., 2014). A recent study (Liu et al., 2022) highlights the advantages of combining bentonite and zeolites in the remediation of contaminated soils, suggesting increased efficiency due to the complementarity of their physicochemical properties.

- *Copper*: activated bentonite ($B_{acff}GS$) and natural zeolite from Zalău ($Zn_{(0-0.4)}ZL$ and $Zn_{(1-3)}ZL$) were most effective in reducing copper mobility, with statistically significant decreases of up to 4.91 mg/kg. Natural zeolite from Rupea (ZnRP) also reduced copper mobility, but to a lesser extent, with decreases ranging from 2.18 to 2.56 mg/kg (Figure 3). The higher efficiency of activated bentonite in immobilizing copper could be attributed to its larger surface area and greater cation exchange capacity compared to the natural zeolites. The activation process may further enhance the adsorption properties of bentonite by increasing its porosity and surface area. The natural zeolites from Zalău, with their smaller particle size, may offer more adsorption sites compared to the zeolite from Rupea, leading to greater reductions in copper mobility.

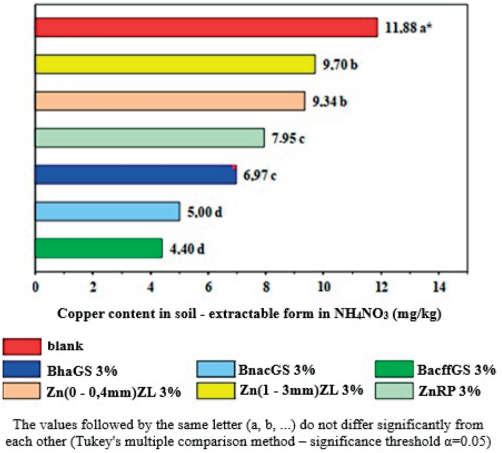

Figure 3. Effects of using bentonite and natural zeolite on the extractable copper content in ammonium nitrate of a soil material contaminated with heavy metals

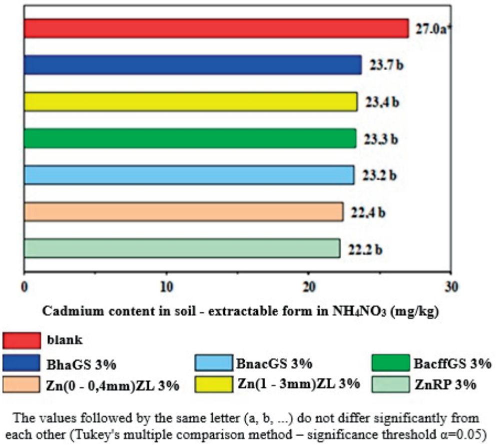

Figure 4. Effects of using bentonite and natural zeolite on the extractable cadmium content in ammonium nitrate of a soil material contaminated with heavy metal

- *Cadmium*: all six additives reduced the mobile concentration of cadmium, but the differences between the additives were not statistically significant (Figure 4). This suggests that the mechanisms responsible for cadmium immobilization may be less influenced by the specific properties of the additives. Possible mechanisms include precipitation of cadmium as insoluble hydroxides or carbonates due to the increase in soil pH, or adsorption onto the surfaces of the additives. The degree of cadmium immobilization at a 3% dose was 17.8% for ZnRP, 17.0% for $Zn_{(0\text{-}0.4mm)}ZL$, 14.0% for $B_{nac}GS$, 13.7% for $B_{acff}GS$, 13.3% for $Zn_{(1\text{-}3mm)}ZL$, and 12.2% for $B_{ha}GS$. As a result of a study conducted by Chen et al. (2000), regarding the evaluation of the effect of different chemical treatments applied to two soils contaminated with cadmium and lead (a clay soil and a sandy soil) cultivated with wheat, they observed that the accumulation of cadmium and lead was significantly reduced with the application of zeolite, calcium carbonate, and manganese oxide in the soil,

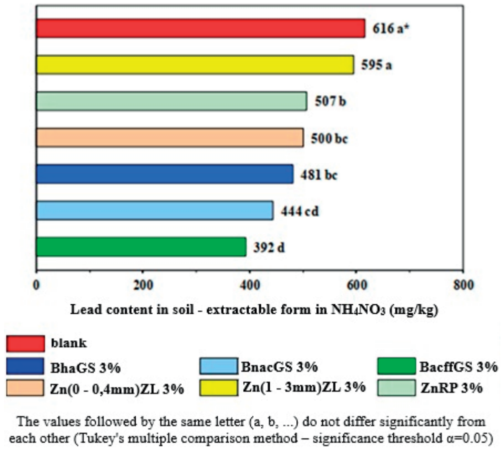

Figure 5. Effects of using bentonite and natural zeolite on the extractable lead content in ammonium nitrate of a soil material contaminated with heavy metals

- *Lead*: activated bentonite for drilling fluids ($B_{acff}GS$) proved to be the most effective additive in reducing mobile lead concentrations, achieving a significant decrease of 224 mg/kg compared to the control. This reduction surpassed the most effective zeolite by 108 mg/kg. In contrast, natural zeolite from Zalău ($Zn_{(1\text{-}3)}ZL$), with a particle size of 1-3 mm, did not yield statistically significant reductions in lead mobility (Figure 5). This superior performance of bentonite in immobilizing lead aligns with previous studies that have highlighted the strong affinity of bentonite for lead and its ability to form stable complexes with this metal. The lower effectiveness of the zeolite, particularly the $Zn_{(1-3)}ZL$, could be attributed to its larger particle size, which may limit its surface area and accessibility to lead ions.

- *Zinc*: similar to lead, activated bentonite ($B_{acff}GS$) demonstrated the most substantial reduction in mobile zinc concentration, with a decrease of 409 mg/kg. While zeolite from Rupea (ZnRP) also reduced zinc mobility, its effectiveness was lower, achieving a reduction of 319 mg/kg (Figure 6). This trend suggests that bentonite may be a more suitable additive for immobilizing both lead and zinc in contaminated soils. The higher efficiency of activated bentonite could be attributed to its greater surface area and cation exchange capacity compared to natural zeolites. Moreover, the activation process may further enhance the adsorption properties of bentonite. The lowest degree of immobilization (18.2%) was observed in soils treated with non-activated bentonite from Gurasada ($B_{nac}GS$).

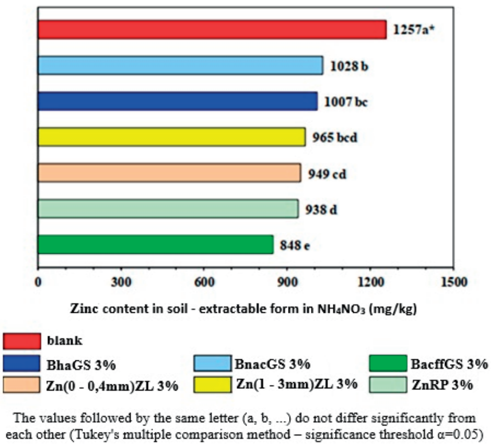

Figure 6. Effects of using bentonite and natural zeolite on the extractable zinc content in ammonium nitrate of a soil material contaminated with heavy metals

CONCLUSIONS

Research has highlighted several important aspects regarding the use of bentonites and natural zeolites for immobilizing metals in contaminated soils. The use of these materials is one of the least expensive and most environmentally friendly practices for reducing the negative effects of soil contamination with heavy metals. By incorporating these materials, which are characterized by a strongly alkaline reaction and high ion-exchange capacity, the aim is to reduce the mobility of heavy metals to limit their transfer from soil to other environmental compartments.

From the incubation tests conducted with 6 indigenous additives (3 bentonites and 3 zeolites) from different sources (Gurasada, Zalău, and Rupea) on a soil contaminated with heavy metals (collected from Copșa Mică), the following observations were made:

pH modification: the application of all tested additives resulted in statistically significant modifications of the soil pH. The most efficient additives in increasing soil pH were activatedbentonite for drilling fluids from Gurasada ($B_{acff}GS$) and natural zeolite from Rupea (ZnRP). At a 3% dose, the pH increase compared to the control was 17.6% ($B_{acff}GS$) and 9.8% (ZnRP).

Copper immobilization: the most efficient additives for copper immobilization were activated bentonite for drilling fluids from Gurasada ($B_{acff}GS$) and non-activated bentonite from Gurasada ($B_{nac}GS$). The incorporation of natural zeolite also led to significant changes in copper immobilization, with the most effective zeolite being the natural zeolite from Rupea.

Cadmium immobilization: all six additives produced statistically significant reductions in cadmium concentrations compared to the control, but there were no significant differences between the additives themselves.

Lead immobilization: the most efficient additives for lead immobilization were activated bentonite for drilling fluids from Gurasada ($B_{acff}GS$) and non-activated bentonite from Gurasada ($B_{nac}GS$). The lowest degree of lead immobilization was observed in soils treated with natural zeolite from Zalău, 1-3mm fraction ($Zn_{(1-3mm)}ZL$). In fact, zeolites were found to be less effective in immobilizing exchangeable lead compared to bentonites.

Zinc immobilization: the most efficient additives for zinc immobilization were activated bentonite for drilling fluids from Gurasada ($B_{acff}GS$) and natural zeolite from Rupea (ZnRP).

Comparison between Bentonites and Zeolites: Bentonites were more efficient in the immobilization of Cu, Zn, and Pb compared to zeolites. For cadmium immobilization, however, no significant differences were found between the additives studied.

Based on these conclusions, the use of these additives for the immobilization of heavy metals in contaminated soils is recommended, with the note that the 3% doses applied were effective for certain additives depending on the metal studied. The issue of using bentonite or zeolite materials to reduce the negative effects of heavy metal pollution in soils remains an open topic due to its complexity. These materials are inexpensive and environmentally friendly, but soil is a dynamic medium that undergoes continuous changes, which may affect the processes in which metals participate, diminishing the effects of immobilization treatments over time. Therefore, long-term monitoring of contaminated soils treated with these additives is necessary, with treatments being repeated if the effect on metal mobility decreases.

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