PRELIMINARY RESEARCH REGARDING THE USE OF EGGSHELL POWDER FOR THE REHABILITATION OF SOILS CONTAMINATED WITH LEAD AND CADMIUM

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Abstract. *The purpose of this paper is to obtain and characterize the chicken eggshells results as domestic waste in order to use them for blocking lead and cadmium in acid soils contaminated with heavy metals. Practically, was determined the effectiveness of fixing lead and cadmium in moderately acidic soil, which contains amounts of lead and cadmium above the intervention level, in the case of using eggshell powder (EGP) in proportions of 1 and 5 percent (compared to soil). The obtained results show different values of the effectiveness of blocking Pb and Cd, depending on the amount of eggshell used and the nature of the metal. Higher values of effectiveness have been reported in the case of using of 5 percent eggshell powder. Comparing the efficiency of using EGP it can be seen that the method is more efficient in case of blocking cadmium. Also, the use of the eggshells powder contributes to reducing the acidity of the soil. The obtained results recommend the use of eggshells for Pb and Cd fixation from acid soils contaminated with such heavy metals contributing to the soils rehabilitation, unsuitable for growing plants. Superior utilization of eggshell waste can be an efficient way of neutralizing them from agro-industrial activities.*

Keywords*: eggshell waste, eggshell powder, calcium, soil rehabilitation, lead, cadmium, effectiveness*

INTRODUCTION

At the global level, agricultural waste management represents an essential and crucial strategy, being a critical factor for humans, animals and vegetation. The nature, quantity and type of waste varies from country to country. Protecting health and environmental quality requires finding an efficient way to properly manage agricultural waste (AL SEADI, HOLM-NIELSEN, 2004). Soil contamination with metals represents an important concern both for human health as well as the environment around the world.

Heavy metals enter in to the food chain through plants, that's why knowledge of the ecology, the storage mechanisms and their metabolism in plants is very important. With the increase in industrialization degree, the abiotic accumulation of heavy metals and the damage caused to plants will be accentuated due to "over-fertilization", by using water with a high load of elements for irrigation purposes, pesticide application, environmental pollution with waste and industrial waters, gases from fossil fuel combustion, traffic, coal and oil combustion, garbage incineration (COZMA ET AL, 2020). The potential toxicity of heavy metals in soil is a function of their mobility but also their bioavailability. Once it reached in the soil, lead and cadmium can be a source of groundwater contamination, being accumulated by absorption in plant tissue directly affecting the human health. Reached into the human body through the consumption of vegetable products, Pb and Cd are accumulated in the body causing severe dysfunctions in the liver, kidneys, lungs or eyes and nervous system (ADRIANO, 1986; AL SEADI, HOLM-NIELSEN, 2004).

To avoid the risk of exposure to Pb and Cd, several remediation techniques have been used including soil washing, stabilization/solidification, electro kinetic bioremediation. To minimize environmental problems, eggshell waste residues should be effectively managed through recycling and reuse, turning them into a valuable product. Nowadays, the use of agricultural residues is a priority for the development of sustainable agriculture (RADULESCU, 2019). Chicken eggshell is composed of water (2%), solid material (98%), protein (5%) and ash (93%) (KHAN ET AL., 2021**).**

The aim of this work is to obtain chicken eggshell powder and using them to block lead and cadmium from soils polluted with such heavy metals. More specifically, the objectives of this study were to evaluate the effectiveness of egg shells as a material for blocking lead and cadmium in acid soils contaminated with heavy metals. For the experiment was used eggshell powder, obtained from the eggshells of chickens raised in the backyard and an average soil sample from a hilly area of Banat. The soil sample was collected from a hilly area in Caraș - Severin County geogenically contaminated with heavy metals.

MATERIAL AND METHODS

The eggshells powder (EGP), taken in the experiment, come from chicken eggshells raised in the backyard, fed with grain. The EGP was obtained in the discipline's laboratory according to a protocol recommended by Platon and collaborators (PLATON ET AL., 2020). Finally, the dried eggshells were ground using a kitchen grinder to a size similar to the soil particles. Until the time of the experiment, the EGP with a size similar to the soil particles was kept in a glass jars at room temperature. To carry out the proposed experiment, an average acid soil sample was used, originating from an area geogenically contaminated with heavy metals.

The soil pH was determined in accordance with the SR ISO 10390:1999 standard. The reaction of the soil was determined by measuring the pH of the aqueous soil suspension in mass ratio, soil: water 1:2.5 using Mettler Toledo type pH meter equipped with combined electrode. The pH of the eggshell powder was carried out under the same conditions as for the soil samples. The determination of the mineral elements concentration in the eggshell samples was made by atomic absorption method after the calcination, followed by ash solubilization in 0.5 N nitric acid and measuring the elements absorbance in the solution (COZMA ET AL., 2023). Total concentrations of Pb and Cd were determined by the extraction method in royal water according to ISO 11466/1999 using the Varian 280 FS Atomic Absorption Spectrophotometer. The concentration of the mobile forms of Pb and Cd were determined using as an extractant the EDTA - ammonium acetate solution with a pH = 7.0 according to the method recommended by Lăcătusu, adapted to the specific working conditions (LACATUSU ET AL., 1996) and also used by Gogoașa, to determine heavy metals in contaminated soils (GOGOASA ET AL., 2009).

RESULTS AND DISCUSSIONS

The average pH value of the eggshell powder prepared under the conditions of this experiment pH = 8.45, shows that it has an alkaline reaction. The EGP prepared under the conditions of this experiment also has an increased mineral content (95.12% ash). Among the analyzed mineral elements, predominates calcium, which was determined in a concentration of 369,870 ppm (36.99%) respectively 92,7% $CaCO_3$. The pH value of the average soil sample determined experimentally, pH = 5.40, shows that the soil of the investigated area is one with a moderately acid reaction.

The total concentrations of lead and cadmium determined in the artificially contaminated soil are presented in table 1.

Table 1

Total concentrations of Pb and Cd in the contaminated soil

Specification	ppm / dry soil	
	Pb	Cd
Total forms, *in royal water*	164	12,6

As can be seen from table 1, the analysed soil samples contain increased amounts of Pb and Cd, with values (164 ppm Pb, respectively 12.6 ppm Cd) above the intervention level provided by the legislation (table 2).

Table 2

Reference values for the heavy metal concentration in soil

Specification	ppm/ dry substance	
	Pb	Cd
Normal values	20	1
Alert level	50	3
Intervention level	100	5

The total content of Pb and Cd cannot provide sufficient information about their different forms, mobility, bioavailability or potential risks regarding their translocation in plants (ASMOAY A. ET AL., 2019). The mobility and bioavailability of accessible metals depend on their specific chemical forms or of the binding capacity to each soil phase. Therefore, to determine the concentrations of the mobile forms of Pb and Cd, the heavy metal extraction method was used in the EDTA - ammonium acetate solution. As mentioned above, only a part of the total soil concentrations are available to the plants, those extracted in the EDTA Therefore, the determination of the mobile forms of Pb and Cd was also necessary.

The results obtained for the determination of Pb and Cd concentrations extracted in EDTA (table 3) : 32.1 ppm Pb and 2.85 ppm Cd, shows that the contaminated soil contains high amounts of Pb and Cd, above the maximum toxicity limits: 18 ppm Pb and 1 ppm Cd (LACATUSU ET AL., 2008).

Table 3

Concentrations of mobile forms of Pb and Cd in the contaminated soil

Specification	ppm/dry soil	
	Pb	Cd
Mobile forms, in EDTA - ammonium acetate	32,1	2,85

The experimentally determined of total and mobile contents of Pb and Cd show that the contaminated soil is unsuitable for plant cultivation. The mineral concentration and the reaction of the eggshell powder are the basis of their use as a stabilizer or as an organic fertilizer for soils with acidic pH (BUREZQ ET AL., 2021). Due to an increased content of calcium, respectively calcium carbonate and the alkaline pH, EGP can block the mobility, considerably reducing the translocation of Pb and Cd from soil to crop plants (OK Y.S. ET AL, 2011). The main purpose of this study was to determine the blocking capacity of Pb and Cd from the soil with a moderate acid reaction. It is important to know that the mobility of heavy metals in soil depends on several factors including pH, aerobic and anaerobic conditions, the

existence of ligands and the composition of ions in the soil solution (ASHRAFI M. ET AL, 2015). The total content as well the mobility of heavy metals must be taken into account when assessing the level of soil contamination. Testing of the blocking capacity of lead and cadmium in the soil was carried out for soils with contents of 1% and 5% eggshell powder. In the selection of the percentage levels of ESP added to the contaminated soil, the recommendations of Yong Sik Ok were taken into account. The results obtained by determining the mobile forms of Pb and Cd extracted from the soil treated with EGP are graphically presented in Figure 1. As can be seen, the Pb and Cd concentrations extracted from the soil with the addition of EGP present different values, depending on the amount of EGP used and the nature of heavy metal in soil.

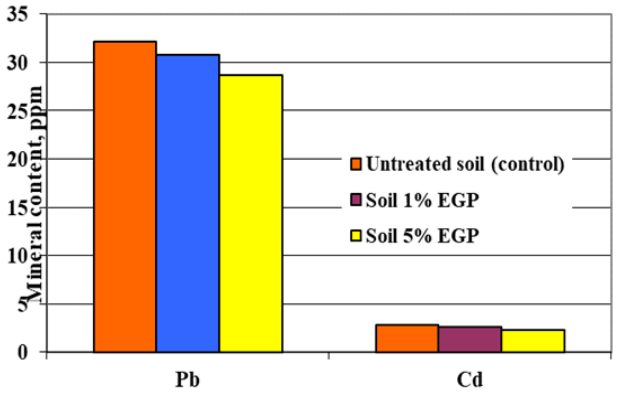

Figure 1. The concentrations of Pb and Cd in the soil treated with EGP, compared to the control sample

The highest amounts of Pb and Cd extracted from the contaminated soil are recorded in case of using a percentage of 1% eggshell while lower amounts in case of using a percentage of 5% eggshell. The quantitative estimation of the efficiency of using EGP to fix Pb and Cd in soils contaminated with heavy metals was done by calculation, using the relationship:

$$E(\%) = \frac{(C1-C2)}{C1} * 100$$

E - the efficiency of the immobilization of Pb or Cd in soil depending on the percentage of added EGP; C1 – concentration of Pb or Cd in the control sample (ppm); C2 - the concentration of Pb or Cd in the soil samples with the addition of EGP. The results obtained by calculating the effectiveness of the immobilization in soil of lead and cadmium using EGP additions with concentrations of 1% and 5% eggshell powder are shown in figure 2. As can be seen from Figure 2, the use of EGP is more efficient in case of the addition of 5% EGP. Using a percentage of 1% EGP, the efficiency decreases substantially.

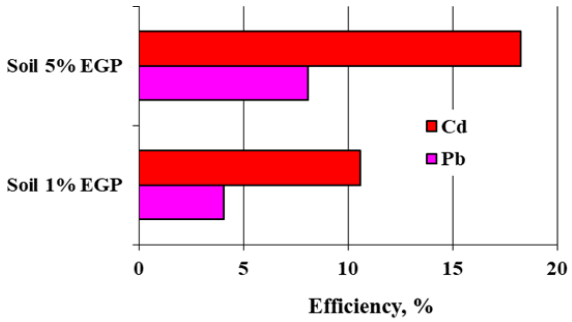

Figure 2. The effectiveness of EGP used for Pb and Cd immobilization in polluted soil

The final results obtained under the conditions of this study shows that EGP can be used to block important amounts of Cd and Pb from soils contaminated with this heavy metals. The procedure is more efficient in case of Cd blocking. The rehabilitation of the acid soils contaminated with Pb and Cd with EGP obtained from household waste or activities of the agro-food industry, contributes to the efficient solution of environmental problems related to waste management.

CONCLUSIONS

The increased content of minerals, especially calcium and the alkaline pH of the eggshell powder experimentally obtained, recommends its use for fixing Pb and Cd in the acid soils contaminated with the toxic metals. In the conditions described in this study, treatment of acid soil contaminated with Pb and Cd with eggshell powder, in a concentration of 1 and 5 mass percent compared to the soil, has the effect of a significant increase in the quantities of Pb and Cd fixed in the soil. Larger quantities of Pb and Cd blocked in the contaminated soil were noted in soils treated with 5 percent of eggshell powder. The use of eggshell powder for blocking Pb and Cd in soil is significantly more efficient for blocking Cd. The obtained results show that the eggshell powder can be used for the rehabilitation of acid soils contaminated with lead and cadmium. In addition, the use of eggshell powder obtained through the superior utilization of the egg waste, it can be an efficient way to dispose the eggshell waste resulting from agro-industrial activities.

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