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RESEARCH REGARDING THE PHYTO-REHABILITATION OF THE SLUDGE STORAGE AREA FROM WASTEWATER TREATMENT PLANTS

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Abstract

The increasing amount of sewage sludge produced in developed countries, especially in metropolitan cities, has been one of the primary environmental issues the European Union has had to deal with. The wastewater and sludge from municipal wastewater treatment plants contain valuable nutrients, yet represent a pollution source because of the heavy metal content. In order to naturally restore the wastewater sludge storage areas, it is necessary to apply rehabilitation technologies. It is important to develop feasible and economical technologies for removing heavy metals from wastewater sludge. Phytoremediation is an alternative technology for the enhanced remediation of environments contaminated with heavy metals. Phytoremediation is a process that uses plants to remove, transfer, stabilize, and destroy contaminants in soils and sediments. The mechanisms include enhanced rhizosphere biodegradation, phyto-extraction (also called "phyto-accumulation"), phyto-degradation, and phyto-stabilization.

The aim of the present study is to illustrate the accumulation of heavy metals through spontaneous flora grown on wastewater sludge storage areas in order to apply phytoremediation as a rehabilitation method.

Keywords: phytoremediation, sewage sludge, heavy metal.

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Introduction

The number, size and efficiency of wastewater treatment plants will become significant through the implementation of the 2015 (for human agglomerations with a population equivalent – p.e. – greater than 10,000) and the 2018 (for human agglomerations with less than 10,000 p.e.), Urban Wastewater DIRECTIVE 91/271/EEC. The sludge production in countries that have already complied with the requirements of the directive above (Austria, Denmark and Germany) was determined as ranging between 23 and 29 kg of dry substance/inhabitant and year. This value is used in the case of Romania where sludge production is relatively low (***PMB, 2009).

Given that wet sludge storage sites have a negative impact on the environment, through gas emissions from anaerobic fermentation, the release of persistent organic (PCBs, PAHs, dioxins) and inorganic (heavy metals, soluble salts) substances, the presence of pathogens and visual discomfort, the closure of these deposits was deemed necessary.

Therefore, in order to return the land occupied by sludge storage areas to the economic cycle, it is necessary for this land to be rehabilitated. There are several ways of achieving this, such as: excavating the mud, after a preliminary drainage, drying and grinding of the sludge in order to be used as a source of nutrients for certain soil types in the region, or covering the sludge storage with various materials, including topsoil, after draining and drying, changing the composition and particle size and increasing the oxidability of the soil.

A possible alternative concerns the use of plants both as green fertilizer for the improvement of the newer soil organic matter, and as a means of extraction of the heavy metals from the solidifying sludge (Lăcătuşu et al., 2005).

The present study details the rehabilitation of the soils affected by sludge through the use of plants (phyto-rehabilitation).

Materials and methods

In order to analyze the sludge, three samples were collected from three different locations. The first sample is a reddish sludge containing trivalent iron hydroxides and oxides resulting from the oxidation of bivalent iron under reduction conditions, found in the presence of excess water. The second sample, dark in color, was collected near a dam and is in a transient state of oxidation. The third sample was collected in a reed-covered area where more reduction conditions are predominant, but where a humification process has begun.

The depth of the sludge samples varied between 20 cm and 30 cm. Additionally, the sampling of plants grown spontaneously on the sludge took place at the same time with the sludge sampling. Samples were collected from seven species, namely: *Atriplex sp., Rumex acetosella, Phragmites australis, Chenopodium album, Aster panonicum, Solanum nigrum and Galinosaga parviflora*. For the purpose of analysis, the plants were separated into vegetative parts: roots, stems and leaves.

The *sludge reaction*, as evidenced by the pH index, was determined potentiometrically in aqueous solution at a 1:5 sludge : water ratio, using a combined glass-calomel electrode.

The estimation of the organic carbon was performed through the Walkley-Black method.

Top mobile forms of P and K were extracted by using a solution of ammonium acetate-lactate with a pH of 3.7, and determinations were performed spectrophotometrically (P) and flamphotometrically (K).

The determination of total nitrogen was carried out by using the Kjeldahl method. The heavy metal content was determined in hydrochloride solution obtained from the disaggregation of the sample using a mixture of perchloric acid and nitric acid, followed by measurements using atomic absorption spectrometry.

The plant samples were dried in the oven for several hours at a temperature of 70°C, after which they were ground. The total amount of nitrogen was determined by using the Kjeldahl method. The other macroelements (P, K, Ca, Mg) and microelements (heavy metals) were determined by using a hydrochloride solution obtained after the solubilization of the ash from the plants. The ash was obtained through incineration at a temperature of 450°C. Measurements were carried out through visible spectrometry (P), flame photometry (K, Ca) and atomic absorption spectrometry for Mg, Cd, Cr, Fe, Mn, Ni, Pb, and Zn.

Results

The chemical composition of sludge

1. Reaction and macroelement content is presented in table 1. The pH values determined in aqueous solution at a dry sludge (water ratio of 1:5) indicate a weak alkaline reaction in the reddish mud, and a weakly acid reaction in the other two samples. The reaction is slightly alkaline due to the presence of hydroxides and carbonates.

Tab. 1 Reaction and macroelement content of sludge samples collected from the sludge storage area

No. samp.	Identification	pH H_2O	Organic matter (%)	N_t (%)	C_{org} (%)	C/N	P_{AL} (ppm)	K_{AL} (ppm)
1	Reddish sludge	7.91	3.06	0.158	1.8	13.1	1233	1526
2	Darker sludge from the dam area	6.75	27.1	4.633	15.7	4.0	504	558
3	Sludge from the middle of the storage within the reed-covered area	6.78	22.4	1.321	13.0	11.5	600	549

The dry organic matter content varies between 3.06% and 27.1% in the sludge collected near the dam. An equally high amount of organic matter is present in the sample taken from the reed-covered area. The presence of reed, which actually reduces the water content in the sludge, has positively influenced the humification process. The value of the C/N ratio (11.5) indicates a good evolution of both the mineralization and humification processes.

The total nitrogen content of the sludge samples, relative to the limits of interpretation of classes of total soil nitrogen content, shows very small nitrogen content for the first sample, small nitrogen content for the third sample, and large nitrogen content for the second sample.

The content of mobile forms of phosphorus and potassium is large.

In conclusion, the sludge has a different reaction, from slightly acid to slightly alkaline, containing a total amount of N from very small to very large, and a very high content of mobile forms of phosphorus and potassium. The sludge sample collected from the reed-covered area is in an advanced stage of humification-mineralization.

2. The values included in table 2 show significant heavy metal content in the sludge.

Tab.2. Total heavy metal content (ppm) of sludge samples compared with clark values (C), normal values in soil (VN), threshold values (PA) and intervention (PI) for a less sensitive use of the land values

No. samp.	Identification	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	Reddish sludge	7	14	106	141	34525	542	65	186	10409
2	Sludge dam area	3	10	52	144	266632	486	39	95	4473
3	Sludge from the middle of the storage with reed vegetation	5	14	107	130	22653	427	134	141	7088
	C[1]	0.13	18	83	47		1000	58	16	83
	VN[2]	0.30	5	30	20		500	20	15	50
	PA[3]	5	100	300	250		2000	200	250	700
	PI[4]	10	250	600	500		4000	500	1000	1500

[1] Fiedler and Rosler (1988); [2] Lăcătuşu et al. (2005); [3,4] Order 756/1997 / MAPPM (1997)

Comparing the analytical data with clark values found in three samples of sludge, the heavy metal content, with the exception of two chemical elements (Co and Mn), is larger than the amount found in the clark.

In comparison to normal values in soils, the heavy metal contents of the sludge are 233 times greater in the case of zinc, than the average found in the three samples, and 16 times greater in the case of cadmium. Values outweigh the other elements in soil average content by 9.4 (Pb), 4.6 (Cu), 3.9 (Ni), 2.9 (Cr), and 2.5 (Co).

A comparison of the values of heavy metals from the sludge with alert values and intervention for a less sensitive use of land thresholds shows that most chemical elements in the sludge samples display values below these thresholds.

An exception is the zinc concentration, which is higher than the intervention threshold in all three sludge samples.

The absorption of chemical elements by plants from spontaneous flora grown in sludge storage

1. Accumulation of macroelements in plants. Analytical data regarding the content of macroelements of primary and secondary order – N, P, K and Ca and Mg, respectively – indicate the presence of these items in bulk, reflected by the amounts of these chemical elements in the substrate composed of sludge at different stages of maturation (tab. 1), and the concentrations of these nutrients in leaves, stems and roots of seven types of ruderal plants analyzed (tab. 3).

Tab. 3 Macroelement content (%) in vegetative organs of plant species collected from sludge storage

Crt. no.	Genus and species		N	P	K	Ca	Mg
1	*Atriplex sp.*	Leaf	3.75	0.339	2.75	2.16	0.598
2		Strain	0.91	0.097	1.25	0.31	0.055
3		Roots	0.92	0.149	1.92	0.27	0.180
4	*Rumex acetosella*	Leaf	3.11	0.237	2.92	2.23	0.569
5		Strain	1.18	0.064	2.62	1.00	0.097
6		Roots	1.77	0.365	1.25	1.72	0.273
7	*Phragmites australis*	Leaf	3.40	0.231	3.10	0.60	0.140
8		Strain	1.07	0.088	1.42	0.18	0.050
9		Roots	2.77	0.331	2.09	0.73	0.180
10	*Chenopodium album*	Leaf	3.22	0.292	5.39	1.99	0.070
11		Strain	0.70	0.070	2.13	0.44	0.085
12		Roots	0.71	0.168	1.21	0.40	0.171
13	*Aster panonicum*	Leaf	3.46	0.257	1.51	2.91	0.503
14		Strain	1.65	0.105	1.95	1.50	0.116
15		Roots	0.80	0.148	1.92	0.57	0.100
16	*Solanum nigrum*	Leaf	6.00	0.462	4.92	3.22	0.344
17		Strain	2.03	0.278	4.25	1.26	0.204
18		Roots	1.31	0.218	2.27	0.97	0.152
19	*Galinosaga parviflora*	Leaf	5.61	0.857	4.86	4.23	1.554
20		Strain	3.22	0.220	4.39	1.10	0.213
21		Roots	2.51	0.379	7.07	5.07	0.311

2. Accumulation of heavy metals (microelements) in plants. Unlike macroelements, microelements such as metals and heavy metal known to environmental protection research, have accumulated in large quantities, some quite large, compared to plants needed for a balanced nutrition.

The analysis of chemical elements indicates that some of them concentrate at a high level, others at a medium level, and some at normal levels. As an example for the first category, zinc shows, in the leaves of *Rumex acetosella*, 37 times higher contents than the normal range limit (60 ppm). Very high zinc values have been recorded in the leaves of *Aster panonicum* and *Galinosaga parviflora* (19 times higher than the normal 60 ppm).

High zinc contents were determined in roots of *Rumex acetosella* and *Galinosaga parviflora*, namely 23 times and 28 times the value of 60 ppm, respectively.

On average, for the seven plant species examined, the zinc content is about 11 times greater than the right limit of the range of content.

Tab. 4 Content (ppm) of microelements (heavy metals) in vegetative organs of plant species collected from sludge storage

Crt. no.	Genus and species		Zn	Cu	Fe	Mn	Pb	Cr	Ni	Cd
1	*Atriplex sp.*	Leaf	664	10	269	242	10	sld	1.60	3.10
2		Strain	147	4	75	20	7	sld	sld	2.36
3		Roots	309	7	135	21	10	sld	sld	3.05
4	*Rumex acetosella*	Leaf	2246	9	349	676	10	sld	0.81	3.53
5		Strain	351	3	98	54	9	sld	sld	2.56
6		Roots	1391	35	121	128	21	15.72	11.32	3.94
7	*Phragmites australis*	Leaf	158	5	191	150	11	sld	1.10	2.81
8		Strain	140	4	88	40	10	sld	sld	2.63
9		Roots	685	13	1043	108	13	2.18	1.38	3.10
10	*Chenopodium album*	Leaf	899	9	291	268	13	sld	sld	2.71
11		Strain	192	4	61	30	13	0.73	sld	4.36
12		Roots	372	7	388	23	13	1.08	sld	2.96
13	*Aster panonicum*	Leaf	1151	12	685	517	14	1.57	sld	3.20
14		Strain	220	3	69	54	141	0.81	sld	2.89
15		Roots	460	9	1136	43	14	2.49	0.81	2.93
16	*Solanum nigrum*	Leaf	608	27	121	505	14	1.46	1.15	3.67
17		Strain	527	7	98	118	13	1.15	sld	3.24
18		Roots	901	17	1670	63	17	6.42	2.49	3.28
19	*Galinosaga parviflora*	Leaf	1171	28	481	252	16	2.91	0.87	3.54
20		Strain	225	5	98	14	14	2.69	sld	4.13
21		Roots	1671	15	1920	50	19	5.90	2.57	3.49
Normal areas contents*			20-60	5-30	20-600	50-200	5-10	0.02-0.2	0.1-2	0.01-0.1

* Kabata-Pendias and Pendias (2001)

Conclusions

Phytorehabilitation/bioremediation can be successfully used to bring normalcy to the affected sludge land disposals from municipal sewage plants.

Through evapotranspiration, plant species developed spontaneously help reduce the amount of water.

Spontaneous vegetation assures, through evapotranspiration, the diminishing of the amount of water. Through specific processes of solubilization, fixation and accumulation of polluting elements, it also ensures the removal of heavy metals. The plants studied accumulated large amounts of zinc and cadmium, in agreement with “dowry” natural mud, and sometimes larger amounts of Fe, Mn, Pb, Cr and Ni, in agreement with the species and organ examined. Between the heavy metal content of the sludge and the one from the plant there is a directly proportional relationship.

The existing vegetation determines the humification and mineralisation of the raw organic matter in the sludge, contributing to the humification by organic matter, through their roots or if incorporated.

The technology necessary for the rehabilitation of the land occupied by sludge will be stored in the optimum conditions required for the development of vegetation.

The use of native species is recommended; „plants by air”, which contain large amounts of heavy metals, will harvest and store the waste dumps. The roots will help the process of mineralization and humification, launching the early stages in the formation of soil materials.

According to the law of ecology, *Nature knows best*.

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