

THE ROLE OF NATURAL ZEOLITE AND OF ZEOLITE MODIFIED WITH AMMONIUM IONS TO REDUCE THE UPTAKE OF LEAD, ZINC, COPPER AND IRON IONS IN *Hieracium aurantium* AND *Rumex acetosella* GROWN ON TAILING PONDS

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Abstract. The objective of this research is to determine if zeolite modified with ammonium ions has a higher capacity than natural zeolite to protect *Hieracium aurantium* and *Rumex acetosella* growing on tailing ponds, by reducing the quantity of metal ions these plants would accumulate in their roots and leaves. The influence of the amount of zeolite in the substrate (5 % and 10 % mass percentage) was also studied. The experiments were carried out in laboratory and the concentration of the ions of heavy metal in roots and leaves, after 38 days of growth was established by Flame Atomic Adsorption Spectroscopy. The pH, conductivity and redox potential for each of the substrate considered were measured. The results were statistically processed using the one-way analysis of variance (one-way ANOVA). FTIR analyses were performed to establish the structural differences between the natural and modified zeolite. *Hieracium aurantium* and *Rumex acetosella* accumulate a smaller quantity of metal ions in roots and leaves in the presence of zeolite modified with ammonium ions than in the presence of natural zeolite. Laboratory tests showed that *Hieracium aurantium* is more tolerant to ions of heavy metals than *Rumex acetosella*, as demonstrated by their translocation factors. In terms of reducing the uptake of ions of heavy metals, only the zeolite modified with ammonium has a significant protective effect on *Hieracium aurantium*, while both natural zeolite and zeolite modified demonstrate a significant role for *Rumex acetosella*, as revealed by statistical tests.

Keywords: natural zeolite, zeolite modified with ammonium ions, *Hieracium*, *Rumex*, heavy metal ions.

INTRODUCTION

The considerable impact on the environment of heavy metals from industrial, agricultural, power sector and municipal sources is a topic of growing concern [1, 2]. A variety of compounds, such as alkaline materials, phosphate minerals, iron and manganese hydroxides, aluminosilicates, zeolites or plant residuals have been used so far in the attempt to reduce the mobility of ions of heavy metals in soil [3-6].

Because of their extremely high cation exchange capacity, their relative high specific surface area, low cost and availability, the use zeolites is probably the most promising solution in the attempt to reduce the pollution of soil and water with heavy metal ions. The modification of zeolite structure with ammonium ions increases its capacity to adsorb heavy metals because the ammonium ions induce the standardization of the ion-exchange surface from an energetic point of view [7]. The zeolite is activated by replacing the sodium, potassium and magnesium ions found in its natural structure with ammonium ions, a mechanism which makes its ion-exchange surface more uniform and which increases its capacity to adsorb ions of heavy metals. Van Herwijnen and coworkers [8] have demonstrated that clinoptilolite and bentonite added to green waste and respectively to sewage sludge composts are efficient in the remediation of metal-contaminated brownfield sites.

Species from *Hieracium* and *Rumex* genus are known as heavy metal tolerant higher plants [9-11]. These plant species growing in the metalliferous soils are often genetically distinct from conspecifics on normal soils. Huang and coworkers [11] studied the effects of copper on the phenology and reproduction of *Rumex dentatus* from metalliferous and non-metalliferous sites. They concluded that *Rumex*

dentatus grown on soil polluted with metals behaved in a significantly different way, in terms of phenologic responses and reproductive traits, as compared to plants of the same species grown on metal – free soil. Compared to the non-metalliferous population, the metalliferous population of *Rumex dentatus* had a shorter life cycle and a larger reproductive effort. Ke and coworkers [12] studied the effects of copper and mineral nutrition on growth, copper accumulation and mineral element uptake in *Rumex japonicus* grown in the neighborhood of a copper mine and in an uncontaminated field. They concluded that at high copper treatment, the contaminated population accumulated less copper in roots than the uncontaminated one, suggesting the root exclusion mechanism existing in the former. The contaminated population was also more tolerant to general nutrient deficiency than the uncontaminated one.

The aims of this study are: (i) to compare the ion exchange capacity of the natural zeolite with that of the zeolite modified with ammonium ions; (ii) to determine if a higher quantity of zeolite in substrate would translate into the accumulation of a smaller quantity of ions of heavy metals in the roots and leaves of the two plant species; (iii) to compare the role of the used amendments in reducing the uptake of the heavy metal ions in the two investigated plants.

MATERIALS AND METHODS

Preparation of the activated amendments

Zeolite with a content of 62% clinoptilolite, originating from a deposit in Stoiana, a village in Cluj County, Romania (coordinates: 46°40'58" N 23°55'45" E), was used for this study. The zeolite samples were grinded in a mortar (Retsch RM 100, Germany) and sieved to separate the fraction ranging from 0.5 to 1

mm by means of mechanical sieves (Retsch AS200 basic). This fraction was washed with distilled water to remove any turbidity and was dried at 105°C for 24 h to remove any adsorbed water. Finally, the zeolite was stored in a desiccator before performing the chemical activation in NH₄-form.

The chemical treatment of the zeolite was performed by adding 1 L of the 2 M solutions of NH₄Cl respectively, to the samples of zeolite fractions of 0.5 - 1 mm (100 g), at room temperature, under stirring at 160 rotations / min, by using a Heidolf stirrer. After 24 h, the solid phase was separated from solution by washing it with ultrapure water, until the removal of the Cl⁻ ions (controlled with AgNO₃ solution) and was dried at 105°C using a Binder oven for 24 h.

The pot experiments

In April 2010, samples of *Hieracium aurantium* and *Rumex acetosella* together with approximately 1 Kg sterile were collected from the Bozanta Mare tailing pond, Maramures County (47°38.579 N 023°28.753 E).

The samples collected were brought in the laboratory and planted in plastic flasks of 400 ml in volume (three plants in each flask), containing sterile amended with natural and modified zeolite (chemically activated in ammonium form). The amount of the amendment in sterile was 5 and 10% percentage mass, respectively. In each flask, the total quantity of sterile-amendment mixture was of 300 g. Sterile without amendment was used as control sample. The flasks were watered with distilled water on a regular basis. The plants were allowed to grow for 38 days, at 20-22°C.

Structural and chemical analyses

Fourier Transformed InfraRed Spectroscopy (FTIR) analyses were performed in order to establish the structural changes occurred during the zeolite modification with ammonium ions. A Perkin Elmer Fourier Transform Infrared Spectrometer BXII was used. Sample wafers consisted in 10% sample in spectral quality KBr.

The concentrations of metal ions in the collected sterile, roots and leaves of *Hieracium aurantium* and *Rumex acetosella* (before and after 38 days of growth in flasks) were measured by atomic absorption spectroscopy (AAS) in air-acetylene flame using a Perkin Elmer Analyst 800 spectrophotometer (Shelton, USA). A Retsch RM-100 grinding machine was used to prepare the samples for mineralization. The mineralization took place in a Berghof MWS-2 (Germany) microwave system. The parameters for vegetal material mineralization were: in stage 1 - 145°C, 5 minutes, power 75%; in stage 2 - 190°C, 10 minutes, power 90%; in stage 3 - 100°C, 10 minutes, power 40%. For the mineralization of sterile the authors have established the following parameters: stage 1 - 180°C, 25 minutes, power 99%; stage 2 - 100°C, 10 minutes and power 99%. A mix of 10 mL HNO₃ 65% (d = 1.4 kg/L, Lach-Ner) with 0.3 g plant

powder, respectively with 1 g of dried sterile was introduced in a microwave system. For the mineralization of all samples, the authors have complied with the methodology provisions in the users' guide of the microwave oven. After mineralization, the samples were brought to 100 ml volumetric flask with distilled water and subjected to AAS-analyse.

The results represent the average value of three determinations, for which the calculated standard deviation was lower than 5%. The Standard Deviation was determined using the Microsoft Excel program.

The pH, conductivity and redox potential of the substrates at the beginning and end of the experiments were performed using Inolab pH-meter pH 730 for pH measurement and Hanna Multimeter Check HI991003 for conductivity and redox potential measurement.

Calculation of translocation factor

The transfer capability of heavy metals from substrate to the edible part of *Hieracium aurantium* and *Rumex acetosella* (roots and leaves) was described using the translocation factor [13-15]. The translocation factors (TF) of Pb, Zn, Cu and Fe were calculated as follows:

$$TF = \frac{\text{metal concentration in edible part of vegetable (FW)}}{\text{metal concentration in substrate (DW) from where the plant was grown}}$$

Statistical analyses

A one-way analysis of variance (one-way ANOVA) was carried out to compare the mean values measured for all the batches tested. When a significant *P*-value (*P*<0.1) was obtained, differences between individual means were compared using the post-hoc Tukey's HSD and Least Significant Difference (LSD) tests (*P*<0.1).

Tukey's HSD (Honestly Significant Difference) test is a single-step multiple comparison procedure and statistical test generally used in conjunction with an ANOVA-based analysis, to find which means are significantly different one from another. It compares all possible pairs of means, and is based on a distribution similar to that of *t* from the *t*-test [16-18].

The correlation coefficients between the concentrations of the heavy metals in roots and respectively leaves grown on different substrates were determined using the Microsoft Excel software.

RESULTS

To establish if the zeolite structure is modified with ammonium ions, FTIR analyses were performed (Figure 1). The peak localized at 1028.68 cm⁻¹ in FTIR spectra of zeolite corresponds to the vibration of the bands connected with the internal Si-O(Si) and Si-O(Al) vibrations in tetrahedra or aluminosilicate oxygen bridges [19]. Introduction of non-tetrahedral cations into aluminosilicate frameworks can change their FTIR spectra in the range of pseudo-lattice vibrations located at about 1028-1036 cm⁻¹ and 700-500 cm⁻¹.

The changes in the FTIR spectra of zeolites exchanged did not result in a distinct shift of these band positions but in changes in their intensity. In this

range a weak but systematic variation was observed in the band at 1028-1036 cm⁻¹ and at 600-602 cm⁻¹, which can be attributed to pseudo-lattice ring vibrations of

SiO₄ or AlO₄ tetrahedra and particularly to the inter-tetrahedral bonds vibrations [19].

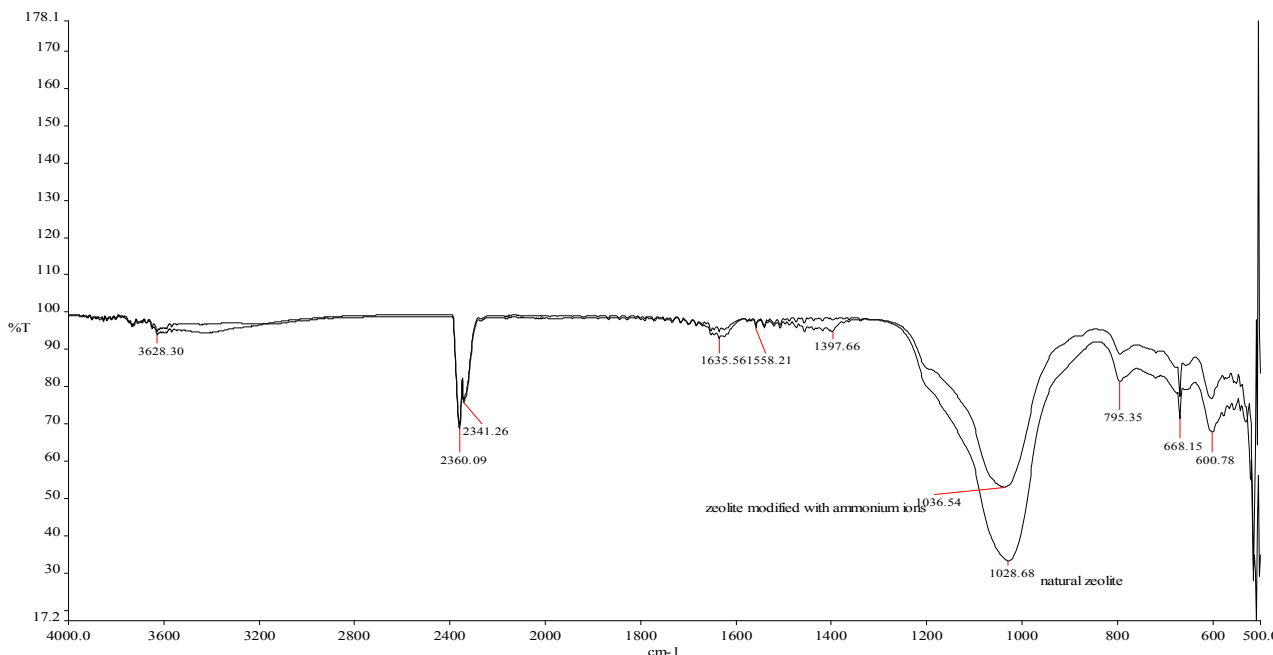


Figure 1. FTIR spectra of the natural zeolite and zeolite modified with ammonium ions.

Table 1 includes details about the area and the length of the peak localized at 1028.68 cm⁻¹ from the FTIR spectra of zeolite and 1036.54 cm⁻¹ from the FTIR spectra of zeolite-NH₄. The variation of the area

and length of the peak of the two samples demonstrates different intensities of vibration of certain bands, thus suggesting generation of different bands (Si-O-NH₄, in the case of zeolite modification with NH₄).

Table 1. Characteristics of the peak from FTIR spectra of the natural and modified zeolite (Figure 1) localized between 1028 and 1036 cm⁻¹.

Amendment	Area of the peak localized between 1028 and 1036 cm ⁻¹ (T % x cm ⁻¹)	Height of the peak at 1028-1036 cm ⁻¹ (T %)
Zeolite	23 502.36	33.28
Zeolite - NH ₄	27 427.21	53.35

In Table 2 are presented the concentrations of heavy metals from the sterile collected together with the *Hieracium aurantium* and *Rumex acetosella*, respectively, from the tailing pond. The highest concentrations correspond to the iron ions (19632.5

mg/Kg DW in the sterile near to the *H. aurantium* and 21630 mg/Kg DW in the sterile near to the *R. acetosella*) and the lower concentrations correspond to the zinc and copper ions.

Table 2. Concentration of the heavy metals in the sterile collected together with the *Hieracium aurantium* and *Rumex acetosella* plants in the tailing pond. The results are the average values of three determinations, for which the calculated standard deviation was lower than 5%.

	Pb	Zn	Cu	Fe
	(mg/Kg DW)			
Sterile near to <i>Hieracium aurantium</i>	483.5	153	111.85	19 632.5
Sterile near to <i>Rumex acetosella</i>	350.8	183.5	157.7	21 630

*DW - dry weight

In Table 3 are presented the values of pH, conductivity and redox potential of the investigated substrates at the beginning and at the end (after 38 days) of the pot experiments.

At the beginning of the experiments, the electrical conductivity of the sterile-zeolite was lower than that of the sterile. Similar behaviour was observed in the case of redox potential, at the beginning of the experiments. The redox potential decreases in the following order: sterile>sterile-zeolite>sterile-zeolite-NH₄⁺. As the quantity of zeolite increases, the redox

potential decreases, because the adsorption capacity grows and, subsequently, the amount of metal ions available for redox reactions (Fe²⁺ and Fe³⁺) is smaller.

At the end of the experiments, all the substrates investigated had a lower pH. The substrates with zeolite have a higher pH than sterile. Moreover, the substrate with modified zeolite has a higher pH than the substrate with natural zeolite. The increase of the amount of zeolite leads to the increase of the pH, due to the basic character of the amendment.

Table 3. Values of pH, conductivity and redox potential of the substrate at the beginning and at the end (after 38 days) of the pot experiments. The results are the average values of three determinations, for which the calculated standard deviation was lower than 5%.

		pH	Electrical conductivity (mS/cm)	Redox potential (mV)
Sterile	Initial	4.45	109.7	356
	Final	3.56	125.4	311
Sterile – zeolite 5%	Initial	4.96	84.3	243
	Final	4.16	97.5	201
Sterile – zeolite 10%	Initial	5.11	70.3	239
	Final	4.50	77.3	178
Sterile - zeolite-NH ₄ ⁺ 5%	Initial	5.07	73.5	240
	Final	4.39	66.4	192
Sterile - zeolite-NH ₄ ⁺ 10%	Initial	5.23	50.7	228
	Final	4.75	21.8	159

The values of the electrical conductivity for the sterile, sterile-zeolite 5% and 10% and sterile-zeolite-NH₄⁺ 5% are higher at the end of the experiments as compared to the initial values.

The concentrations of different heavy metals in roots and leaves of *Hieracium aurantium* and *Rumex acetosella* grown on different substrates are indicated in Table 4. The highest concentrations of heavy metals

were accumulated in organs grown on sterile without zeolite, being smaller in the organs grown on substrate with natural zeolite. The organs grown on substrate with modified zeolite have accumulated the lowest amount of heavy metal ions. The concentrations of the heavy metal ions accumulated in organs of *Hieracium aurantium* and *Rumex acetosella* were used for the determination of the soil-to-plant translocation factors.

Table 4. Concentration of the heavy metals in roots and leaves of *Hieracium aurantium* and *Rumex acetosella* grown for 38 days on different substrates containing 5% and 10% (w/w) zeolite and sterile. The results are the average values of three determinations, for which the calculated standard deviation was lower than 5%.

		Pb	Zn	Cu	Fe
		mg/Kg DW*			
<i>Hieracium aurantium</i>					
Sterile	Root	289.25	112.44	82.7	8741.78
	Leave	106.56	54.32	27.5	539.08
Sterile – zeolite 5%	Root	220.56	90.43	63.43	6734.67
	Leave	80.43	32.14	10.23	223.5
Sterile – zeolite 10%	Root	180.56	60.21	57.45	4806.33
	Leave	72.43	12.11	6.45	114.3
Sterile-zeolite-NH ₄ ⁺ 5%	Root	115.43	50.14	32.14	2754.65
	Leave	37.67	13.21	5.43	97.5
Sterile-zeolite-NH ₄ ⁺ 10%	Root	49.63	23.51	13.21	843.32
	Leave	0.67	5.22	1.46	76.43
<i>Rumex acetosella</i>					
Sterile	Root	87.56	143.62	70.37	3037.5
	Leave	5.38	71.44	19.51	1167.54
Sterile – zeolite 5%	Root	61.45	111.67	55.21	2567.2
	Leave	3.21	50.2	9.44	795.21
Sterile – zeolite 10%	Root	55.21	93.28	34.12	2122.4
	Leave	1.42	24.37	7.83	556.23
Sterile-zeolite-NH ₄ ⁺ 5%	Root	22.41	65.71	20.45	1433.2
	Leave	2.39	20.45	5.42	237.12
Sterile-zeolite-NH ₄ ⁺ 10%	Root	9.43	24.21	7.14	969.67
	Leave	0.71	9.81	1.11	157.4

*DW – dry weight

Soil-to-plant translocation factors (Fig. 2 & 3) were used to evaluate the metal uptake ability of roots and leaves of *Hieracium aurantium* and *Rumex acetosella* respectively, after 38 days of growth in different substrates. The translocation factors of the heavy metal ions in roots and leaves grown on sterile are higher than those calculated for the samples grown on substrates with zeolite. Furthermore, the translocation factor of the metals in roots and leaves grown on substrates with zeolite, decreases as the percentage of zeolite increases. These results are confirmed by Shi and coworkers [5] who studied the effect of different doses of zeolite in reducing the lead accumulation in

roots and aerial parts of grape. They are in agreement with the fact that the potential environmental availability of metals from contaminated soil may be controlled by soil amendments with exogenous zeolite or humic substances [5].

The graph in Figure 4 shows the variation of the correlation coefficients between the concentrations of the heavy metals investigated. All the values are positive (between 0.93 and 0.98), suggesting the change in same direction of the concentrations of heavy metals (if the concentration of a heavy metal ion from the above mentioned pair increases, an increase of the concentration of the other ion will occur).

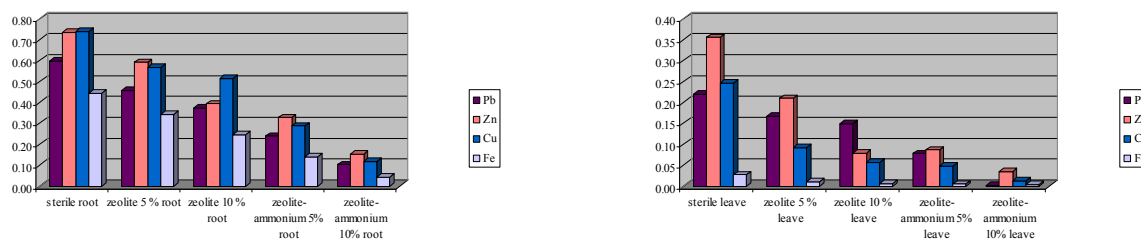


Figure 2. Variation of the translocation factors (TF) depending on the substrate in which *Hieracium aurantium* samples were grown (a) variation of the TF in roots; (b) variation of the TF in leaves.

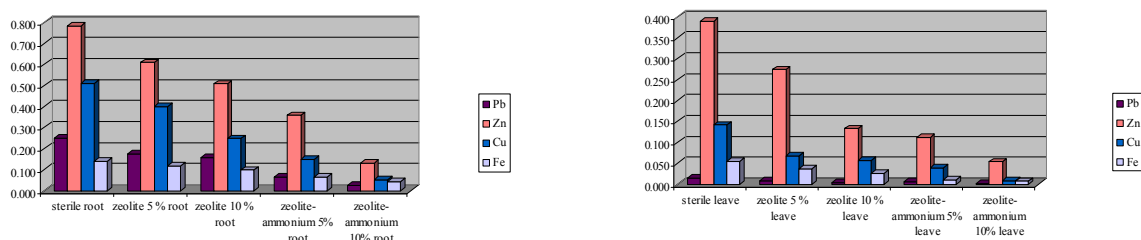


Figure 3. Variation of the translocation factors (TF) depending on the substrate in which *Rumex acetosella* samples were grown (a) variation of the TF in roots; (b) variation of the TF in leaves.

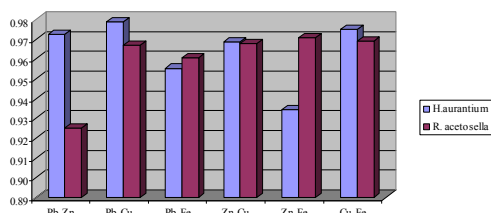


Figure 4. Variation of the correlation coefficients between the concentrations of heavy metals in roots and leaves respectively, grown on different substrates, for 38 days.

As the ANOVA tests reveal (Table 5), the differences between individual means for each of the ions of heavy metals investigated are significant (all the significance (Sig.) values obtained were lower than 0.1) suggesting that the variation of the heavy metal concentration in roots and leaves, depending on the substrate is significant.

Tukey HSD and LSD tests were performed to establish if the decrease of heavy metal concentration in roots and leaves grown on sterile with zeolite is sig-

Table 5. Parameters of the One-Way ANOVA statistical analyses performed for each metal ion found in *Hieracium aurantium* and *Rumex acetosella*.

<i>Hieracium aurantium</i>					
LEAD					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	33246.714	2	16623.357	7.138	0.072*
Within Groups	6986.701	3	2328.900		
Total	40233.416	5			
ZINC					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5718.383	2	2859.192	10.625	0.044*
Within Groups	807.283	3	269.094		
Total	6525.666	5			
COPPER					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3683.136	2	1841.568	28.037	0.011*
Within Groups	197.053	3	65.684		
Total	3880.188	5			
IRON					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	48531266	2	24265633.01	19.750	0.019*
Within Groups	3685839	3	1228613.002		
Total	52217105	5			

<i>Rumex acetosella</i>					
LEAD					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5190.194	2	2595.097	75.069	0.003*
Within Groups	103.709	3	34.570		
Total	5293.903	5			
ZINC					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	9823.121	2	4911.561	14.302	0.029*
Within Groups	1030.221	3	343.407		
Total	10853.342	5			
COPPER					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3209.623	2	1604.812	15.482	0.026*
Within Groups	310.972	3	103.657		
Total	3520.595	5			
IRON					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3438834	2	1719417.166	24.997	0.013*
Within Groups	206353.6	3	68784.517		
Total	3645188	5			

* The mean difference is significant at the 0.1 level.

nificant as compared to sterile without zeolite (Table 6). If the significance values are lower than 0.1, the variations of the heavy metal concentrations are significant. The values marked (*) are smaller than 0.1,

which means the reduction of the concentration of lead, zinc and iron accumulated in roots and leaves of *Hieracium aurantium* and *Rumex acetosella*, by using zeolite modified with ammonium ions is significant.

The natural zeolites have no significant impact when used in the attempt to reduce the concentration of the heavy metal ions in the organs of *Hieracium aurantium*. In contrast, the fact that the values of the significance corresponding to *Rumex acetosella* grown

on natural zeolite are lower than 0.1, reveals that the natural zeolite is an efficient amendment in reducing the accumulation of lead, copper and iron in roots and leaves.

Table 6. The significance values obtained by using the Tukey HSD and LSD tests.

			Pb	Zn	Cu	Fe
<i>Hieracium aurantium</i>						
Tukey HSD	Sterile	Sterile - Zeolite	0.560	0.279	0.536	0.145
		Sterile - Zeolite-NH ₄ ⁺	0.065*	0.045*	0.117	0.017*
LSD	Sterile	Sterile - Zeolite	0.317	0.135	0.299	0.075*
		Sterile - Zeolite-NH ₄ ⁺	0.028*	0.019*	0.052*	0.080*
<i>Rumex acetosella</i>						
Tukey HSD	Sterile	Sterile - Zeolite	0.032*	0.213	0.165	0.150
		Sterile - Zeolite-NH ₄ ⁺	0.002*	0.026*	0.023*	0.012*
LSD	Sterile	Sterile - Zeolite	0.016*	0.113	0.086*	0.078*
		Sterile - Zeolite-NH ₄ ⁺	0.001*	0.013*	0.011*	0.006*

* The mean difference is significant at the 0.1 level.

DISCUSSION

The pH values revealed that, at the beginning of the experiments, all the investigated substrates are slightly acid (in the 4.45 to 5.37 range), due to the presence of the pyrite, chalcopyrite, galena and blend, which in reaction with oxygen, generate sulphides. Because of the basic character of zeolite, the sterile-zeolite substrate has a higher pH than the sterile. The pH of the zeolite modified with ammonium ions is even higher, for the same reason. These results are in agreement with those of Leggo and coworkers [20] which studied the role of clinoptilolite in organo-zeolitic-soil systems for phytoremediation.

The zeolite acts to diminish the electrical conductivity to a minimum limit of 50.7 mS/cm, behaviour which is in agreement with that established by Leggo and coworkers [20]. At the beginning of the experiments, the electrical conductivity of the substrates with modified zeolite was lower as compared with the substrate with natural zeolite, due to the higher adsorption capacity of the modified zeolite and has induced the decrease of the amount of the heavy metal ions in solutions responsible for the electrical conductivity.

The increase of the pH, at the end of the experiments, in all the substrates investigated was explained by two reasons: the presence of humic acids generated during the degradation of the organic and of the pyrite materials, on one hand, and the rhizosphere effect, on the other hand. The rhizosphere effect consists in the local acidification of the environment due to the adsorption of the heavy metal ions on the cell walls by replacing the protons from -COOH, -OH, -SH, and -NH₂ groups with heavy metal ions. The protons increase the acidity and, subsequently, lead to the decrease of the pH [21].

The values of the electrical conductivity for the sterile, sterile-zeolite 5% and 10% and sterile-zeolite-NH₄⁺ 5% are higher at the end of the experiments as compared to the initial values, due to the increase of the concentrations of the humic acids and protons. In the other cases, the electrical conductivity is lower at

the end of the experiments as compared with the initial values.

The redox potential decreases, in all cases, at the end of the experiments as compared with the initial values, due to the decrease of the amount of the metal ions available for redox reactions.

The comparison of the amount of heavy metals accumulated in roots with the amount accumulated in leaves reveals that, in all the cases investigated, the leaves accumulated a lower amount of heavy metals than roots, due to the inhibition mechanism that almost all of the plants develop as protection against the destructive effect of the heavy metal ions [22].

The variation of the translocation factors of heavy metal ions uptake in roots and leaves grown on different substrates (sterile with natural zeolite and sterile with modified zeolite) demonstrates the impact of ammonium ions on zeolite in terms of enhancing its capacity to adsorb ions of heavy metals. Cations such as ammonium and potassium have smaller hydrated radius and lower hydration energy than the calcium and magnesium ions [23-25]. Increasing the adsorption capacity of zeolite by activation (replacing the magnesium and calcium ions characteristic to natural zeolite with activation cations such as ammonium and potassium), can be explained by the fact that the new cations show a greater availability to ion exchange and higher mobility [26].

It was established by comparison that *Rumex acetosella* has a higher TF for lead and iron than *Hieracium aurantium*. This happens because the tolerance to metals of *Rumex acetosella* is slightly smaller than the tolerance of *Hieracium aurantium*, on one hand, and because the natural and the modified zeolite have a stronger protective effect (smaller uptake of lead and iron) on *Rumex acetosella* than on *Hieracium aurantium*, on the other hand. The presence of phosphorus in the cells of *Rumex acetosella* explains its smaller TF. Ke et al. [12] found that under severe stress by copper (100 μM), the populations of *Rumex japonicus* growing in contaminated zones maintain higher quantities of phosphorus than the populations in non-contaminated areas. Because a higher

accumulation of phosphorus determines a higher tolerance to copper, the transport and accumulation of copper, as well as of other metal ions, in *Rumex japonicus* might be controlled by adjusting the content of phosphorus. The research studies demonstrated that the tolerance of plants to different heavy metal ions is controlled by the metallothionein gene, *SvMT2b*, which behaves as a hypostatic enhancer of the degree of tolerance [12]. Additionally, it was observed that mucilages of plant root exudates may play a role of filter in heavy metal absorption. The mucilages are deposited outside the root hairs forming a gelatinous envelope known as "mucigel". Mucilages constitute an important fraction of the apoplast and rhizosphere and possess a high ability to complex and immobilize metals in the reticulating sites of the root free space [12].

We can conclude that natural zeolite or zeolite modified with ammonium can be used to reduce the uptake of heavy metal ions in the roots and leaves of *Hieracium aurantium* and *Rumex acetosella*. The adsorption capacity of zeolite increases by changing its structure with ammonium ions. Thus, the modified zeolite is a more efficient amendment more efficient than the natural zeolite in reducing the accumulation of heavy metal ions in plants. Because *Hieracium aurantium* has a higher translocation factor than *Rumex acetosella*, the former has a higher tolerance to heavy metals than the later. As the statistical analyses reveal, *Hieracium aurantium*'s uptake of ions of heavy metals is significantly reduced only by the zeolite modified with ammonium ions. Both natural zeolite and zeolite modified with ammonium ions can significantly influence the uptake capacity of *Rumex acetosella*.

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