MIXTURE SUPPORT FOR ESSENTIAL ELEMENTS AND ITS EFFECT ON ZN AND CD SORPTION

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Abstract

Zinc and Cadmium are elements similar in chemical properties but different in mobility and availability, used as stress factors and contaminants. The aim of the study was to establish the sorption capacity of Zn (II) and Cd (II) on a nutrient mixture, the conditions under which the process is maximal and the changes that undergo in the chemical composition of the mixture. The mixture consists in eutrophic peat and compost (60:40%), which contains in addition to organic matter, macronutrients (N, P, K) and certain content of inorganic contaminants (Ni, Pb, Co, Cd, Zn). The parameters that influence the sorption process on nutrient mixture were: initial solution pH (1.0-9.0), contact time (0-1200 min), Zn and Cd concentrations (50-250 mg/l) and organic matter content (52%). The results show that certain characteristics such as phosphorus and potassium content did not change significantly, while the organic matter content decreased to 45%. The humic acids from the organic matter composition caused a significant immobilization of Zn (II) and only a slight immobilization of Cd (II). The values of Cd and Zn from nutritive solution are higher (42.24 mg/kg Zn and 11.69 mg/kg C) than accessible fraction (19.26 mg/kg Zn and 1.4675 mg/kg Cd). The heavy metals content decreases with the increase of pH (5.0 mg/kg Cd, 3.0 mg/kg Zn). The content of accessible fraction reveal reduced values of Cd and Zn that does not represent a threat for human health. These organic materials improve soil fertility, can change the availability of heavy metals and increase crop production.

Key words: zinc, cadmium, compost, peat, sorption

Apart from an increased content of organic matter and nutrients, the role of the nutrient mixture is to partially immobilize heavy metals and block their transfer to plants, and food chain (Bulgariu L., Bulgariu D., 2018). Heavy metals are transition metals with an atomic density above 5.0 g.cm, which, released into the environment, accumulate continuously and their concentration will not decrease over time. Zinc is an essential nutrient for plants, however, present in excessive amounts it turns it into a heavy metal with toxic effects on plant development and affecting animal and human health. But Zn (II) deficiency is a major problem facing many countries. The total zinc content of soil varies between 10 and 300 ppm (Lăcătușu R., 2003). When added to soil or a nutrient mixture, there is a rapid initial reaction in which the trace elements are absorbed, followed by slower reactions that remove the metal from the soluble pool in a process called fixation. Through this process the fixed fraction increases, the fraction that can no longer be easily changed in the solution phase. (Legret P., 2006).

Cadmium is non-essential metal element, but it has been detected in many plant species, making it one of the most dangerous pollutants. The normal contents of Cd (II) in the soil are between 0.1 and 0.5 mg/kg, but it easily accumulates in plants due to its increased mobility and availability. In agriculture, Cd (II) comes from mineral fertilizers, especially from ammonium phosphate and superphosphate (0.05-0.71 mg/kg Cd) organic fertilizers (0.25-36 mg/kg Cd), sludge from city sewage used as fertilizer (300 mg/kg C) (Holm P.E., 2003). A sustainable method to maximize soil fertility and quality, change the availability of heavy metals and increase of crop production is the use of the nutrient mixture that consists in compost and peat (60:40%). The compost item, obtained by mixing organic materials in conditions favorable to microbial decomposition, can increase the degree of heavy metals immobilization and mineral fertilizers assimilation. The presence of iron oxides and humic substances in the structure of compost can achieve these challenging issues. The optimal stage when heavy metals can be immobilized is when the compost is stabilized (Kabata P., Mukherjee., 2007). This slow acting organic fertilizer fails to degrade inorganic contaminants such as heavy

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metals but reduces their availability to be absorbed by plants.

Peat is a natural material, with a neutral reaction, high hydration capacity, rich in humic acids, black in color and high ash content (Arikibe J.E., Prasad S., 2020). Peat performs better in certain toxicity categories duet to its low content of heavy metals. In general, chemical elements have an affinity for organic matter. The organic component in peat is made up of a complex mixture of substances containing the majority of elements such as C, H, O, N, to which small amounts of Ca, Mg, Fe, K, P, S are added.

The study was carried out with the aim of following the sorption process of cadmium metal and zinc ions, on nutrient mixture consisting of peat and compost.

MATERIAL AND METHOD

The nutrient mixture was obtained from the Experimental Farm of USV Iasi. Approximately one kilogram of the nutrient mixture was washed with ultra-pure water to remove the dust and other adhered materials. It was dried for 48 h at 75 ^{0}C in an oven. The dried nutrient mixture was ground at 0.1-0.15 mm size and used for sorption studies. The properties of the nutrient mixture are shown in *table 1*. In the laboratory, the samples were analyzed for pH, the content of organic matter, phosphorus, potassium and heavy metals (total content, accessible and soluble forms). The solubility and mobility of heavy metal is closely related to the processes of adsorption, desorption, complexation, reactions of oxidation-reduction, precipitation and dissolution, reactions that depend on the character of the environment in which these processes take place (Barman *et al,* 2000, Quartacci *et al*, 2005).

Table 1

The characteristics of the nutrient mixture from a chemical point of view

No. crt	Analysis name	Unit of measure	Results obtained
1.	pH	-	4.94
2.	Total phosphorus	mg/100 g mixture	9.62
3.	Total potassium	mg/100 g mixture	25.7
4.	Accessible phosphorus	ppm	310
5.	Available potassium	ppm	720
6.	Organic matter	%	51.95
7.	Accessible zinc	ppm	0.388
8.	Accessible copper	ppm	0.63
9.	Accessible lead	ppm	0.254
10.	Accessible nickel	ppm	0.877
11.	Accessible cadmium	ppm	0.052

The pH of the samples was analyzed in an aqueous suspension and determined potentiometrically using a glass-calomel combined electrode, WTW; The content in organic matter was carried out by loss on calcination, a method that consists in measuring the loss in weight upon calcination of the sample at a temperature of 450^{0}C; the content of mobile phosphorus and potassium soluble in the ammonium acetate-lactate solution, was carried out according to the Egner-Riehm-Domingo method; the determination of mobile zinc and cadmium contents was carried out by extraction in EDTA-ammonium acetate solution at pH=7.0 (Lăcătușu R. *et al*, 1987).

In order to assess the contamination level of the nutrient mixture with these metals, it was necessary to put the solid phase in contact with the liquid phase, in which some parameters varied while others remained constant. To study the behavior of Cd (II) and Zn (II) on nutrient mixture, it is necessary to determine and quantify the total forms of heavy metals from the soil solution. The total content of heavy metals was analyzed with the help of X-ray fluorescence spectrometry, which provides information relative fast and accurate using a non-invasive technique that can be easily applied to different types of samples. The device used for XRF analysis is an S8 Tiger spectrometer produced by Bruker, Germany;

The studies on the sorption of cadmium and zinc on nutrient mixture were carried out by contacting the two heavy metals in different concentrations. The necessary concentrations were obtained by diluting the stock solution 1g/l of Cd (II) and 1g/l of Zn (II), to the desired concentrations in the range between 20-150 mg/l. Metals in the soil solution are found in the form of free ions, or in the form of soluble complex combinations, or associated with the mobile colloidal phase. To evaluate the adsorptive potential of the nutrient mixture under static conditions, it is necessary to contact the aqueous solution containing the polluting species (Zn and Cd) with the adsorbent.

RESULTS AND DISCUSSIONS

For optimal parameters required to increase the adsorptive potential of the nutrient mixture under static conditions, were evaluated the following parameters: initial pH of the solution, nutrient mixture dose, contact time and concentration of heavy metals.

The influence of pH on the adsorption process of Cd (II) and Zn (II)

The nutrient mixture surface properties and ionization level can be conditioned by pH optimization. For the influence of pH, a dose of 5.0 g of the nutrient mixture was used, placed in contact with an aqueous solution of Cd (II) and Zn (II) at an initial concentration of 25 mg/l.

The optimum pH value for pollutant adsorption has been established through trials. The modified pH values were obtained with the help of diluted solutions of acids and bases HCl 1n, NH_3 1:1, NaOH 1n, $CaCl_2$ 0.1n, in a range between 1.3 and 9.6 at room temperature. After 24 hours, the two phases were separated by filtration, at which time the metal ion concentration in the filtrate was also determined. The obtained results are represented in *figure 1* and it is found that regardless of the initial pH value, following the sorption process of Cd (II) and Zn (II) ions, the final pH value decreases.

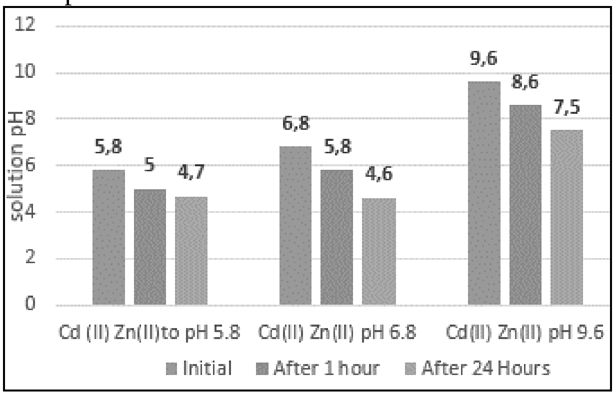

Figure 1**Initial and final pH values over a 24 hour interval**

The results regarding the variation of the Cd (II) and Zn (II) concentration retained on the nutrient mixture depending on the pH of the initial solution. By adding calcium, association with chlorine, using low concentrations of phosphate, the metal adsorption process is intensified and mobility is influenced (Kocher *et al*, 2005; Kluge, Wessolck, 2012). Hydrogen ions have a metal complexing and ion exchange effect; this finding reflected in the influence of cadmium and zinc concentration retained on the nutrient mixture. The phenomenon of the removal of Cd (II) and Zn (II) ions is observed with the increase of the initial pH values. It is noted that in the pH range between 5.0 and 6.7 a greater amount of Cd (II) and Zn (II) is absorbed, and around the pH value of 9.5 the whole process intensifies, and concentrations of cadmium ions and of zinc retained on the organic matter is maximum.

The influence of the amount of nutrient mixture on the sorption of Cd and Zn

To follow the activity of the two metals depending on the amount of mixture used the dose varied from 5 g to 10 g, adding 50 ml of 50 mg/l solution of cadmium and zinc for 24 hours at room temperature. *Table 2* show the values of the amount of metal ion retained on the absorbent mass. It can be observed that 10 g of the mixture the maximum effect is obtained, when the largest amount of cadmium and zinc is retained. Increasing the dose of nutrient mixture can no longer have an effect, due to the phenomenon of agglomeration, which can lead to the blocking of superficial functional groups.

Table 2

The concentration of Cd(II) and Zn (II)ions in the nutrient mixture

No. crt.	Zn mg/Kg	Cd mg/Kg	Contact time	Mixture dose g
1.	17.32	6.22	24 hours	5
2.	18.70	7.36	24 hours	6
3.	20.8	8.54	24 hours	7
4.	21.1	9.96	24 hours	8
5.	21.9	10.8	24 hours	10

The influence of contact time on the sorption process

The experiment was carried out for a period of 1200 minutes, using a dose of 5 g placed in contact with a solution of Cd (II) whose concentration was 50 mg/l and Zn (II) of 100 mg/l, having a pH of 6.3. It was found that the sorption rate of Cd (II) is very high in the first 15-17 minutes, and of Zn (II) after which it starts to decrease followed by reaching equilibrium after about 140-150 minutes.

Table 3

The concentrations of metal ions as a function of time

Solution concentration	After 20 minutes		After 140 minutes		After 1200 minutes	
	Zn^{2+}	Cd^{2+}	Zn^{2+}	Cd^{2+}	Zn^{2+}	Cd^{2+}
	mg/kg					
50 mg/l Cd		28		35		37
100mg/l Zn	27		56		62	

Influence of organic matter content

Humus/organic matter is considered the stabilized organic component of soil. The presence of organic matter in the nutrient mixture has the ability to accumulate, immobilize and block heavy metals. The humic acids from the organic matter can affect the solubility and mobility of heavy metals. It is considered that mature compost from the nutrient mixture, which has increased moisture and high content of organic matter, can reduce the bioavailability of heavy metals due to the phenomenon of adsorption. Organic matter can form very stable complexes with zinc and cadmium. The total content of Cd (II) and Zn (II) have high values (Cd=21.67 mg/kg and Zn=112.20 mg/kg) while the values obtained from the nutrient mixture solutions (Cd=11.69 µg/l and Zn= 42.24 µg/l) and those from the accessible fraction (Cd=1.468 mg/kg and Zn=19.26 mg/kg) have lower concentrations, which means that mostly the metal ions were retained in the nutrient mixture *(table 4)*. Zinc establishes durable forms, which often accumulate in horizons with increased content of organic matter. The fractions that control the concentration of zinc in the soil solution are those retained by surface processes (adsorption, exchange and specific) and by complexation reactions with organic matter. The mobility and ability of cadmium to accumulate are enhanced under conditions of low pH, the retention capacity of the absorbing metal and the low content of organic matter. Between Cd and Zn there is an interdependence related to the adsorption in the plant, which manifests itself especially when the phenomenon of over-phosphating of the soil occurs *(table 5)*.

Table 4

Chemical analyses of samples of the nutrient mixture in contact with contamination solutions (microelements)

Sample	Total forms		Mobile forms		Nutrient solution	
	Zn	Cd	Zn	Cd	Zn µg/L	Cd µg/L
	mg/kg				µg/L	
1	112.20	21.67	19.26	1.468	42.24	11.69
2	94.54	17.36	16.16	1.034	40.25	10.74
3	74.51	9.32	11.80	0.87	28.54	5.30

Table 5

Chemical analyses of samples of the nutrient mixture in contact with contamination solutions (macroelements)

Sample number	OM %	P ppm	K ppm
1	51.95	300	700
2	47.30	288	630
3	45.13	271	421

CONCLUSIONS

The results obtained provide an image of the adsorption process, which allows the establishment of conditions in which the adsorption process is maximum. Compost can contribute decisively to the reintegration of organic matter into the soil, so it represents a cost-effective way to restore the soil. Compost is able to biodegrade on its own, while heavy metals tend to persist and accumulate. As the main disadvantage of the repeated use of large doses of composts involves the danger of enriching the soil in heavy metals (Pb, Cd, Cu, Ni, Zn). Knowing the processes that build the behavior of heavy metals and the factors that influence this process, will allow for preventing or mitigating the negative effects characteristic of heavy metal pollution. In general, the parameters that characterize the soil reserve are the total forms of metal, and the amount of metal that can be assimilated by plants is represented by the mobility of the metal. When heavy metals are closely related to the constituents of the nutrient mixture, they become less accessible and therefore less toxic, but when conditions allow their passage into the soil solution, the risk of pollution arises. The nutrient mixture represents a valuable resource in soil practices due to its increased organic matter content and nutrient supply. The ultimate goal of this study was to reduce the level of contaminants in the nutrient mixture.

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REFERENCES

Arikibe, J.E., Prasad, S., 2020 - *Determination and comparison of selected heavy metal concentrations in seawater and sediment samples in the coastal area of Suva, Fiji*. Mar. Pollut. Bull. 157,111157.

Barman S.C., Sahu R.K., Bhargava S.K., Chaterjee C., 2000 - *Distribution of Heavy Metals in Wheat, Mustard, and Weed Grown in Field Irrigated with Industrial Effluents.* Bull. Environ. Contam. Toxicol. (2000) 64:489-496.

Bulgariu Laura, **Bulgariu D.**, **2018** - *Functionalized soy waste biomass - A novel environmental-friendly biosorbent for the removal of heavy metals from aqueous solution*, Journal of Cleaner Production, 197(1), (2018), 875-885.

Holm P.E., Rootzen H., Borggard O.K., Moberg J.P., Christensen T.H., 2003 - *Correlation of cadmium distribution coefficients to soils characteristics*. J. Environ. Qual. 32:138-145.

Kabata Pendias, Mukherjee A.B., 2007 - *Trace elements from Soil to Human***.** Springer – Verlag, Berlin.pp.540-32714-1.

Kluge, Wessolek, 2012 - *Heavy metal retention of different embankments*. Conference EGU 2013.

Legret, Pagotto, 2006 – *Heavy metal retention of different embankments*. Conference EGU 2013.

Quartacci M.F., Barbara Irtelli, Baker J.M., Flavia Navari Izo, 2007 - *The use of NTA and EDDS for enhanced phytoextraction of metals from a multiply contaminated soil by Brassica carinata.* Volume 68, Issue 10, August 2007, Pp 1920-192.