Studies Regarding the Use of Ash from Pyrolysis Rubber as an Amendment to Soils Used to Cover Waste Dumps, with *Phalaris Arundinacea*

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The aim of the study was to stabilize waste dumps (ash) from rubber pyrolysis using a plant called Phalaris Arundinacea. Also was studied the possibility of using ash from the pyrolysis of waste rubber, as a soil amendment used to cover the heaps of waste. For ash from rubber pyrolysis, were conducted leaching tests in view depositories at sites licensed for arranged, setting the as waste rubber pyrolysis originated corresponds to the hazardous waste and it can be accepted for storage in warehouses specially designated waste. Following an initial analysis of the ash it was observed that it has high metals content, especially zinc, which allows use as an amendment for mixing the with soils, in order to use of this mixture to cover waste dumps or bioremediation processes.

Key words: waste dumps, bioremediation, metals, Phalaris arundinacea

Waste from burning in form of ash (approximately 80%) and slag (15%), irrecoverable for the station, shall be removed and stored. The annual amount of waste varies depending on power station, the quality and degree from spraying of product burned and the characteristics of the boiler furnace [1-3]. The land on which are stored are not devoid of vegetation, each other showing plant populations including dozens of species. Some species show genetic variability, large enough, that some genotypes to adapt to survive in these soils with excess heavy metals [4-6]. At low concentrations of metals in soil solution more intense absorption occurs, and at high concentrations, the absorption is reduced [7-9]. Determinations have shown that species adapted to take soil and accumulates heavy metals in amounts that would result in death for most other species, with specific physiological mechanisms to counteract the toxic effects of heavy metals [10-12]. The absorption of the various heavy metals in the soil solution or extra root is selective for the majority of plant species. Accumulation of heavy metals in plants depends on their concentration in the soil solution, interactions between these elements and their physiological role [13-16]. Phytoremediation has been proposed as an alternative to restoration practices soils polluted with heavy metals; because the environmental impact of this method is much smaller and also the costs are lower [17-20]. Phytoremediation is defined as the removal of heavy metals from the soil through aboveground biomass, which by different mechanisms extract from soil polluting substances (heavy metals) and they accumulate in various parts of the plant [21-24].

The paper checking the possibility of using ash from the pyrolysis of waste rubber (ash containing zinc oxide, carbon black and other metal oxides, which mixture of natural rubber may be used as the starting material), as well as soil amendment used to cover waste dumps (tailings and ash), by using plant of *P. arundinacea var. Premier* and *Pollycross.*

Experimental part

Materials and methods

Leaching Test Methods

In order to establish grade of waste, it has been carried out leaching test, according to the Official Monitor no.194 bis/ March 8, 2005. Thus, it took well-defined quantities of waste (100 g, 500 g) above which have been have added 1 L water, such as to have the report L:S = 10:1 and L:S = 2:1. Samples were homogenized for 24 h, after which were filtered and has been analyzed metals content. Metals content was determined by atomic absorption spectrometry, using spectrophotometer VARIAN Spectr AA 280FS [25].

Initial content of heavy metals (in ash)

Metals content in ash was determined by X-ray fluorescence, using spectral analyzer NITON Instruments. Equipment is designed for analysis by X-ray fluorescence, quantitative and qualitative elementary (chemical composition) of precision (at level of ppm), in-situ of environmental samples, the geological, biological, different in nature - liquid and solid and diverse forms, without processing [27].

Studies regarding the use of ash from pyrolysis rubber as a amendments to soils used to cover waste dumps, with *P. arundinacea*

Ash and soil samples were mixed in the ratio 1:3, arranged in the pots, in which has been planter *Premier* and *Pollycross.* The samples obtained were regularly doused with water. After a period of 8 months, the plants

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were separated and dried at room temperature (20°C). Dried plants were separated into roots and stems, and calcined, after analyzing heavy metal content by X-ray fluorescence, using spectral fluorescence analyzer RX (FRX). The initial and final samples, to follow the migration of metal from the soil in the plant have been carried out Dispersive X-ray analysis (EDX), using the microscope QUANTA FEG 250 [28, 29].

Results and discussions

Experimental data on leaching test for establishing class for accepting waste in specially designated warehouses are shown in table 1.

Are noticed from the experimental data, as waste rubber pyrolysis originated corresponds to the hazardous waste and can be accepted for storage in warehouses specially designated waste, according to Order no. 95/ February 12, 2005 establishing acceptance criteria and preliminary procedures for the acceptance of waste storage and the national list of waste accepted in each class of deposited into landfill [28-30]. The initial content of metals in the ash is shown in table 2.

It can be noted experimental data as ash presents a high metals content, in particular zinc, which requires the need application of remediation methods. Has been found that the contents in the case Cu^{2+}, Co^{2+}, Cr_{total}, Pb^{2+} and Zn^{2+} is greater than the maximum allowed by law. Because of high zinc content, we will further study the possibility of using ash from rubber pyrolysis as a soil amendment used to cover waste dumps (sterile and ash), with the help against plants, such as *P. arundinacea.* The plants used in this study are *Premier* and *Pollycross*. Calcining a vegetable product is designed to remove organic part thereof, in the subsequent analysis purposes. The plant material weighed, sat down in a crucible is heated to carbonization, after which the crucible is allowed to cool in the desiccator, and then will perform again weighing the crucible with ash after carbonisation plant [31-33]. The difference between the initial mass and the mass remaining after calcination plant is the loss on calcination. The loss on calcination of the plant is presented in table 3.

Table 1
LEACHING TEST METHODS

Indicator	L/S=2:1		L/S=10:1	
	M.A.C. [mg/kg D.M.]	Experimental value [mg/kg D.M.]	M.A.C. [mg/kg D.M.]	Experimental value [mg/kg D.M.]
As	0.4	0.5	2	3.2
Cd	0.6	0.8	1	2.5
Cr_{total}	4	5.2	10	14.7
Cu	25	36.2	50	53.7
Hg	0.05	0.13	0.2	0.35
Ni	5	7.5	10	13.7
Pb	5	9.8	10	12.3
Zn	25	32.7	50	65.7
Mo	5	8.3	10	12.17
Chlorides	10.000	12.351	15.000	17.325
Sulphates	10.000	11.432	20.000	21.450
M.A.C.-maximum allowable concentration; D.M.- dry matter				

Table 2
THE INITIAL CONTENT OF HEAVY METALS IN ASH

The metal	M.A.C. [mg/kg D.M.]	Content of heavy metals in ash. [mg/kg D.M.]
Cu^{2+}	20	482
Co^{2+}	15	672
Cr_{total}	30	136
Pb^{2+}	20	61
Zn^{2+}	100	$55 \cdot 10^3$
Fe^{n+}	-	$4.5 \cdot 10^3$
Ca^{2+}	-	$17 \cdot 10^3$
K^+	-	$2.8 \cdot 10^3$

Table 3
LOSS ON CALCINATION OF THE PLANTS

The sample	The content of copper, mg/Kg D.M.		The degree extraction, %
	M.A.C.	The experimental value	
The initial sample PREMIER Soil Vegetation	20	23 192	-
The final sample PREMIER Soil Vegetation		330 239	72.4
The initial sample POLLYCROSS Soil Vegetation		30 202	-
The final sample POLLYCROSS Soil Vegetation		292 239	81.8

Table 4
THE CONTENT OF COPPER

The sample	The content of copper, mg/Kg D.M.		The degree extraction, %
	M.A.C.	The experimental value	
The initial sample PREMIER Soil Vegetation	20	23 192	-
The final sample PREMIER Soil Vegetation		330 239	72.4
The initial sample POLLYCROSS Soil Vegetation		30 202	-
The final sample POLLYCROSS Soil Vegetation		292 239	81.8

The experimental data are noticed as loss on calcination ranges between ≈70 and 90%. Experimental data on the copper content and degree of its extraction following the studies are presented in table 4.

It is noted from the experimental data that the initial samples of soil in which plants are growing, as well as in the plant, there is a copper content of which slightly exceeds the maximum permissible value. After 8 months of vegetation in both cases it appears that plants accumulate copper, showing a degree of extraction of 70-80%, more accumulate in *Pollycross*.

Experimental data on zinc content and degree of its extraction are shown in table 5.

From experimental data, it appears that initial samples of soil and in plant, containing zinc greatly exceed maximum permissible value. After 8 months of vegetation in both cases it appears that plants accumulate zinc, showing a degree of extraction of 50-60%, more accumulate in *Pollycross*. Experimental data on content of lead are presented in table 6.

It is observed from experimental data that the initial soil samples in developing plants, no exceedances of lead

Table 5
THE ZINC CONTENT

The sample	The zinc content, mg/Kg D.M.		The degree extraction, %
	M.A.C.	The experimental value	
The initial sample PREMIER Soil Vegetation	100	$1.35 \cdot 10^3$ $1.47 \cdot 10^3$	-
The final sample PREMIER Soil Vegetation		$10.7 \cdot 10^3$ $6.02 \cdot 10^3$	56.3
The initial sample POLLYCROSS Soil Vegetation		$1.22 \cdot 10^3$ $1.24 \cdot 10^3$	-
The final sample POLLYCROSS Soil Vegetation		$24.4 \cdot 10^3$ $16.9 \cdot 10^3$	69.3

Table 6
THE LEAD CONTENT

The sample	The lead content, mg/Kg D.M.		The degree extraction, %
	M.A.C.	The experimental value	
The initial sample PREMIER Soil Vegetation	20	14 32	-
The final sample PREMIER Soil Vegetation		64 25	39
The initial sample POLLYCROSS Soil Vegetation		16 10.9	-
The final sample POLLYCROSS Soil Vegetation		47 38	80.8

Table 7
THE COBALT CONTENT

The sample	The cobalt content, mg/Kg D.M.		The degree extraction, %
	M.A.C.	The experimental value	
The initial sample PREMIER Soil Vegetation	15	153 58	-
The final sample PREMIER Soil Vegetation		167 74	44.3
The initial sample POLLYCROSS Soil Vegetation		23 159	-
The final sample POLLYCROSS Soil Vegetation		253 168	66.4

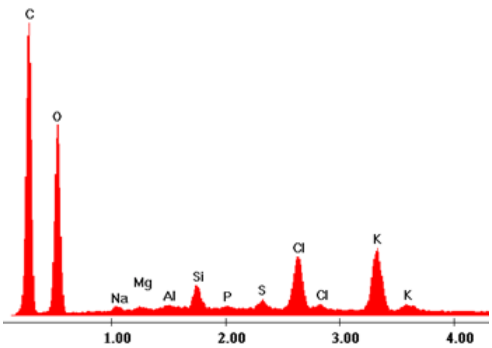
Table 8
THE CHROMIUM CONTENT

The sample	The chromium content, mg/Kg D.M.		The degree extraction, %
	M.A.C.	The experimental value	
The initial sample PREMIER Soil Vegetation	30	 79 69	-
The final sample PREMIER Soil Vegetation		 171 141	82.5
The initial sample POLLYCROSS Soil Vegetation		 38 36	-
The final sample POLLYCROSS Soil Vegetation		 147 128	87.1

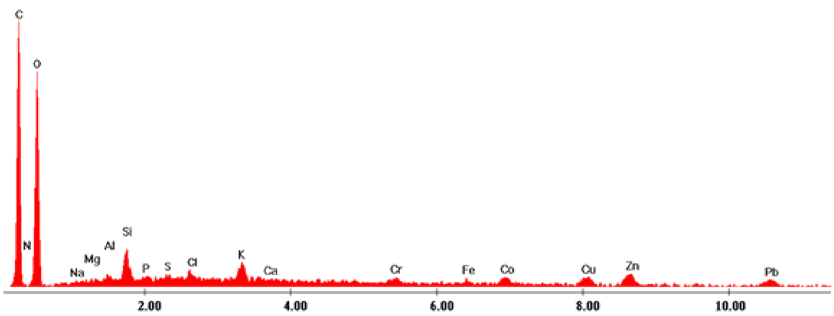
content, but after mixing with ash from rubber pyrolysis lead content exceeds the maximum permissible. Following the time of vegetation in both cases it appears that plants accumulate lead, showing a degree of extraction of 40-80%, more accumulate in *Pollycross*. The experimental data on the content of cobalt are shown in table 7.

From experimental data, it appears that initial sample of soil and in plant; cobalt content far exceeds maximum permissible value. After 8 months of vegetation in both cases it appears that plants accumulate cobalt, showing a degree of extraction of 40-65%, more accumulate in *Pollycross*. Experimental data on the chromium content is shown in table 8.

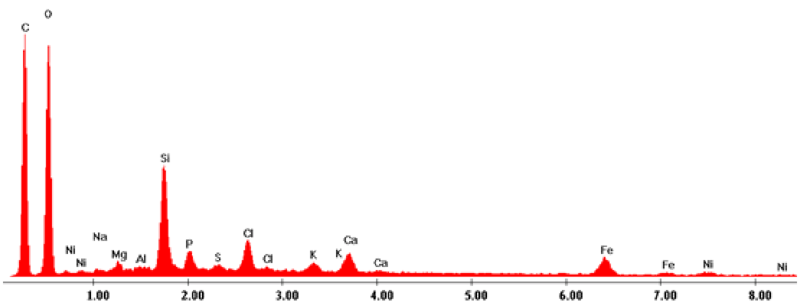
It is observed from the experimental data that initial samples of soil and in the plant, total chromium content far exceeds the maximum permissible value. After 8 months of vegetation in both cases it appears that plants accumulate chromium, showing a degree of extraction of ~80%, accumulation in both plants was about the same. Was studied the migration of metals from soil to the plants by dispersive X-ray (EDX). To follow the migration of metals in soil in plants (*Premier* and *Pollycross*), the initial and final samples were carried out Dispersive X-ray analysis, using the microscope QUANTA FEG 250. EDX spectra obtained are shown in figures 1 (a, b and c) and 2 (a, b and c).



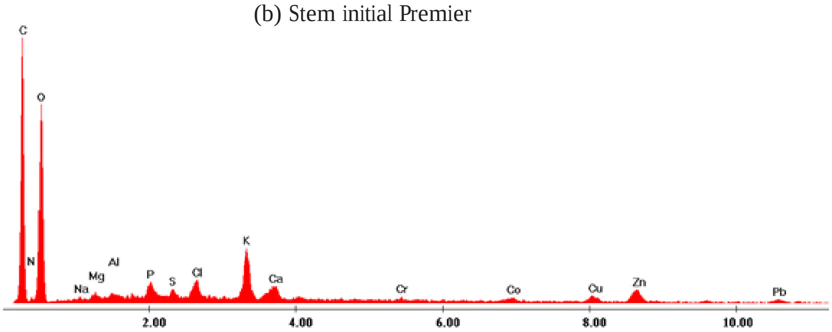
(a) Root initial Premier



(a) Root final Premier



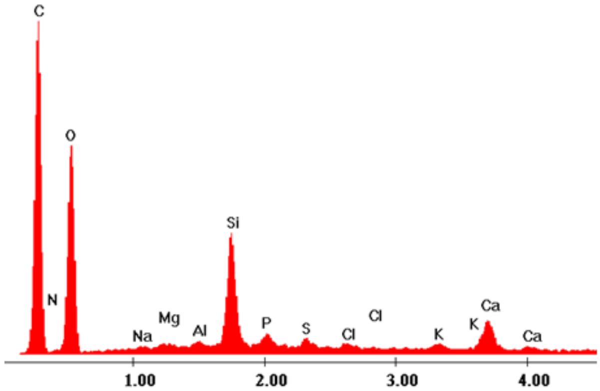
(b) Stem initial Premier



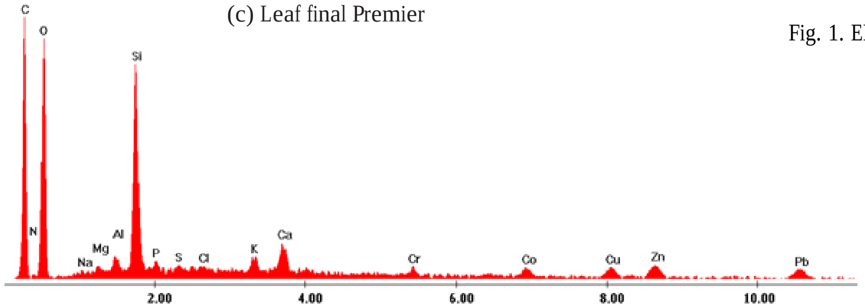
(b) Stem final Premier

Fig. 1. EDX spectra of the plant *P. arundinacea Premier* (initial and final)
(a). root; (b). stem

From Dispersive X-ray spectra (EDX), it can be observed qualitatively metals in soil migrates the two plant species that is to say: *Premier* and *Pollycross*, both the initial and final samples. This analysis may be useful to follow the behaviour of plants in the process of bioremediation (migration of metals) of soils polluted with heavy metals and waste dumps.

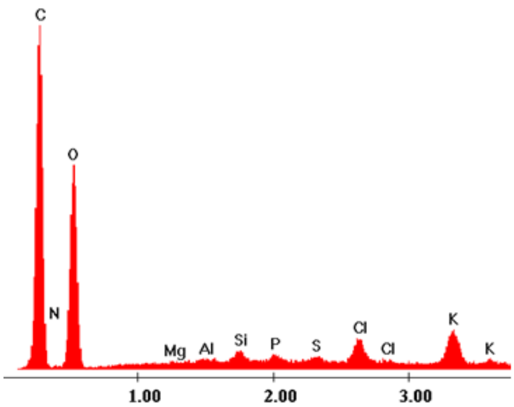


(c) Leaf final Premier

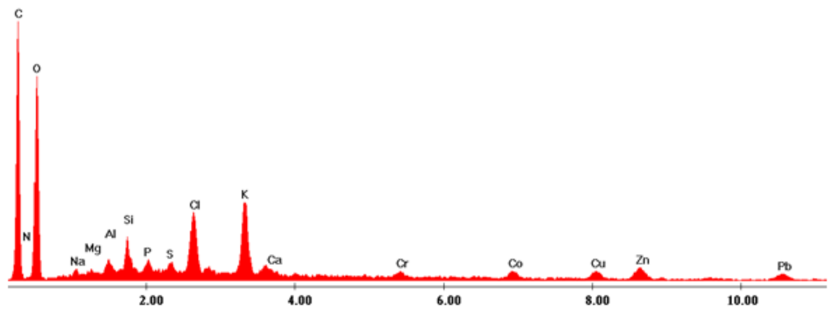


(c) Leaf final Premier

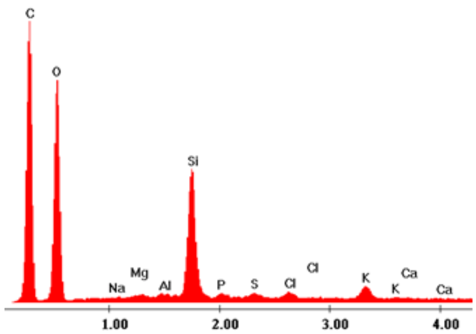
Fig. 1. EDX spectra of the plant *P. arundinacea Premier* (initial and final) (c). leaf



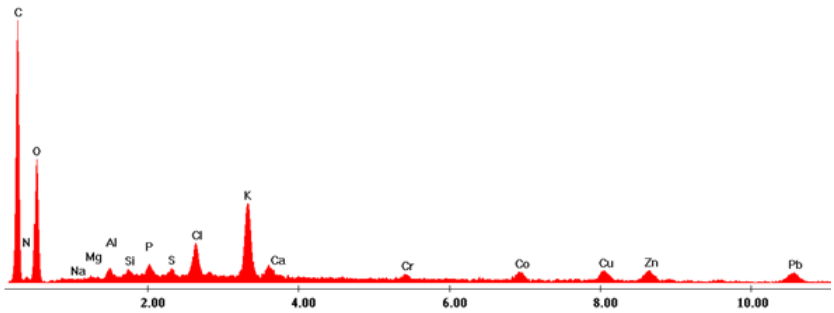
(a) Root initial Pollycross



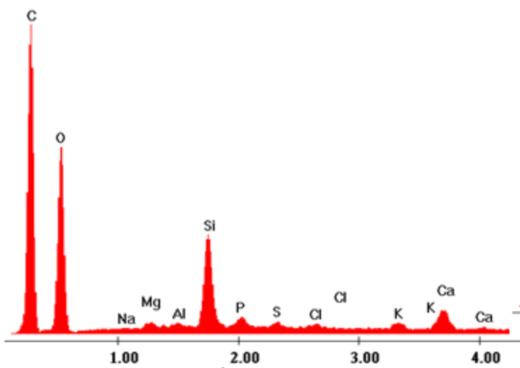
(a) Root final Pollycross



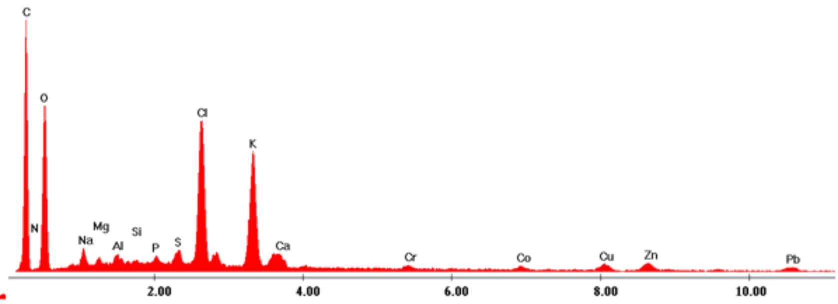
(b) Stem initial Pollycross



(b) Steam final Pollycross



(c) Leaf initial Pollycross



(c) Leaf final Pollycross

Fig.2. EDX spectra of the plant *P. arundinacea Pollycross* (initial and final)(a). root; (b). stem; (c). leaf

Conclusions

Following an initial analysis of ash it was observed that it has a high content of metals, particularly zinc, which allows us to use as amendment for mixing with soil in order to use this mixture to cover waste dumps or in the process of bioremediation. Has been found that the contents in the case Cu^{2+}, Co^{2+}, Cr_{total}, Pb^{2+} and Zn^{2+} is greater than the maximum allowed by law. It studied possibility of using ash from rubber pyrolysis as a soil amendment used to cover waste dumps (sterile and ash), with plants (*P. arundinacea*). The experimental data following were found: loss on calcination ranges between ≈70 and 90%; in initial sample of soil in which plants are growing studied, as well as in plant, there is a content of copper, cobalt and chromium which exceed maximum permissible value. After 8 months of vegetation in all cases it is found that plants accumulate metal, showing a degree of extraction of 40-80%, more accumulate in *Pollycross*. Initial samples of soil and in plant, containing zinc greatly exceed maximum permissible value. After 8 months of vegetation in both cases it appears that plants accumulate zinc, showing a degree of extraction of 50-60%, more accumulate in *Pollycross*. In initial sample of soil in which plants are growing studied, no exceedances of levels of lead, but after mixing with ash from rubber pyrolysis, lead content exceeds maximum permissible. At the end of growing season in both cases it appears that plants accumulate lead, showing a degree of extraction of 40-80%, more accumulate in *Pollycross*. From EDX, was observed migration metals from soil the two species of plants: *Premier* and *Pollycross*, both the initial and final samples. This analysis may be useful to follow the behaviour of plants in process of bioremediation of soils polluted with metals and waste dumps. In conclusion, it was found that ash from pyrolysis of rubber, which is a raw material, it can be successfully used as a soil amendment used to cover waste dumps (ash, sterile *etc.*), as a result of content of micro- (Zn^{2+}, Co^{2+}, Cu^{2+}) and macronutrients (Ca^{2+}, K^{+}, Fe^{2+}). At the same time it was found that plants studied, properties of bio-accumulation of heavy metals may also be used for stabilization and covering with *inert* material waste dumps since these plants tend to reach heights of over 2 m.

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Manuscript received: 18.08.2015