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THE CONTRIBUTION OF NATURAL SORBENTS TO THE IMPROVEMENT OF THE PROPERTIES OF CONTAMINATED TECHNOSOLS EVALUATED BY THE DEVELOPMENT OF VEGETATION COVER

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Abstract: Mining spoil heaps, as a remnant of extensive mining activity in many parts of the world, are considered as a serious contaminated site especially due to the high content of potentially toxic elements (PTEs) and acidic soil pH which also inhibits the development of vegetation cover. The aim of our paper was to experimentally test the effectiveness of natural sorbents (biochar, bentonite, organo-zeolitic substrate 1 – 20 wt%, chicken manure) on pH technosol taken from two abandoned mining localities - Cu mine waste dump Maximilián (Slovakia) and Fe – Cu sulphide mine waste dump Libiola (Italy) and their impact to the support of grass mixture growth. We evaluated the height of plants, the weight of fresh aerial biomass and dry matter. Testing of the effectiveness of individual sorbents was performed by a pot experiment. The results showed that all tested sorbents statistically significantly ($P < 0.001$) increase the pH from technosols initially strong to ultra-acid (Maximilian heap – pH 5.17; Libiola – 3.42), which statistically significantly supports the development of vegetation cover ($P < 0.05 – 0.001$). The growth of aboveground biomass is significantly more effective in a weakly acidic soil reaction (pH 6.5 – 6.7). However, the choice of sorbent depends on the character of the geological basement and the properties of technosol on its surface. Organo-zeolitic substrate was the most effective for ultra-acid soil from Libiola, influenced by oxidation of the basalt- and serpentinite-hosted Cu-ores. On the other hands, bentonite was proved as the most useful on Maximilián heap with much more acidic geological basement built by siderite, tetrahedrite and chalcopyrite. This knowledge can be used in practice in the ecological restoration of surfaces of disturbed mining or other toxic soils.

Keywords: mining area, technosol, potentially toxic elements, organo-zeolitic substrate, chicken manure, bentonite, biochar, pot experiment

1. INTRODUCTION

Mining activity is an integral part of human history, which helps to meet the basic material needs of mankind. On the other side, it was changed the original structure of the country due to deforestation, changing geomorphology, hydrological and hydrogeological regime (Križáni et al., 2007). Up to now, we observe its negative impact on the state of the environment, such as an increased amount of potentially toxic elements (PTEs) in soil, sparse or even absent vegetation cover due to lack of soil matrix, water, nutrients, excess coarse tailings, and other environmental and ecological factors (Turisová et al., 2016). The pollution caused by PTEs leads to decrease activity of plant enzymes, disorders of stoma function, chlorophyll metabolism and suppression of photosynthesis. The growth of vegetation may be slowed down or even completely stopped (Banásová, 2006; Bini, 2011).

There are several physical, biological and chemical methods that help reduce these negative impacts. Physical methods most often use covering the surface of the heap with soil without PTEs contamination or inert materials, or soil replacement, vitrification, etc. Chemical methods include oxidation-reduction processes, ion exchange, extraction, precipitation, and biological use of microorganisms or plants to regenerate contaminated soil (Frankovská et al., 2010; Ye et al., 2017; Liu et al., 2018).

In recent years, the use of sorbents for soil recovery has come to the forefront. A sorbent is a natural or artificial substance of an inorganic or organic nature, most often in a solid state, capable of absorbing or adsorbing another substance, solid, liquid or gaseous (Fingas, 2002; Deng, 2006; Chen et al., 2019). The application of natural sorbents has proven to be a suitable ecological, less material-intensive and relatively fast-acting variant.

We tested the effect of four natural sorbents in the present study (bentonite – BE, biochar – BCH, chicken manure – CHM and organo-zeolitic substrate – OZS) on improving the properties of technosol from mining sites with a high PTE content and on supporting the development of vegetation cover contributing to the restoration of the ecosystem and the landscape.

2. MATERIALS AND METHODS

In April 2019, technosols were collected by stratified sampling from 0 – 20 cm depth from two historically significant abandoned European deposits with different geological basement and chemism: i) Libiola (Italy, Eastern Liguria, village Sestri Levante), which is built by basalts and serpentinites with absence of rocks (e.g. carbonates) able to neutralize the high acidity caused by oxidation of Fe-Cu ores (Marescotti et al., 2012); ii) Cu dump field Maximilián (Slovakia, Banská Bystrica County, village Špania Dolina) which consist of acidic geological subsoil formatted with gray ores with siderite, tetrahedrite and chalcopyrite ore. The soils were homogenized to one complex sample from each locality by mixing and not further treated. The contents of PTEs were determined by multi-acid ICP-ES method in certificated Bureau Veritas Laboratory in Canada.

2.1. Natural sorbents and soil treatments

Experiment was realised with four natural sorbents – chicken manure (CHM), bentonite (BE), biochar (BCH), organo-zeolitic substrate (OZS). The average chemical composition of following substances in bentonite are: SiO_2 57 – 61%, Al_2O_3 18 – 21%, Fe_2O_3 2 – 3%, FeO 0.1 – 0.5%, TiO_2 0.2 – 0.3%, CaO 1.9 – 2.6%, MgO 3.0 – 5.0%, K_2O 0.4 – 1.0%, Na_2O 0.2 – 0.7%. We obtained chicken manure from domestic breeding of domestic fowl (*Gallus gallus domesticus*). We bought the charcoal commercially as charcoal for grilling. These sorbents were dried at room temperature, crushed and sieved through a 2 mm sieve. Perlite had an average chemical composition as follows: SiO_2 68.0 – 73.0%, Al_2O_3 7.5 – 15.0%, Fe_2O_3 1.0 – 2.0%, Na_2O 1.0 – 2.0%, K_2O 2.5 – 5.0%, CaO 0.5 – 2.0%, MnO max. 0.3%, TiO_2 max. 1.0%, P_2O_5 max. 0.2%, MgO max. 1.0%. Its size did not need to be adjusted. Calcium carbonate ($CaCO_3$) was pure and in the form of a fine powder.

2.2. Pot experiment

In June 2019, we implemented a pot experiment, taking place in a greenhouse. We used a self-watering pots measuring 40 × 17 × 15 cm for this experiment. We put a mixture of contaminated soil and sorbents in the pot, with weight percentage – bentonite 10%, chicken manure 1%, biochar 20%, organo-zeolitic substrate (perlite 5%, chicken manure 1%, $CaCO_3$ 3%) in a total weight of 4 kg.

We established control samples, as well (technosol from the heap without added sorbents) and reference samples of uncontaminated soil from the vicinity of the Maximilián heap. The chicken manure variant and reference samples were not established for the Libiola site due to the smaller weight volume of the soil taken. Each variant was realized in three parallel repetitions.

We let the prepared soil substrates rest for a week, subsequently, 60 g of soil were taken from each pot to determine the active soil reaction (pH) and 7 g of grass mixture sown from *Agrostis capillaris* L., *A. stolonifera* L., *Festuca rubra* L. and *Poa pratensis* L. which were mixed in a weight ratio of 2: 2: 1: 1. These species occur naturally in both localities (in situ), especially in the early successive stages of heap overgrowth (Širka et al., 2018). After 11 weeks, we divided the pot area into 36 rectangles measuring 3 × 4.5 cm. In 34 rectangles (in 2 corner rectangles with holes for water replenishment not measured) we measured the height of the highest leaf and calculated the average highest height of grown grasses per pot. At the end of the 12th week, we cut and weighed the aerial biomass and again took 60 g of soil for pH determination. The biomass and soil were dried at room temperature for 30 minutes in a BINDER Drying and heating chambers FD115 with forced convection (BINDER GmbH, Tuttlingen, Germany) at 30 °C. The dry matter was weighed on laboratory balances KERN 440-51N (KERN & SOHN GmbH, Balingen, Germany). The active soil response of soil samples was determined according to Sobek et al., (1978). Soil reaction classification terms follow Soil Survey Manual (Soil Science Division Staff, 2017).

2.3. Statistical analyses

The differences between the effects of natural sorbents on the pH of the soil samples and plant variables were evaluated using one-way analysis of variance (ANOVA) with an a posteriori Bonferroni test. Pearson's correlation coefficients were used to assess the relationship between pH of the soil samples and plant metric data. Data are presented as mean, standard deviation (SD) and 95% confidence interval (95% CI). A two-tailed P value of $P < 0.05$ was considered statistically significant. Statistical analysis was performed using the IBM SPSS software, version 20.0 (SPSS, Armonk, NY, USA).

3. RESULTS

3.1. Soil analyses and pH

The high contents of Cu, As, Sb are recorded in the Maximilián heap, while in the Libiola deposit it is possible to observe contamination by Cu, Pb, Zn, Ni, Co, Cr and Mn. The soil analyses are presented in Table 1. The result of soil analyses is presented in Table 1.

The natural sorbents used in the controlled pot experiment changed the soil reaction from strongly acid (Maximilián – 5.17) or ultra-acid (Libiola – 3.42) to neutral (Libiola after 12 days – pH 6.8) or slightly alkaline (Maximilián after 12 weeks – pH 7.57). In soil from the Maximilián heap, the efficiency of sorbents decreased in the order BCH (7.57) > OZS (7.22) > BE (6.73) > CHM (6.62). Bentonite has been shown to be less efficient as the difference from the pH of the control sample was only 0.15 units. The pH value ± increased until the end of the experiment (except for the variant with BE and BCH in soil from Libiola). In general, the differences in the change in soil reaction in both localities varied from ~ 0.5 to 3.0 pH units, which represents a 3- to 1000-fold reduction in the concentration of H_3O^+ ions in the soil. This fact has a significant effect on the biogeochemical soil processes demonstrated in our experiment through the evaluation of vegetation cover development. An overview of changes in soil reaction after sorbent application to the soils from two dump fields is presented in Table 2.

Table 1. The contents of potentially toxic elements in soils from locality Maximilián and Libiola

samples	**Cu** [ppm]	**Pb** [ppm]	**Zn** [ppm]	**Ni** [ppm]	**Co** [ppm]	**Mn** [ppm]	**As** [ppm]	**Cr** [ppm]	**Sb** [ppm]	**Al** [%]
Maximilián (Slovakia)										
1	1179	26	38	25	28	271	275	19	405	7,53
2	1017	26	39	24	27	264	273	19	390	8,58
3	1101	23	36	22	24	239	255	17	367	7,15
Average	**1099**	**25,00**	**37,67**	**23,67**	**26,33**	**258,00**	**267,67**	**18,33**	**387,33**	**7,75**
Libiola (Italy)										
1	2842	40	345	341	69	915	10	771	<5	6,22
2	2360	54	359	272	54	1094	8	691	<5	6,54
2	2577	39	368	289	52	824	10	754	<5	6,25
Average	**2593**	**44,33**	**357,33**	**300,67**	**58,33**	**944,33**	**9,33**	**738,67**	**<5**	**6,34**

Table 2. Statistical description of soil pH characteristics at the beginning of the experiment and at the end of the experiment after 12 weeks

Substrate	Maximilián (Slovakia)					Libiola (Italy)				
		Beginning		After 12 weeks			Beginning		After 12 weeks	
	N	Mean ± SD	95% CI	Mean ± SD	95% CI	N	Mean ± SD	95% CI	Mean ± SD	95% CI
C	9	**5.17 ± 0.03**	**5.15 – 5.19**	**5.87 ± 0.02**	**5.86 – 5.88**	9	**3.42 ± 0.02**	**3.41 – 3.43**	**3.43 ± 0.01**	**3.42 – 3.44**
BE	9	6.72 ± 0.09*	6.65 – 6.78	6.73 ± 0.02*	6.72 – 6.74	9	3.90 ± 0.02*	3.88 – 3.92	3.68 ± 0.02*	3.67 – 3.69
BCH	9	7.06 ± 0.07*	7.01 – 7.11	7.57 ± 0.03*	7.55 – 7.59	9	6.21 ± 0.07*	6.16 – 6.26	5.41 ± 0.15*	5.31 – 5.51
OZS	9	6.91 ± 0.03*	6.89 – 6.93	7.22 ± 0.02*	7.21 – 7.23	9	6.46 ± 0.02*	6.45 – 6.47	6.81 ± 0.05*	6.78 – 6.84
CHM	9	6.51 ± 0.03*	6.49 – 6.53	6.62 ± 0.07*	6.57 – 6.67	–	–	–	–	–

C – control sample, BE – technosol + bentonite, CHM – technosol + chicken manure, OZS – technosol + organo-zeolitic substrate, BCH – technosol + biochar; *P < 0.001 – significant difference between control and treatment (ANOVA with Bonferroni *post hoc* test); N – number of samples; SD – standard deviation; CI – confidence interval

3.2. Plants

The positive effect of the sorbents on promoting the growth of the grass mixture was visible after only a few days, when the seeds began to germinate. After 12 weeks, differences in density and total vegetation cover were also visible (Fig. 1, Fig. 2). The obtained values of the average highest height of grasses, weight of fresh biomass after 12 weeks of the experiment and dry matter with soils from both localities are presented in Table 3.

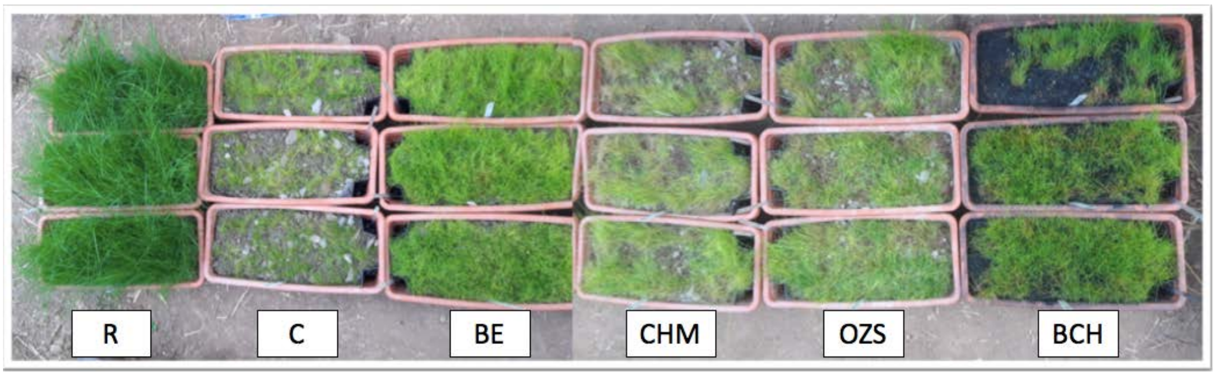

Figure 1. Pot experiment with soils from the Maximilián heap 12 weeks after its establishment (R – reference sample from uncontaminated site, C – control sample, BE – technosol + bentonite, CHM – technosol + chicken manure, OZS – technosol + organo-zeolitic substrate, BCH – technosol + biochar).

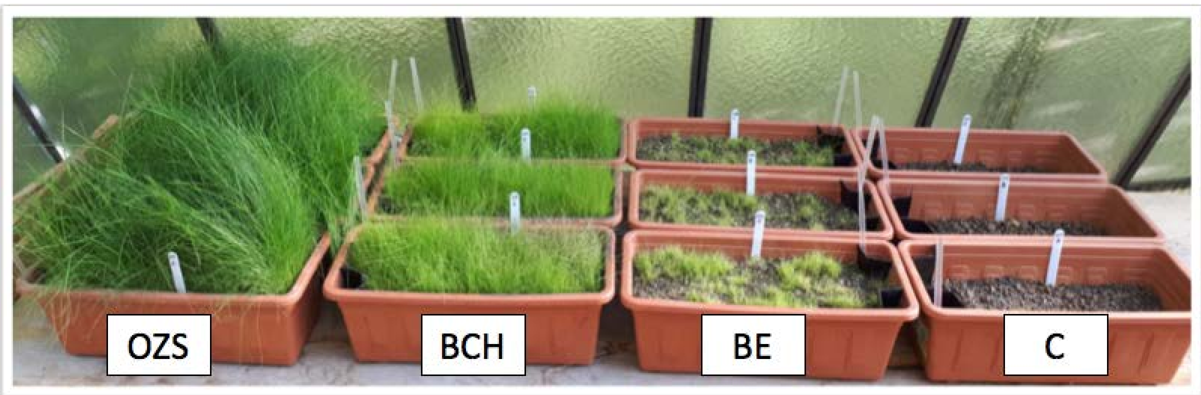

Figure 2. Pot experiment with soils from Libiola 12 weeks after its establishment (OZS – technosol + organo-zeolitic substrate, BCH – technosol + biochar, BE – technosol + bentonite, C – control sample)

Table 3. Statistical description of plant samples (the highest grasses, fresh aerial biomass, dry matter) 12 weeks after

Treatment	**Plant height** (cm)			**Fresh aerial biomass** (g)			**Dry aerial matter** (g)		
	N	Mean ± SD	95% CI	N	Mean ± SD	95% CI	N	Mean ± SD	95% CI
				Maximilián (Slovakia)					
Control	**102**	**5.2 ± 2.6**	**4.7 – 5.7**	**3**	**4.3 ± 1.2**	**2.9 – 5.7**	**3**	**1.7 ± 0.6**	**1.0 – 2.4**
Bentonite	102	10.1 ± 2.5¶	9.6 – 10.6	3	23.3 ± 0.6¶	22.6 – 24.0	3	6.0 ± 0.1¶	5.9 – 6.1
Biochar	102	7.7 ± 3.5¶	7.0 – 8.4	3	11.3 ± 4.6*	6.1 – 16.5	3	3.3 ± 1.2	1.9 – 4.7
Organo-zeolitic substrate	102	7.2 ± 3.4¶	6.5 – 7.9	3	10.0 ± 1.0	8.9 – 11.1	3	2.7 ± 0.6	2.0 – 3.4
Chicken manure	102	6.8 ± 3.2§	6.2 – 7.4	3	5.7 ± 2.1	3.3 – 8.1	3	1.8 ± 0.3	1.5 – 2.1
				Libiola (Italy)					
Control	**102**	**1.0 ± 0.7**	**0.9 – 1.1**	**3**	**< 1.0**	**–**	**3**	**< 1.0**	**–**
Bentonite	102	3.3 ± 1.4	3.0 – 3.6	3	2.7 ± 0.6	2.0 – 3.4	3	< 1.0	–
Biochar	102	13.5 ± 3.3¶	12.9 – 14.1	3	21.3 ± 2.3¶	18.7 – 23.9	3	5.3 ± 0.6¶	4.6 – 6.0
Organo-zeolitic substrate	102	34.0 ± 4.6¶	33.1 – 34.9	3	69.7 ± 3.2¶	66.1 – 73.3	3	15.3 ± 1.2¶	13.9 – 16.7

*P < 0.05, §P < 0.01, ¶P < 0.001 – significant difference between control and treatment (ANOVA with Bonferroni *post hoc* test); N – number of samples, SD – standard deviation, CI – confidence interval.

Plants in pots with soil from surrounding of mine waste dump Maximilián (reference sample) had an average maximum grass height of 23 cm, in pots with soil from the landfill without treatment (control sample) 5.21 cm. The highest average stand height decreased in the order BE (10.1 cm) > BCH (7.7 cm) > OZS (7.2 cm) > CHM (6.8 cm).

In the experiment with technosol from Libiola, all variants of natural sorbents had a positive effect on plants compared to the control sample, where the plants hardly germinated and reached an average maximum height of 1.0 cm. The efficiency of sorbents decreased in the order OZS (34.0 cm) > BCH (13.5 cm) > BE (3.3 cm). The results of growth characteristics show that the grass mixture is able to grow on soil with different pH, but its growth assessed by the height of aboveground biomass is significantly more effective in a weakly acidic soil reaction (pH 6.5 – 6.7). This finding is valid for both sites examined. Vegetation growth and development was statistically significantly supported by the use of each sorbent. The most significant effect was recorded in OZS in pots with in pots with technosol from Libiola, where the height of the plants was 3 times bigger than when BE was added to the soil from the Maximilián heap - the most effective sorbent for this heap. The values of the weight of fresh and dry above-ground biomass followed the trend of the values of the stand height, i.e. decreased in the order BE > BCH > OZS > CHM on soils from the heap Maximilián, or, OZS > BCH > BE on soils from Libiola. Biomass weights varied depending on soil reaction. The average drying ratio between dry matter and fresh biomass was 1: 3.46.

4. DISCUSSION

The geological basement and the properties of technosol on its surface play the most important role in sorbent selection which we experimentally confirmed using two chemically different types of technosols from mining spoil heaps. Although we worked with only three replicates for each treatment due to the financial complexity of the analyses, we captured statistically significant trends in the effect of sorbents on soil healing assessed through pH change (from strongly to ultra-acid technosols to neutral soil reaction), as well as and vegetation cover development. Probably by evaluating the average peak heights of the plants based on 102 measured values for each treatment and when determining the change in pH, and based only on three values found for each treatment, the same or approximately the same statistically significant difference in the influence of individual sorbents on these 2 traits in comparison with the control sample was not shown. At the same time, other studies point to a close relationship between soil pH and plant growth, when the best plant development takes place at pH 5(-5.5) – 6(-7) (Soti et al., 2015; McCauley et al., 2017; Gentili et al., 2018), which also follows from our experiment, namely from absolutely measured values.

4.1. Experimental plants

In the pot experiment, we used a mix of four common Eurasian grass as model plants *Agrostis capillaris*, *A. stolonifera*, *Festuca rubra* and *Poa pratensis* with broad ecological tolerances. So far, these species have been studied mostly individually. For example, *Agrostis capillaris* served as one of the model plants in investigating the effect of biochar on the root-induced changes of metal dynamics in the rhizosphere (Houben & Sonnet, 2015). Whiteley & Williams (1993) tested various cultivars of *Agrostis capillaris* in metalliferous mine spoil treatment with lignite derived humic substances. *Festuca rubra* is used as a useful grass for phytostabilization of technosol after As extraction (Dradrach et al., 2020). Indices of tolerance of her cultivars to increased amounts of copper, lead and zinc were also found and compared (Wong, 1982). Liu et al. (2006) have confirmed good metal-enrichment and metal-tolerant traits in *Poa pratensis*. Based on these studies, we can also refer to the species we use as facultative metallophytes.

Sorbents are also being tested for application to agricultural soils with an increased content of PTEs, which is accumulated here mainly due to the proximity of industrial factories. Therefore, in several studies, crops have also been used as model plants, for example *Oryza sativa* L. (Bian et al., 2013; Zhou et al., 2014; Sun et al., 2015), *Triticum aestivum* L. (Li et al., 2016; Qayyum et al., 2017), *Hordeum vulgare* L. (Moreno-Jiménez et al., 2016.), *Lactuca sativa* L. (Basta et al., 2001), *Vicia faba* L. (Lucchini et al., 2014), etc.

Woody plants have also been tested with various successes for phytoremediation purposes, e.g. in recent years pioneer species like *Pinus sylvestris* L. (Bęś et al., 2019; Zaitsev et al., 2020), *Betula pendula* Roth (Lewis et al., 2015), *Alnus glutinosa* (L.) Gaertn. (Desai et al., 2019), *Quercus* spp. (Dadea et al., 2016; Benhachem & Harrache, 2019) and so on.

4.2. Natural sorbents

The application of natural sorbents has proved to be a suitable ecological, materially less demanding and relatively fast-acting variant, tested inorganic (bentonite) and organic (biochar, chicken manure) sorbents, also their mix as organo-zeolitic substrate (perlite+$CaCO_3$+chicken manure). Bentonite is a clay rock consisting mainly of the montmorillonite mineral (Kraus & Kužvart, 1987). Bentonite clay exhibits ionic exchange, sorption and intercalation as the main reactions leading to the removal of heavy metals (Ntwampe & Moothi, 2018). It was successfully tested within experiments of for example Houben et al., (2012), Ma et al., (2012), Argiri et al., (2013). According to Xu et al., (2017) bentonite is more effective at remedying more acidic soils as it is an alkaline mineral. It was proved as a sorbent which is able to increase the soil reaction in our experiment, but is less effective in promoting growth compared to other sorbents used. Biochar is a porous substance of fine-grained structure, produced by pyrolysis of organic residues (Lehmann & Joseph, 2009), which has seized interest because of its significant effect on the remediation of heavy-metal-contaminated soil, which is confirmed by many studies (e. g. Bian et al., 2014; Lucchini et al., 2014; Chen et al., 2016; Cui et al., 2016; Wang et al., 2019). Biochar contributed to the increase in pH in our experiment, but it had an average effect on the growth of the grass mixture. Perlite is a volcanic rock, an amorphous volcanic glass formed by rapid cooling of the rhyolite melt during volcanic activity (Zuberec et al., 2005; Jeleň et al., 2009). It is characterized by low bulk density, high water retention capacity, high air-filled porosity, high sorption ions Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, therefore is recently used as a substrate additive to support vegetation in green roofs, vertical gardens and biofilters (Vijayaraghavan & Raja, 2014). However, perlite has not been used separately as environmental cleanup material, because its ion exchange capacity is very low (Kasai et al., 2019). However, perlite is a starting material in the synthesis of zeolites, what increases the potential environmental applications. Calcium carbonate is found in nature in the form of calcite or aragonite, which are the main constituent of limestone. It has been also successfully applied in remediation procedure (Chen & Lee, 1999; Hong et al., 2011; Wang et al., 2017). Chicken or poultry manure is commonly used to increase productivity and fruit or vegetable quality, also as suitable sorbent of PTEs, but with differential responses of crops to this organic amendment (Siddiqui et al., 2021). As with perlite, its use in combination with another sorbent or fertilizer is recommended (Moore et al., 1998; Ramadan & Adam, 2007). Ramadan & Adam (2007) confirmed the positive effect of chicken manure on the distribution of PTEs, soil pH and fruit yields of tomato. The influence on phytotoxicity and phytoavailability of Cd in plants was confirmed also in pot experiment with *Raphanus sativus* L. (Liu et al., 2006). Wasilkowski et al., (2019) indicate that the application of manure contributes to a significant increase in the yield of sown biomass *Festuca arundinacea* Schreb. after ecological restoration of heavy metal-contaminated soil. We used chicken manure in our research as organic component into the organo-zeolitic material together with perlite and calcium carbonate, which has proved to be most effective to raise the pH and promote growth in comparison with other sorbents. Organo-zeolitic materials are used as a comprehensive fertilizer provided a natural source of plant nutrients by greatly increasing the population of soil nitrifying microorganisms (Leggo, 2014) or in removal of heavy metals from soil or water (Coppola et al., 2003; Yuna, 2016; Damian et al., 2018, 2019).

The soil sorbents are currently widely and effectively used in remediation processes for immobilizing of PTEs. Selecting proper immobilizing agents can yield cost-effective remediation techniques and fulfill green and sustainable remediation principles. Furthermore, long-term stability of immobilized PTEs compounds and the environmental impacts and cost effectiveness of the amendments should be considered before application (Palansooriya et al., 2020).

5. CONCLUSION

The study demonstrated the importance of sorbents during remediation of soils with a high content of PTEs and their selective effect on this process conditioned by a specific chemical soil and geological basement. Each of the sorbents had a positive effect on the change in pH, which was subsequently reflected in the support of the development of vegetation cover using the seeds of metal-tolerant, autochthonous grass species. Organo-zeolitic substrate was the most effective for ultra-acid soil from Libiola, influenced by oxidation of the basalt- and serpentinite-hosted Cu-ores. On the other hands, bentonite was proved as the most useful on Maximilián heap with much more acidic geological basement built by siderite, tetrahedrite and chalcopyrite. This knowledge can be used in practice in the ecological restoration of surfaces of disturbed mining or other toxic soils.

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