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Heavy Metals Immobilization in Soils by Using of Supported Volcanic Tuff and of Biosolid

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Abstract: The using of biosolid and of supported tuff for decreasing metals availability from soil polluted with waste mining was tested in this paper, by using of two grass plants, *Medicago sativa* and *Festuca arundinaceea*. In case of *Festuca arundinacea*, the decreasing of Zn and Mn accumulation in plant tissues took place about 1.8 - 2.3 times, and 3.5 - 5.0 respectively; Cu and Pb concentrations decreased 2.6 - 3.2 times and 7.6 - 10.7, respectively. Similar results were obtained for *Medicago sativa.* It was determined that using of biosoild and supported tuff, allowed important immobilization of metals in polluted soils.

Keywords: heavy metals, soil, volcanic tuff, biosolid

1. Introduction

Heavy metals are important pollutants in environment. They are present in great concentrations, both in polluted soils and in waste mining deposits. For decreasing of metals bioavailability from polluted soils are used different materials, like sludges from municipal waste water treatment, native zeolites and native modified zeolites [1-5]. These materials immobilize heavy metals in polluted sites. Thus, the concentrations of pollutants availably to cultivated plants decrease in great extent [6-10].

Some grass plants species may grow on soils polluted with heavy metals, and tolerate them. E.g., *Medicago sativa* or alfalfa can grow onto soils polluted with metals. It was showed that this plant may concentrate heavy metals in its tissues. Medicago sativa may be used for metal extraction and recovery from polluted sites. The other plant, Festuca arundinaceea, was also tested for phytoremediation.

The using of biosolid and of supported tuff for decreasing metals availability from soil polluted with waste mining was tested in this paper by using of two grass plants, Medicago sativa and Festuca arundinaceea.

2. Materials and methods

In order to determine the efficiency of biosolid and of supported volcanic tuff for immobilization of heavy metals in polluted soils, experiments were undertaken at Banat University of Agricultural Science and Veterinary Medicine, in Timisoara. The preparation of experimental parcels was realized during 16-19.03.2007. Experimental block consisted of 6 parcels, as follows:

- 3 parcels cultivated with Festuca arundinacea: (1) soil containing waste mining as blank sample; (2) soil containing waste mining, fertilized with biosolid; (3) soil containing waste mining, fertilized with biosolid and supported tuff; -3 identical parcels, cultivated with Medicago sativa.

As biosolid was used municipal sludge, resulted from waste water treatment plant from Timisoara. The composition of waste minig used for experimental parcels pollution was: Cu - 669 mg/kg d.s., Zn - 610 mg/kg d.s., Mn - 676 mg/Kg d.s., Cd – 2.7mg/Kg d.s. Pb -110 mg/Kg d.s. This waste was taken of waste mining deposit from Molodova Noua.

The amounts of waste mining and of biosolid introduced in soil were 20 kg/m^2, and 8 kg/m^2, respectively; volcanic tuff was supported with aluminium basic polychloride, and 5 kg/m^2 was applied.

First harvesting of plants was done in the beginning of July, and the second in September. The determination of heavy metals from dried plants was undertaken by their mineralization, followed by AAS spectrophotometry analysis.

3. Results and Discussion

The evolution of concentrations for metals accumulated in grass plants cultivated onto (1) soil containing waste mining, blank sample, (2) soil containing waste mining, fertilized with biosolid, and (3) soil containing waste mining, fertilized with biosolid and supported tuff, are presented in tables 1-4. At the first harvesting were not determined decreasing of metals accumulation in plants, due to using of volcanic tuff.

TABLE 1. Metal accumulation in Festuca arundinacea, cultivated on different experimental parcels, first harvesting, July 2007

experimental parcels	concentration of metals from aerial parts of *Festuca arundinacea*, mg/kg d.s.				
	Zn	Cd	Cu	Mn	Pb
(1) blank sample: soil containing waste mining	26.4	0.9	10.13	30.8	49.10
(2) soil containing waste mining, fertilized with biosolid	32.3	0.39	7.18	37.17	5.04
(3) soil containing waste mining, fertilized with biosolid and supported tuff	51.88	1.83	10.3	48.32	10.30

TABLE 2. Metal accumulation in Medicago sativa, cultivated on different experimental parcels, first harvesting, July 2007

experiment parcels	concentration of metals from aerial parts of *Medicago sativa*, mg/kg d.s.				
	Zn	Cd	Cu	Mn	Pb
(1) blank sample: soil containing waste mining	21.60	0.31	10.74	29.8	38.2
(2) soil containing waste mining, fertilized with biosolid	33.6	1.59	5.68	15.9	17.2
(3) soil containing waste mining, fertilized with biosolid and supported tuff	31.78	-	14.27	33.8	17.2

TABLE 3. Metal accumulation in Festuca arundinacea, cultivated on different experimental parcels, second harvesting, September 2007

experiment parcels	concentration of metals from aerial parts of *Festuca arundinacea*, mg/kg d.s.				
	Zn	Cd	Cu	Mn	Pb
(1) blank sample: soil containing waste mining	63.7	-	56.8	59.8	63.7
(2) soil containing waste mining, fertilized with biosolid	34.7	-	21.3	16.7	8.3
(3) soil containing waste mining, fertilized with biosolid and supported tuff	27.9	-	17.8	11.9	5.9

TABLE 4. Metal accumulation in Medicago sativa, cultivated on different experimental parcels, first harvesting, September 2007

experiment parcels	concentration of metals from aerial parts of *Medicago sativa*, mg/kg d.s.				
	Zn	Cd	Cu	Mn	Pb
(1) blank sample: soil containing waste mining	74.5	-	65.10	137.4	49.6
(2) soil containing waste mining, fertilized with biosolid	40.0	-	34.10	39.8	19.5
(3) soil containing waste mining, fertilized with biosolid and supported tuff	20.4	-	29.20	41.2	14.0

By using of supported volcanic tuff synergic effects were determined, concerning heavy metals accumulation in plants, obtained after the second harvesting. Thus, by adding of volcanic tuff in experimental parcels containing waste mining and biosolid, an advanced decreasing of metals accumulation into plants from the second harvesting, took place.

In case of Festuca arundinaceea, the following concentrations were accumulated in the experiment (3) from the second harvesting: zinc – 27.9 mg/kg d.s., copper - 17.8 mg/kg d.s., manganese - 11.9 mg/kg d.s., lead - 5.9 mg/kg d.s. Similar concentrations were accumulated in Medicago sativa, zinc 20.4 mg/kg d.s., copper 29.2 mg/kg d.s, manganese 41.2 mg/kg d.s., lead 14 mg/kg d.s. Due to using of supported zeolite, zinc and copper significantly decreased in Festuca arundinaceea cultivated on experimental parcels with 56.2 % and 68.6 % respectively, comparatively with plants from parcels containing waste mining only. Similar results were obtained for Medicago sativa, 72.6 % and 55.1 %, respectively.

In table 5 are presented the decreasing degrees of metals concentrations from plants, after the second harvesting, by reporting of concentrations from experiments (2) to those of (3) – case a, and of concentrations from experiments (1) to (3), case - b. It may be observed that for *Festuca arundinacea*, the using of biosolid and volcanic tuff in soil polluted with waste mining, decreased Zn and Mn accumulation in plant tissues of 1.8-2.3 times, and 3.5 – 5.0 respectively; also, Cu and Pb concentrations decreased of 2.6-3.2 times and 7.6-10.7, respectively. Similar results were determined for *Medicago sativa*.

TABLE 5. The evolution of accumulation degree of heavy metals in grass plants of the second harvesting, by using of biosolid (a) only, and of biosolid together with supported volcanic tuff (b) in experimental parcels

analysis cases	decreasing of metals concentrations accumulated in plants				
	Zn	Cd	Cu	Mn	Pb
	Festuca arundinacea				
case a	1.8	-	2.6	3.5	7.6
case b	2.3	-	3.2	5.0	10.7
	Medicago sativa				
case a	1.8	-	1.9	-	2.5
case b	3.6	-	2.2	3.3	3.5

By adding of supported volcanic tuff, the accumulation of heavy metals in plant tissues cultivated on parcels containing waste mining, took place in the following order: *Festuca arundinacea*, Mn ≅ Zn > Cu ≅ Pb, for the first harvesting, and Zn > Cu > Mn > Pb for the second harvesting; *Medicago sativa,* Zn ≅ Mn > Pb ≅ Cu, the first harvesting, and Mn > Cu > Zn > Pb for the second harvesting.

It may be observed that by using of biosolids together with volcanic tuff, allowed higher accumulation of Mn and Cu in Medicago sativa, and of Zn in Festuca arundinaceea. Pb, was accumulated in smallest concentrations by both plants.

4. Conclusions

By using of supported volcanic tuff and of biosolid in experimental parcels containing waste mining, the decreasing of metals accumulation in grass plants from the second harvesting, was determined. In case of *Festuca arundinacea*, the decreasing of Zn and Mn accumulation in plant tissues took place of about 1.8-2.3 times, and 3.5 - 5.0 respectively; also, Cu and Pb concentrations decreased 2.6 - 3.2 times and 7.6 - 10.7, respectively. Similar results were determined for *Medicago sativa.* It was proved that important immobilization of metals in polluted soils, took place.

By adding of supported volcanic tuff, the accumulation of heavy metals in plant tissues cultivated on soil parcels containing waste mining, took place in the following order: *Festuca arundinacea*, Mn ≅ Zn > Cu ≅ Pb, for the first harvesting, and Zn > Cu > Mn > Pb for the second harvesting; *Medicago sativa,* Zn ≅ Mn > Pb ≅ Cu , the first harvesting, and Mn > Cu > Zn > Pb, for the second harvesting.

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