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Mobilization of Heavy Metals From Mining Wastes by their Covering with Soil and Phytoremediation

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Abstract: This paper deals with the evolution of the transport processes for Cu, Zn, Mn and Fe from a waste mining deposit, resulted by copper ore processing at Moldova Noua enterprise, in south – west part of Romania. Some areas of the deposit were covered with non-polluted soil layers, thickness of 5 and 10 cm from deposit neighbourhood, which were cultivated with grass plants like Festuca arundinaceea and Hippophae rhamnoides, in order to evaluate efficiency of metals separation. Metals transport took place by their accumulation in organic matter from soil, and concentration decresing from the other fractions of soil. Separation efficiencies of metals after five years, due to mining waste covering with soil and grass plants cultivation, were: Cu – 52 %, Zn – 70 %, Fe – 39.2 %, Mn – 77 %. The order of metals accumulation in leaves of grass plants was Fe > Zn > Mn > Cu.

Keywords: heavy metals, mining wastes, transport processes, phytoremediation.

1. Introduction

Metals are presented in polluted soils in different forms: dissolved, colloidal, and particulate. Soil pollution with heavy metals are due to soluble forms and potential soluble, like ionic exchangeable, adsorbed onto surfaces, or soluble organometallic compounds, especially complexes of fulvic acids. Metals solubility in soil and ground water is dependent on pH, redox potential, soil texture, biocenosis composition, and plants grown in polluted areas [1, 2, 3]. Metals mobility in soil is influenced by their releasing and retaining, from soil matrix into soil solution.

The other form is represented by organic soluble complexes, as are derivatives of fulvic acids, or less soluble compounds like derivatives of humic acids. It is well known that by adding organic matter in soil, like organic fertilizers, the fraction of organometallic compounds will increase. Metals that are not available, are those from mineral networks of aluminomsilicates [4, 5].

Due to specific activities of biocenosis in plants rizosphere from soil, or due to exudates released from plant roots, solubilization or immobilization of metals takes place. This paper deals with the transport processes evolution for Cu, Zn, Mn and Fe from a waste mining deposit, resulted by copper ore processing at Moldova Noua enterprise, in south – west part of Romania.

2. Experimental

Some areas of deposit were covered with non-polluted soil layers, thickness of 5 and 10 cm from deposit neighbourhood, which were cultivated with grass plants like Festuca arundinaceea and Hippophae rhamnoides in order to evaluate efficiency of metals separation. The following areas were took into consideration for the analysis:

- waste mining deposit Bosneag 2 (B2), covered with spontaneous vegetation of Festuca (l);
- two areas from B2 deposit, which were covered with layers of vegetal soil, thickness of 5 cm (lla) and 10 cm (llb), cultivated with Festuca arundinaceea for one year;
- waste mining deposit Lunca Dunarii (LD), covered with vegetal soil for 5 years, and cultivated with grass plants and bushes (Salix babylonica, Robinia pseudoacacia, Hippophae rhamnoides).

Metals concentrations from soil were analysed by using of sequential extraction method proposed by European Community Bureau of Reference (BCR). This method allows determination of metals from operationally defined fractions: l - exchangeable fraction (extraction with acetic acid); ll - fraction adsorbed onto iron and manganese oxyhydroxide surfaces (extraction with hydroxylamine hydrochloride); lll - fraction linked by organic matter (oxidation with hydrogen peroxide, extraction with ammonium acetate); lV - fraction linked by mineral network (treatment with aqua regia) [4,5,6].

3. Results and Discussion

Total initial concentration of copper, 1408 mg/Kg d.s. from waste mining area, table 1, had the following distribution in soil fractions: l – 94 mg/Kg d.s., ll – 303 mg/Kg d.s., lll – 462 mg/Kg d.s., lV – 549 mg/Kg d.s. In areas covered with 5 and 10 cm soil cultivated with Festuca arundinaceea, copper concentrations decreased up to 1280 mg/Kg d.s. and 912 mg/Kg d.s., respectively, after one year. In area covered with 10 cm soil cultivated with Hippophae rhamnoides and bushes, total copper concentration decreased up to 675 mg / Kg d.s., after 5 years.

The influence of soil thickness is revealed by different distribution of copper in the four fractions, after one year. Copper concentration linked by organic matter increased more intense in case of area covered with 10 cm (llb) vegetal soil, 26 %, than for that covered with 5 cm (la) vegetal soil, 3.6%.

TABLE 1. Distribution of the sequential repartition onto solid fractions (l, ll, lll, lV) for Cu, from mining waste deposits

Experiment	I		II		III		IV		Total
	mg/kg d.s.	%	mg/kg d.s.	%	mg/kg d.s.	%	mg/kg d.s.	%	mg/kg d.s..
deposit B2	94.0	7.3	303.2	21.5	462.0	32.8	542.0	38.4	1408.2
deposit B2, 5 cm soil layer	74.2	5.8	419.7	32.8	466.1	36.4	320.2	25.0	1280.2
deposit B2, 10 cm soil layer	40.1	4.4	126.2	13.8	526.8	57.8	218.3	24.0	911.4
deposit LD, 10 cm soil layer	97.7	14.5	92.4	13.7	352.1	52.1	132.9	19.7	675.1

TABLE 2. Distribution of the sequential repartition onto solid fractions (l, ll, lll, lV) for Mn, from mining waste deposits

Experiment	I		II		III		IV		Total
	mg/kg d.s.	%	mg/kg d.s.	%	mg/kg d.s.	%	mg/kg . d.s.	%	mg/kg d.s.
deposit B2	276.8	31.7	364	41.7	95.9	11.0	136.8	15.6	872.8
deposit B2, 5 cm soil layer	260.8	31.7	304	37	132	16.0	126.0	15.3	822.0
deposit B2, 10 cm soil layer	215	27.6	365	46.6	107.8	13.7	95	12.1	782.4
deposit LD, 10 cm soil layer	82.0	45.4	61.2	34	7.5	4.1	28.9	16.5	180.5

TABLE 3. Distribution of the sequential repartition onto solid fractions (l, ll, lll, lV) for Zn, from mining waste deposits

Experiment	I		II		III		IV		Total
	mg/kg d.s.	%	mg/kg d.s.	%	mg/kg d.s.	%	mg/kg . d.s.	%	mg/kg d.s.
deposit B2	68.8	14.3	72.5	15,1	139,3	29	201	41,6	481.6
deposit B2, 5 cm soil layer	56	13.7	52.8	13.0	154	37.6	146	35.7	408.8
deposit B2, 10 cm soil layer	51.6	13.5	54	14.2	172	45.3	102,4	27	380.0
deposit LD, 10 cm soil layer	32	22,1	33.8	23.5	33.5	23,1	45.4	31.3	144.7

TABLE 4. Distribution of the sequential repartition onto solid fractions (l, ll, lll, lV) for Fe, from mining waste deposits

Experiment	I		II		III		IV		Total
	mg/kg d.s.	%	mg/kg d.s.	%	mg/kg d.s.	%	mg/kg . d.s.	%	mg/kg d.s.
deposit B2	193.3	0.4	528.7	1.0	4200	8.2	46000	90.3	50922
deposit B2, 5 cm soil layer	76	0.2	501	1.1	14350	30,9	31380	67.7	46307
deposit B2, 10 cm soil layer	82	0.2	496	1.4	3913	10,7	32150	87,7	36641
deposit LD, 10 cm soil layer	36.3	0.2	748.8	2.2	13534	43.6	16799.5	54	31110.2

The increasing of organic content from vegetal soil for areas ll b and lll, determined the increasing of copper accumulation in fraction linked by organic matter, more than 50 % from total copper concentration, especially by decreasing of copper concentration from fraction adsorbed onto oxyhydroxide surfaces.

The concentration of copper from ionic exchangeable fraction, is smaller than from the other fractions. Decreasing of copper linked by mineral networks and ionic exchangeable was about the same after one year, for the covered areas.

Separation efficiencies for copper from the horizon 10 - 20 cm was 52 %, after five years.

Festuca arundinaceea accumulated in vegetation period of 3 - 4 months, 10 - 25 mg Cu/kg d.s. in areas ll a and ll b, and 10.6 mg Cu/kg d.s. in area lll (LD).

In table 2 are presented both total manganese concentrations from studied areas, and metal distribution in soil fractions. In waste minig deposit B2, manganese concentrations of 780 - 870 mg/kg d.s., were distributed mostly in fractions l and ll: the content of ionic exchangeable fraction ranged in 215 – 277 mg Mn/kg d.s., and that adsorbed onto oxyhydroxides surface between 304 - 365 mg/kg d.s. Manganese concentration from fractions l and ll, represent about 70-80 % of total Mn concentration.

After one year, manganese concentration from area covered with vegetable soil (10 cm thickness), decreased with 10.3 %. Transport process is more evident after five years, when decreasing of manganese concentrations in all fractions was recorded, 79.3%, in area LD. The most important decreasing was determined in case of organic fraction, 92.8%, showing its dominant role in metal transport process.

Manganese was accumulated in leaves of Festuca arundinaceea during vegetation period, up to 45 – 65 mg Mn/kg, and in those of Hippophae rhamnoides, 23 mg Mn/kg s.u.

By analysis of zinc concentration evolutions from soil fractions, versus thickness of vegetal soil and time of cultivation, table 3, the following remarks were evidenced:

- zinc content from mineral networks decreased with increasing of vegetal soil thickness, and time of cultivation;
- concentration of zinc linked by organic matter, after an initial increasing with 19.1 % after first year of cultivation, decreased in great extent in the following four years, with 80.5 %.

Initial, in the waste mining deposit, content of zinc linked by organic matter and by mineral networks, was 2 -3 times greater then content from ionic exchangeable and adsorbed onto oxyhydroxide surfaces. After five years, the concentrations from the four fractions are closed, and efficiency for total zinc separation was about 70 %.

Festuca arundinceea accumulated up to100 mg Zn/kg d.s., and Hippophae rhamnoides 60 mgZn /kg d.s.

TABLE 5. Heavy metals accumulation in leaves of Festuca arundinaceea and Hippophae rhamnoides, cultivated on waste mining areas covered with vegetal soil layers

Grass plants	Cu	Mn	Zn	Fe
Leaves of Festuca arundinaceea, B2, 10 cm soil	10	45	75	710
Leaves of Festuca arundinaceea,B 2, 10 cm soil	25	65	105	855
Leaves of Hippophae rhamnoides (LD area)	10.6	23.3	60.35	656.7
Fruits of Hippophae rhamnoides (LD area)	1.61	2.75	7.3	78.9

In table 4, iron content from soil fractions is presented. Iron is distributed especially in fraction linked by mineral networks, 46 g/kg d.s., and by organic matter, 4.1 g /kg d.s. In areas covered with vegetal soil, variation of concentrations from ionic exchangeable and adsorbed onto oxyhydroxide surfaces, were insignificant.

Continuous decreasing of iron from mineral networks, and variations of concentrations from fraction linked by mineral networks, showed that mobilization of iron is due to metal transport processes between these two fractions.

After five years, iron content of fraction linked by organic matter was 43.6 %, (13.5 g /kg d.s.) and that from mineral networks, 54 % (16.7 g/kg d.s). Efficiency of iron separation after five years was 39 %. With increasing of soil thickness and time of cultivation, a greater concentration of iron is linked by organic matter.

Festuca arundinaceea accumulated 710 – 850 mg Fe/kg d.s. in leaves, and Hippophae rhamnoides 655.7 mgZn/kg d.s.

4. Conclusions

1. Concentration of manganese from polluted areas is distributed mostly in ionic exchangeable and adsorbed onto oxyhydroxide surface fractions, about 70 - 80 % of total Mn concentration. The analysis of transport process revealed decreasing of manganese concentrations in all fractions of soil. The most important decreasing was determined in case of organic fraction, 92.8 %, after five years.

2. Excangeable copper and zinc were in small quantities, than in the other fractions. Copper was linked especially by organic matter, and zinc by mineral networks.

3. Iron was presented in high quantities, 31.1 – 50.9 g/kg d.s. Organic matter from vegetal soil is responsible by transport process of iron between the other fractions. It can mobilize up to 13.5 g iron /Kg d.s. Festuca arundinaceea accumulated 853 mg/kg d.s., and fruit of Hippophae rhamnoides about 700 mg Fe/kg d.s.

4. Separation efficiencies of metals after five years, due to mining waste covering with soil and grass plants cultivation, were: Cu – 52 %, Zn – 70 %, Fe – 39.2 %, Mn – 77 %. The order of metals accumulation in leaves of grass plants was Fe > Zn > Mn > Cu.

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