

Experimental study of polluted sediment and As elimination from the pit water in the locality of Zlatá Idka-Rieka, Slovakia

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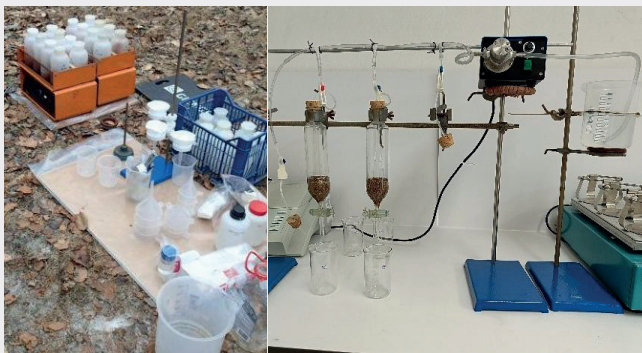
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Abstract: The study presents introductory laboratory and in-situ experiments focused on elimination of As from the pit water in locality Zlatá Idka-Rieka, Slovakia, as well as on characterization of the sediment parameters in this locality from the viewpoint of their eventual toxicity. The mobility of As from the sediment is dependent on the chemical bonds with non-stable Fe oxides/hydroxides, creating surface coatings on the grains of minerals and soil, present in the lake of pit water. Leachates after the Simply Bioavailability Extraction Test contained high concentrations of Fe (223 mg.l⁻¹), Mn (165 mg.l⁻¹), as well as As (11.1 mg.l⁻¹), which are potential toxic for people in case of contamination of the soil attached to vegetables, or from coarse dust that can be inhaled and then swallowed. The batch adsorption experiments were performed in the laboratory and next in in-situ conditions. As adsorbents natural zeolite, terra rossa and their mixture were used. In laboratory the As adsorption was fast, reached equilibrium almost after 4 hours. The adsorption capacity of zeolite and terra rossa was 18.3 and 25,3 µg.g⁻¹, respectively. Effect of in-situ As removal was the highest for terra rossa (almost 85 %) and the concentration of As in leachate after the experiment was slightly higher than required limited value. The promising results for future in-situ applications brought laboratory column experiments, where after 4 cycles of adsorption the effectivity of columns was still 95 % independently on the columns filling (layers or mixture of studied adsorbents).

Key words: pit water, adsorption, zeolite, terra rossa

Graphical abstract



Highlights

- Arsenic present in the sediment in studied locality is easy mobile and potential toxic for local population.
- Laboratory adsorption experiments decreased the As content in the pit water to concentration applicable for irrigation waters.
- Laboratory experiments in dynamic conditions demonstrated high potential of column filling – beds of zeolite and terra rossa for in-situ applications.

1 Introduction

In Slovakia, the source of contamination of the natural environment with arsenic is mainly anthropogenic or caused by mining activity, which adversely affects the ore deposits in all components of the environment. Its impact may appear immediately, but also with a delay of several years. The presence of arsenic (As) in surface water and

groundwater, and associated stream sediments and soils represents a serious environmental concern. In territory of Slovakia the highest concentrations of As contaminant are present in the ore deposits areas of Slovenské rudohorie Mts., Nízke Tatry Mts. and Malé Karpaty Mts. (Fľaková et al., 2017).

In old mining village of Zlatá Idka the silver and antimony ores were extensively mined and processed. Waters,

soil and stream sediments in this area are contaminated by arsenic. High contents of this potential toxic element are present especially in the outflows of pit waters and consequently in surface water of the Ida creek. Exploration was realized within the frame of geological project of the State Geological Institute of Dionýz Štúr (SGIDS) Evaluation of potential impact of the geochemical environment on the health state of inhabitants in the area of the Spiš-Gemer Ore Mts. (Rapant et al., 2004). Chemical analyses of water proved high concentrations of As in almost all water sources used in area, with the exception of some shallow based mines (adits) and springs. The arsenic is present in less toxic form of pentavalent ions, what suggests the presence of **oxidizing conditions** – probably in the final stage of pit water outflow to the surface (Cicmanová & Baláz, 2007).

Arsenic and its compounds represent persistent mobile pollutants, which cannot be destroyed, but their negative impact can be reduced by immobilization (adsorption). Between pH 2.2 to 11.5 the arsenate oxyanion ($pK_a = 2.2, 7.0, 11.5$) dissociates in aqueous solutions in two forms: $H_2AsO_4^-$ (pH 2.2–7.0 and $HAsO_4^{2-}$ (pH 7.0–11.5) (Ho & McKay, 1999).

Oxidation-reduction potential (Eh) and pH are the most important factors that control the forms of As occurrence. Both parameters must be measured directly in the field and simultaneously. Arsenic is a special element among the elements forming complex anions (e.g. As, Se, Sb, Mo, V, Cr) in its sensitivity to mobilization at pH values that are typical for the groundwater (6.5–8.5), and this in both oxidation and reduction conditions (Smedley and Kinniburgh, 2002; Sracek et al., 2004a, b). Arsenic can occur in the natural environment in several oxidation stages (– III, 0, + III and + V), but in natural waters it is predominantly found as an inorganic form in a complex anion such as trivalent arsenite (As (+ III)) or pentavalent arsenate [As (+ V)]. Under oxidizing conditions, $H_2AsO_4^-$ is dominant at low pH (less than 6.9), whilst at higher pH, the $HAsO_4^{2-}$ becomes dominant.

The work of Cicmanová and Baláz (2007) showed that in terms of the level of content and bioavailability of As in river sediments of streams, the whole Ida stream can be described as an area of high environmental risk. These are indicated results of the sequential extraction method of metals, where decisive proportions of As in the sediment is in the 5th residual fraction (41–54 %) and the 3rd reducible fraction (33–53 %). Particularly problematic is the high proportion of the 3rd reducible fraction, representing the metal content bound to the thermodynamically unstable Fe and Mn oxides. For this reason, there is a probability of variability in the processes of metal binding in the sediment and its release into water depending on changes in the redox conditions of the aqueous environment. These changes are directly related to seasonal regime conditions – strength of pit and surface water flows.

The study is focused in the characterization of sediment contaminated by arsenic containing pit water in locality Zlatá Idka-Rieka. The mobility and bioavailability of potential toxic elements in living environment were tested and evaluated by known methods for contaminated soils and sediments. The elimination of high content of arsenic (concentration changed in dependence on climate and weathering conditions from 300 up to 380 $\mu\text{g.l}^{-1}$) from the pit water was studied in laboratory within static and dynamic regimes, as well as in-situ in batch conditions using natural adsorbent of zeolite and decorative clay terra rossa. For all test both materials were used separately, as well as applied was also their mixture.

2 Materials and methods

2.1 Pit water sample

Laboratory, as well as, in situ experiments were performed applying the pit water, flowing out from the Hauser adit in the Zlatá Idka-Rieka locality. The pit water in this locality is characterized by very high concentrations of As and Fe, what is expressed by the rusty red colour



Fig. 1. Regulated flow of pit water on the locality of Hauser adit with formed lake under the drain of pit water.

of precipitates in drained water and coatings on the surrounding rocks and soil. The concentration of As in the pit water varied depending on the year season and climate conditions. The As concentrations of 200 up to 360 $\mu\text{g.l}^{-1}$ were measured on the locality, what is several times higher than required value applicable for irrigation waters 50 $\mu\text{g.l}^{-1}$ (according to the Regulation of Government of the Slovak Republic No. 269/2010 Coll. (next only “regulation”) – Part B – Surface waters for irrigation. Except of As and Fe, other analysed elements (Ba, Co, Cr, Cu, Mn, Ni, Zn, Pb, Sb, Cd) in the pit water did not exceed the limit value (not shown here). The flow of pit water is regulated and the water is cumulated in the plane under the previous heap forming small lake.

2.2 Sediment sample

The sediment sample, denoted as H1, was taken from the lake with pit water under its drain in the Hauser adit locality. The sample of sediment was wet sieved to grain size below 2 mm. The oversized product and product of fraction 1.0–2.0 mm consisted of organic material (leaves, springs, cons). The sludge below 1 mm was analysed by laser granulometer (defined below) to determine the particle size distribution and used for the experimental purposes.



Fig. 2. Fractions of sediment H1: fraction +2.0 mm and 1.0–2.0 mm created by organic matter, fraction below 1.0 mm consisted of fine particles with high content of Fe.

2.3 Adsorbents

As the adsorbents, domestic natural materials with good adsorption expectations were chosen: zeolite from the Majerovce locality and decoration clay terra rossa from the Včeláre locality.

2.4 Adsorbents and sediment characterization

The powder X-ray diffraction (XRD) patterns of adsorbent samples and sediment sample were recorded

using a diffractometer D2 Phaser (Bruker, Germany), equipped with a $\text{CuK}\alpha$ radiation source (30 kV, 10 mA) and Lynxeye detector. The data were qualitatively and quantitatively analysed using Software DIFFRAC.EVA with PDF-2 Database.

Differential thermal analysis (DTA) was carried out using the derivatograph STA 449 F3 Jupiter (Netzsch, Germany). Measurement was done in real atmosphere up to the temperature 1000 °C with heating gradient 10 °C/min. Obtained data were processed by the Proteus software.

Particle size distribution of sediment sample in the range 0.01–1000 μm was analysed by laser light scattering analyser Mastersize 3000 (Malvern, UK)

The iron oxide coatings of sediment were studied by scanning electron microscopy FE MIRA 3 (Tescan, Czech Republic) equipped by XRD energy-dispersive (EDX) analyser of chemical composition (Oxford Instruments).

2.5 Mobility of toxic elements and bioassessability testing

Mobility of toxic elements present in the sediment was tested using Synthetic Precipitation Leaching Procedure (SPLP), Method 1312 based on the acid rain leaching (Method 1312, 1994; Fey et al., 2011). The sediment sample of 5 grams was extracted by solution of H_2SO_4 and HNO_3 (weight ratio 3 : 2). The sediment and extraction solution were placed into the extraction bottle and shaken for 18 hours on the laboratory shaker. Then the leachate was filtered and analysed.

The bioassessability of the toxic elements present in the sediment H1 was tested by Simply Bioavailability Extraction Test (SBET). The sediment sample of 5 grams was extracted by solution of 0.4 M glycine of pH 1.5 (adjusted by HCl) under the vigorous stirring for 1 hour at 37 °C (Report No.: 1542820-003-R-Rev0, 2016; Kim et al., 2009).

2.6 Adsorption experiments

First, the laboratory adsorption experiments were made by batch technique. The adsorbents dose was 10 g. l^{-1} . 1 g of adsorbents was added into the glass bottles containing 100 ml of pit water. The initial pH of the pit water was 7.15. The suspensions were shaken for 20 hours at the ambient temperature (25 °C) at 200 rpm to reach equilibrium and then consequently filtered using the filter paper. The experiments were performed duplicate.

In situ batch adsorption experiments were realized during one day on locality Zlatá Idka. The plastic bottles were filled by adsorbents: zeolite (fraction 1.0–2.0 mm), terra rossa and mixture of both (adsorbents concentration 10 g. l^{-1}). The pit water of 500 ml was added into bottles and shaken onto terrain shakers for 15 up to 120 minutes.

The experiments were performed duplicate. The effect of contact time was studied to determine the rate constant as well as possible mechanism of adsorption.

All column experiments in laboratory conditions were performed using glass columns: inner diameter of 5 cm and 18 cm high. The columns were filled by different layers: quartz sand (60 g), zeolite from the Majerovce locality (20 g) and terra rossa from the Včeláre locality (20 g). During one adsorption cycle, 150 ml of pit water was percolated through the columns at constant flow 2.8 ml per minute. The initial As concentration of pit water varied from 104 to 387 $\mu\text{g.l}^{-1}$ for different cycles, pH from 7.07 up to 7.8. The initial As concentration changed in dependence of time of its storage in plastic bottles. The higher precipitation of iron hydroxides with As occurred, leading to the increase of pH value. The experiments were performed duplicate. For each cycle, the initial As concentration of pit water was analysed.

For all adsorption experiments the supernatant solutions were analysed by the inductively coupled plasma mass spectrometry ICP-MS (Agilent 7900).

3 Results

3.1 Sediment characterization

Particle size analyses of sediment sample showed wide distribution in the range of 1–500 μm , with the maximum at 63 μm , Fig. 3. The results of analyses are listed also in Tab. 1.

The sediment sample was processed by wet magnetic separation and dried at 60 °C for the purpose of mineralogical characterization. The X-ray diffraction analyses (XRD) of magnetic and non-magnetic fractions of this sample are in Fig. 4. Both fractions contained quartz, muscovite, plagioclase and in the case of magnetic fraction also chlorite. But, the XRD analysis did not confirm the presence of expected iron oxide or hydroxide crystalline phases. Therefore the rusty red coatings of rocks and sediment surfaces were further investigated by EDX analyses by scanning electron microscope.

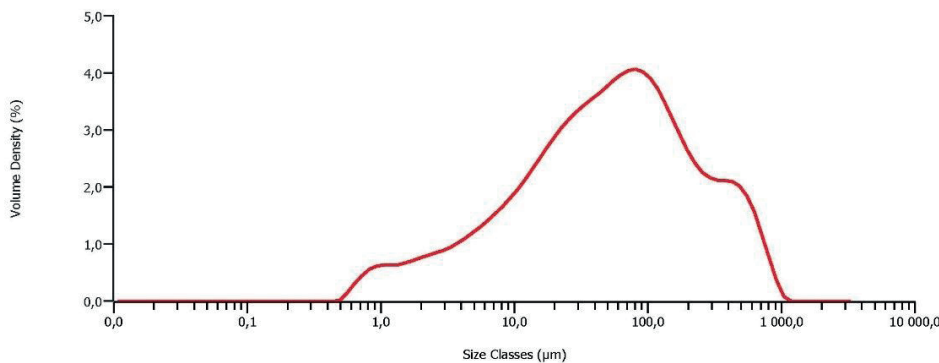


Fig. 3. Particle size distribution of sediment sample H1.

Tab. 1
Particle size analyses of sediment sample H1.

Sample	H1 below 1 mm		
Specific surface area ($\text{m}^2.\text{kg}^{-1}$) of sample of grain size below 1mm	203.2		
Granular class [μm]	volume [%]		
	fraction	over	below
over 2 000	–	0.00	–
2 000–1 000	0.04	0.04	100.00
1 000–500	5.23	5.27	99.96
500–250	9.64	14.91	94.73
250–125	13.12	28.03	85.09
125–63	17.73	45.76	71.97
63–31	17.03	62.79	54.24
31–16	12.98	75.77	37.21
16–8	9.35	85.12	24.23
8–4	6.03	91.15	14.88
4–2	4.04	95.19	8.85
2–1	3.04	98.23	4.81
1–0.010	1.77	100.00	1.77
below 0.010	–	–	0.00
Sum	100.00		

The point EDX analyses showed the presence of Fe and O (41.6 and 40.1 weight %, respectively), as well as expressed higher content of As in the analysed sample (Fig. 5). The content of Mn is also interesting from the environmental point of view.

On the basis of results of XRD and EDX analyses it can be assumed that rusty red colour of sediment as well as surface coatings of rocks in the surrounding lake is caused by amorphous phases of iron compounds (hydroxides, oxyhydroxides), also binding negligible content of As from the outflowing pit water.

During the water sampling also the presence of small precipitates was observed, that were unstable under the water stirring. Longer term of water accumulation (in the lake) and its slower drain into local stream lead to the precipitation of iron compounds caused the expressed sediment colouring.

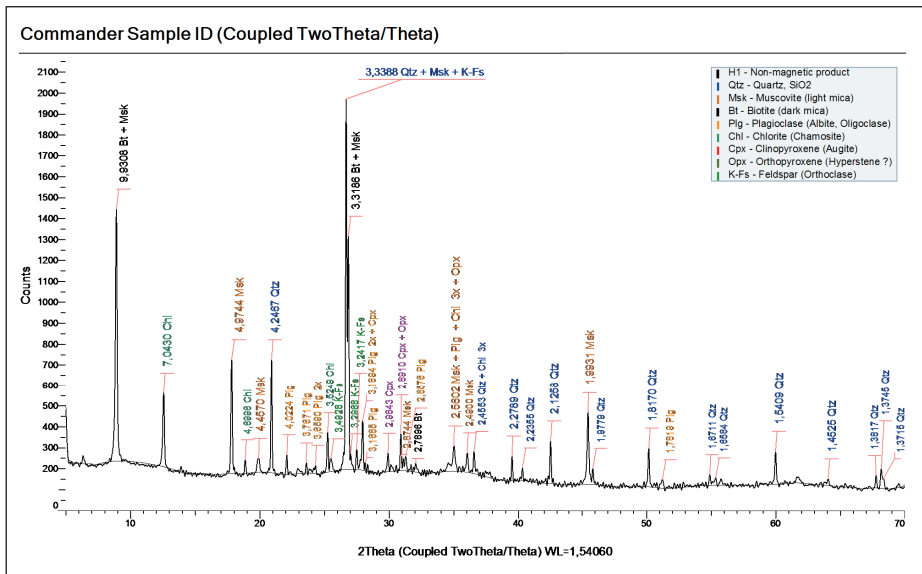


Fig. 4. XRD patterns of magnetic and non-magnetic fraction of sediment sample H1.

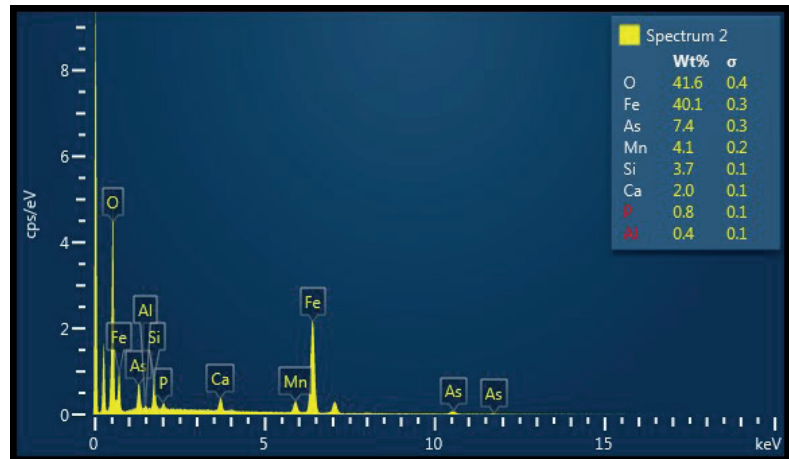
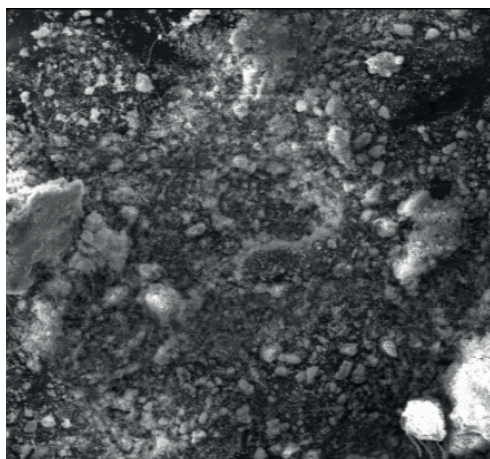
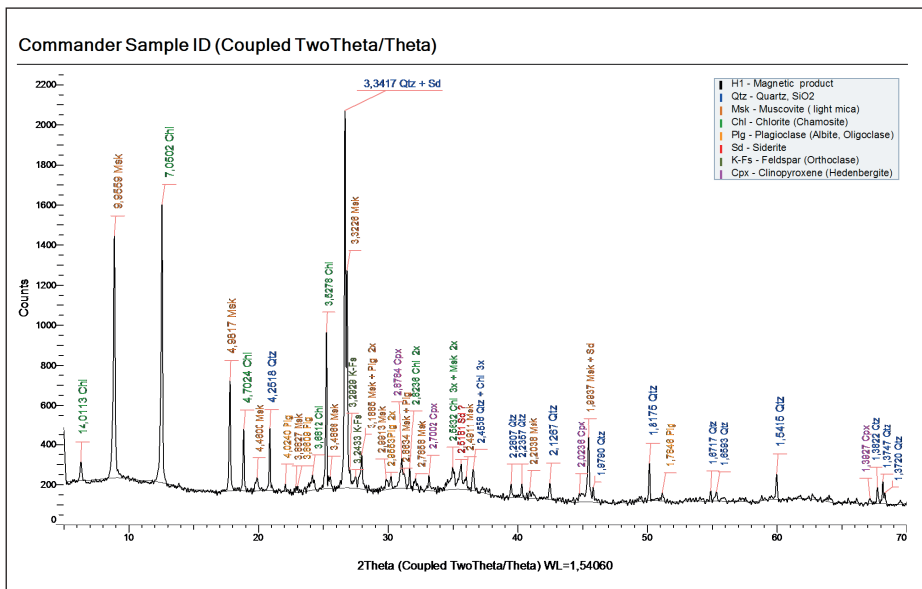


Fig. 5. Point EDX analysis of iron oxide surface coatings.

Tab. 2
Concentration of potential toxic elements in sediment and comparison with the permissible and critical limits according to the guideline.

Element	Permissible limit (ID)	Critical limit		H1 sediment
		Residential districts	Industrial districts	
	[mg.kg ⁻¹]	[mg.kg ⁻¹]	[mg.kg ⁻¹]	[mg.kg ⁻¹]
As	65	70	140	26 032
Ba	900	1 000	2 800	330
Cd	10	20	30	3
Co	180	300	450	28
Cr	12	20	50	34
Cu	500	600	1 500	46
Ni	180	250	500	25
Pb	250	300	800	624
Sb	25	40	80	444
Zn	1 500	2 500	5 000	411

- ID – Permissible limit of contaminant concentration in soils according to the Methodical Instruction of Ministry of Environment of the Slovak Republic, No. 1/2012-7
- IT – Critical limit of contaminant concentration in soils according to the Methodical Instruction of Ministry of Environment of the Slovak Republic, No. 1/2012-7
- 34 – value of contaminant over the critical limit (IT) according to the Methodical Instruction of Ministry of Environment of the Slovak Republic, No. 1/2012-7 for residential districts
- 444 – value of contaminant over the critical limit (IT) according to the Methodical Instruction of Ministry of Environment of the Slovak Republic, No. 1/2012-7 for industrial districts

The presence of potential toxic elements in the sediment represents a risk of their liberation and mobilization. They can be considerable toxic also at low concentrations and should negatively influence the living environment.

Concentrations of risk elements in sediment were evaluated on the basis of chemical analyses according with the Appendix No. 12 of the “Methodical Instruction of Ministry of Environment of the Slovak Republic from the January, 28th 2015, No.1/2015-7” (next only “guideline”).

According the chemical analyses, the concentrations of Cr and Pb provide the values over the critical limits of contaminant in soil in residential districts. The concentration values of As and Sb were over the critical limits of contaminant in soil in industrial districts, Tab. 2.

High concentration of As should be released from the soil matrix by the biological-chemical processes and lead to gradual contamination of plants and groundwaters. Together with other elements it should expose the living environment.

Next the mobility of contaminants in sediment was studied – case study for potential acidification of sediment by acid rains. Acid-forming matters as SO₂ and nitrogen oxides (NO_x) in the atmosphere and on the surface of vegetation react with the air humidity forming the sulphuric and azotic acid. Presence of both acids in the rainfall water leads to decreasing of pH and to reactions causing the acidification of waters and soils (Hruška et al., 1996).

The mobility of sediment contaminants was tested in laboratory conditions according to the Method 1312. Average values of cumulative concentrations of contaminants (mg.g⁻¹) in sediment after the leaching were used to calculate the mobility of indicators (%), Fig. 6.

Mobility of studied contaminants was not very expressive and ranged from 0.02 up to 0.38 %. The most

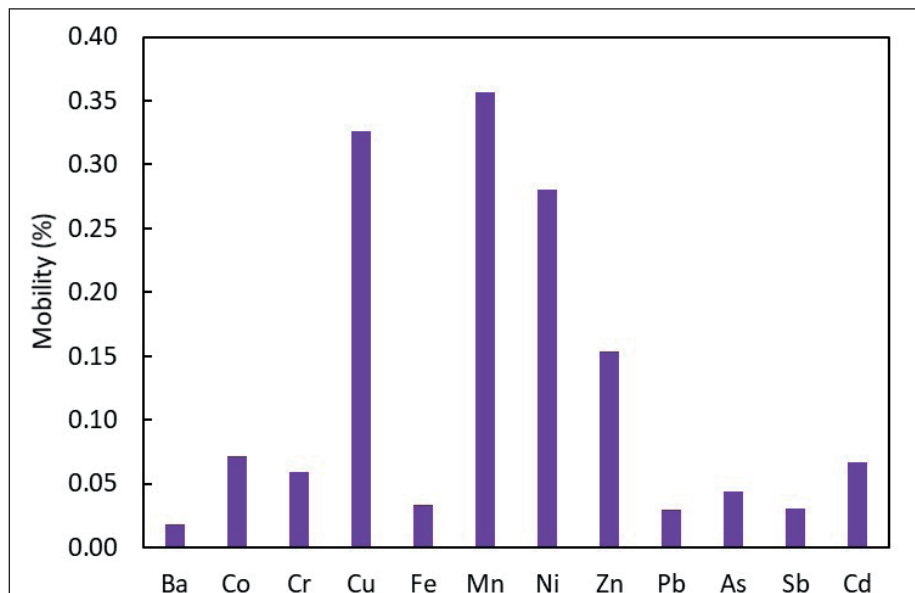


Fig. 6. Mobility of contaminants in studied sediment sample.

mobile seems to be Mn, the least Ba (Fig. 6). In spite of low mobility of As and Fe (0.03 and 0.04 %, respectively), their concentration in leachate after the test represented high values (2.602 mg_{Fe}·l⁻¹ and 0.568 mg_{As}·l⁻¹) due to initial As and Fe concentrations in sediment. It pointed at unstable forms of Fe (Fe, Mn) oxy-hydroxides/hydroxides in sediment binding As.

The bioavailability of a trace element is the proportion of that element being absorbed from soil by the digestive system into body. Laboratory-based extraction procedures

have been developed by researchers to mimic biological extraction using simulated digestive fluids. The bioaccessibility of a trace element is the proportion of that element that can be extracted under simulated digestive conditions. Soil ingestion is thought to be the dominant health risk exposure pathway for many trace elements in soils, including arsenic. Small amounts of contaminated soil and soil-derived dust can adhere to children's hands and to toys, which are then intentionally or accidentally put in the mouth. For both children and adults, some

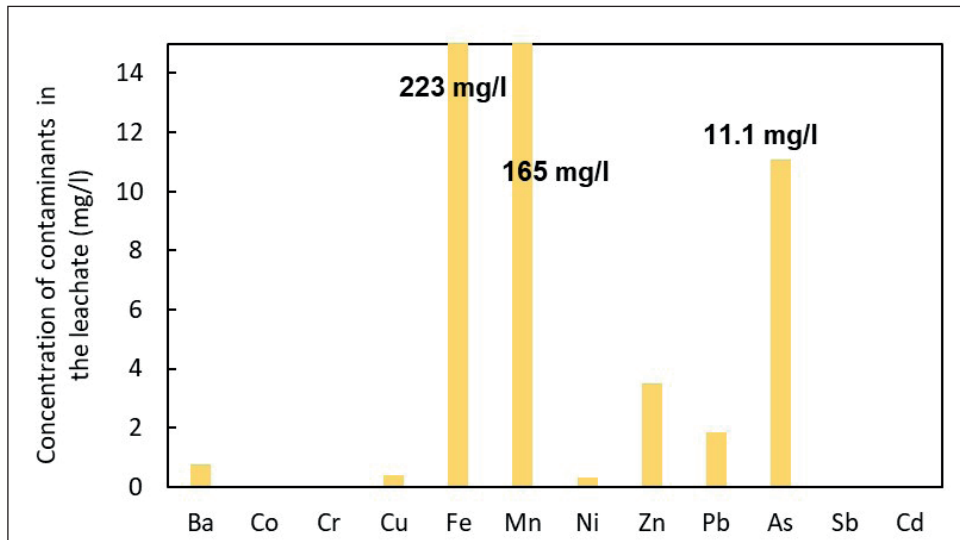


Fig. 7. Concentration of studied contaminants in leachates after the SBET test.

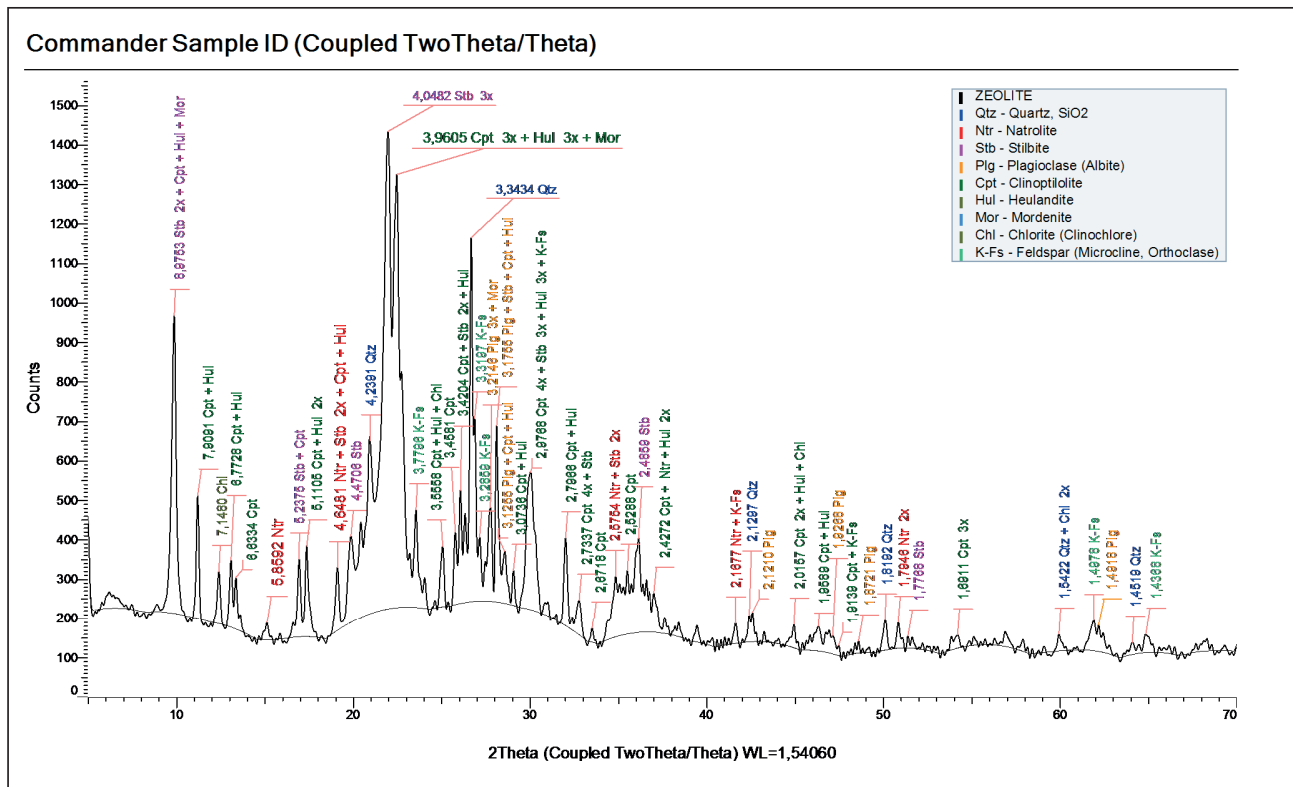


Fig. 8. XRD pattern of zeolite.

contribution may come from soil attached to vegetables, and from coarse dust that is inhaled and then swallowed.

Method Physiologically Based Bioavailability Extraction Test, PBET, is based on two sequential extractions simulating parameters for gastric and small intestinal pH, soil mass, fluid volume, stomach mixing and emptying rate, and small intestinal transit time. Simplified method Simply Bioavailability Extraction Test, SBET simulates only the stomach activity.

Leachates after the SBET test contained high concentrations of Fe (223 mg.l⁻¹), Mn (165 mg.l⁻¹), as well as As (11.1 mg.l⁻¹), also smaller concentrations of Zn, Pb, Ba, Cu (Fig. 7). Expressive acid environment led to the extraction of Fe, Mn and As into the leachate. Obtained results of chemical analyses correspond with the EDX analyses. Hereby, also pointed at the weak stability of Fe (Fe, Mn) precipitated bonding As.

3.2 Adsorbents characterization

For sorption experiments, two types of adsorbents were selected, zeolite and decorative clay terra rossa. X-ray diffraction patterns of used materials are shown in Figs. 8–9. Main mineralogical phases of zeolite sample are represented by clinoptilolite, stilbite, natrolite, present are also plagioclase, chlorite and mordenite. Main mineralogical phases detected in terra rossa sample were kaolinite, hematite and goethite. This material was

selected due to the presence of Fe oxides, known as good adsorbents of As from the water environment. Except drying and fraction grading these adsorbents were not modified or activated for experimental purposes.

3.3 Batch sorption-experiments in laboratory conditions

First, the kinetic of the sorption process was studied in the batch conditions. From the reason that As is considered as potential toxic element, the elimination of this selected indicator was solved and discussed. Sorption capacity of zeolite and terra rossa increased rapidly during the first minutes of experiment and reached equilibrium after 240 minutes. It stayed unchanged up to the end of experiment (Fig. 11), where higher sorption capacity was obtained for the terra rossa.

Adsorption kinetics controls the rate of adsorption, which determines the time required for reaching equilibrium for the adsorption process. Kinetic models can give information regarding adsorption pathways and probable mechanism involved. This is also an important data for the development of the process and the adsorption system design.

It was found, that the Lagergren-first-order kinetic model is not suitable to describe these adsorption systems (not shown here). Therefore the pseudo-second-order (PSO) model was used to interpret the experimental data:

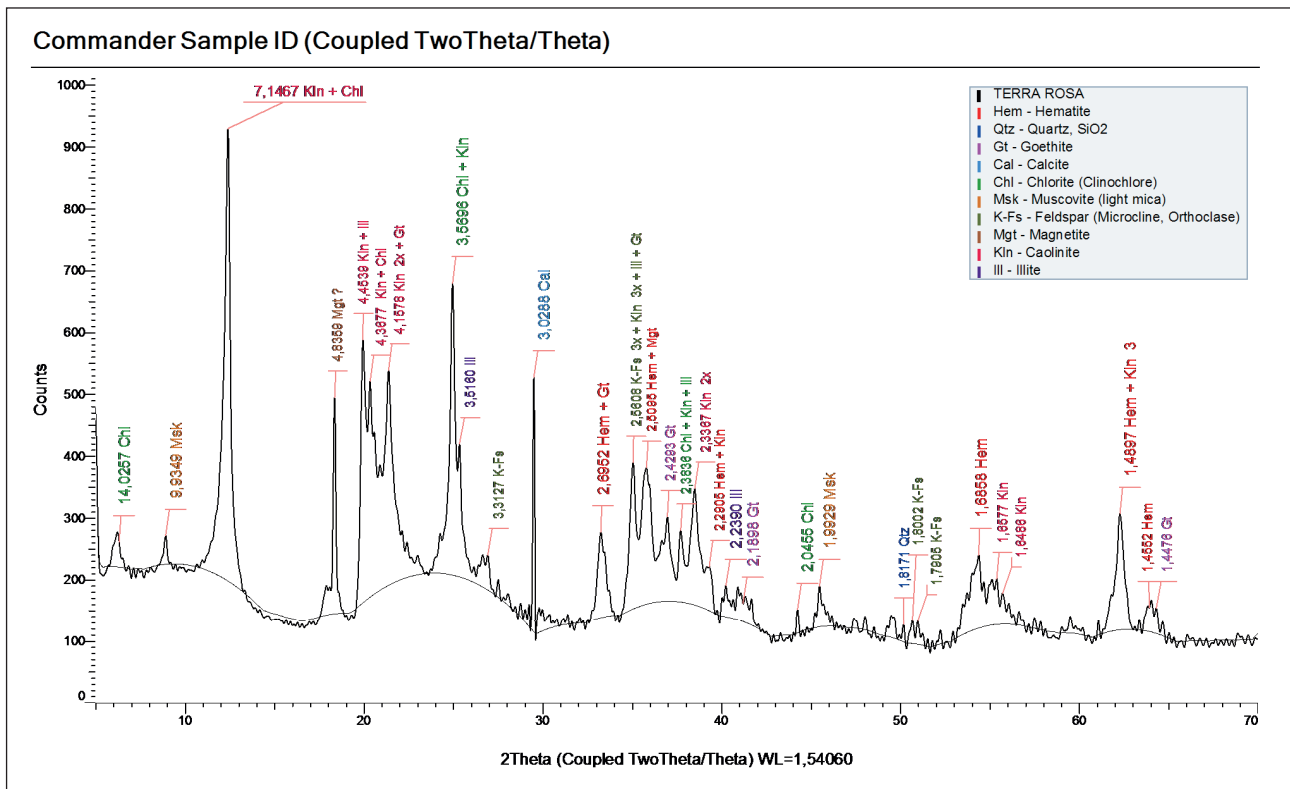


Fig. 9. XRD pattern of terra rossa.

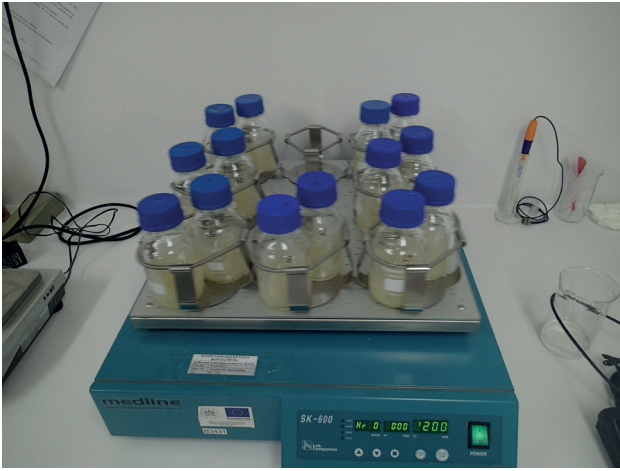


Fig. 10. Kinetic study of As sorption onto zeolite in batch conditions.

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t,$$

where q_e and q_t are the amounts of ions adsorbed on the adsorbent at equilibrium and at various times t ($\text{mg}\cdot\text{g}^{-1}$), k is the rate constant of the pseudo-second-order model for the adsorption process ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) (Erdem et al., 2009).

Tab. 3

Kinetic parameters of pseudo-second-order model for the adsorption of As onto studied adsorbents.

Adsorbent	k [$\text{g}\cdot\mu\text{g}^{-1}\cdot\text{min}^{-1}$]	q_e [$\mu\text{g}\cdot\text{g}^{-1}$] cal.	q_e [$\mu\text{g}\cdot\text{g}^{-1}$] exp.	R^2
Zeolite	0.0466	22.42	18.3	0.9999
Terra rossa	0.0078	29.49	25.3	0.9985

q_e [$\mu\text{g}\cdot\text{g}^{-1}$] – equilibrium amount of ions adsorbed per unit mass, k – rate constant [$\text{min}\cdot\text{g}\cdot\mu\text{g}^{-1}$], R^2 – correlation coefficient

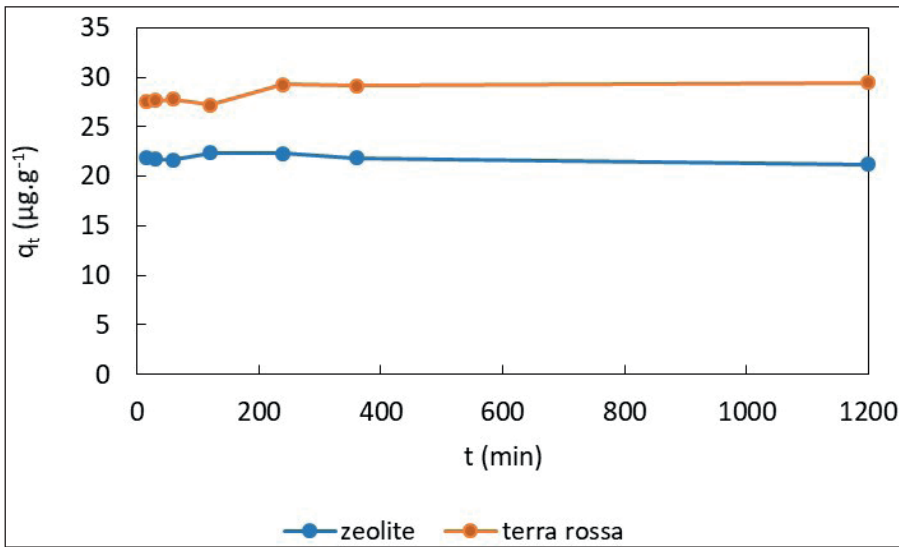


Fig. 11. Dependence of As adsorption on time in batch conditions.

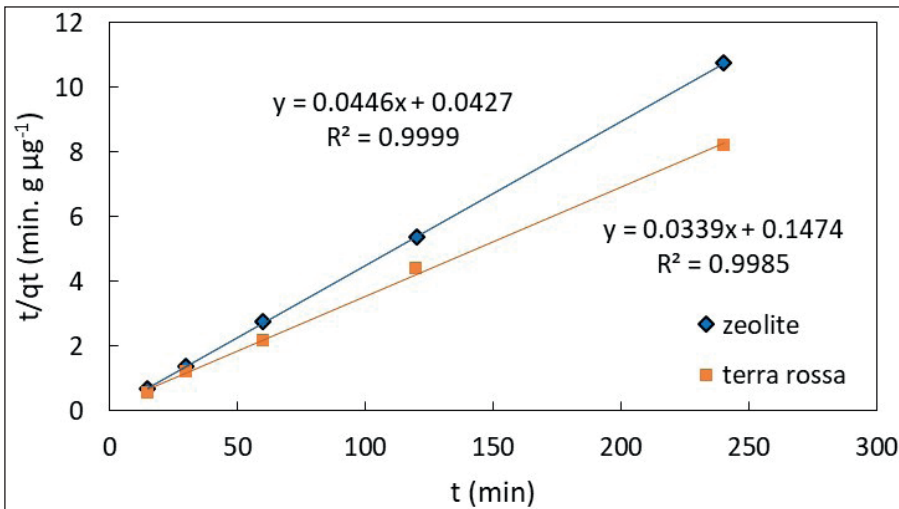


Fig. 12. Pseudo-second-order kinetic plots for the adsorption of As onto zeolite and terra rossa.

The kinetics parameters of As adsorption onto zeolite and terra rossa were calculated from the plots shown in Fig. 12 and are given in Table 3. From the obtained results it can be concluded that the dominant mechanism is external surface adsorption. Kinetic process was not evaluated from a diffusion point of view in regard to small calculated values of intercept. Higher values of intercepts suggests that surface diffusion has a larger role as the rate-limiting step (Boparai et al., 2011).

According to the kinetic study, zeolite (Z), terra rossa (TR) and mixture of both adsorbents (Z + TR) were tested for As elimination in batch sorption experiment. After 20 hours of adsorption the highest effect of removal was obtained for the mixture of adsorbents, where more than 90 % of As was removed from the pit water in laboratory conditions (Fig. 13).

The kinetic study of As removal was also tested in-situ, using terrain shaker (Fig. 14). The pit water was added into the plastic bottles with adsorbents and shaken for selected time periods. Then the leachates were filtered

and stabilized for chemical analyses. Three bottles with each kind of adsorbent were after 120 minutes of shaking taken into laboratory and storage in refrigerator to remain the in-situ temperature up to 24 hours. Then they were also filtered and sent for chemical analyses.

The in-situ adsorption experiment was performed in January, when the pit water flow was quite strong, the As concentration was $380 \mu\text{g.l}^{-1}$, temperature varied between -7 up to -4 °C and temperature of pit water decreased in dependence of shaking time from 7.5 up to 0 °C.

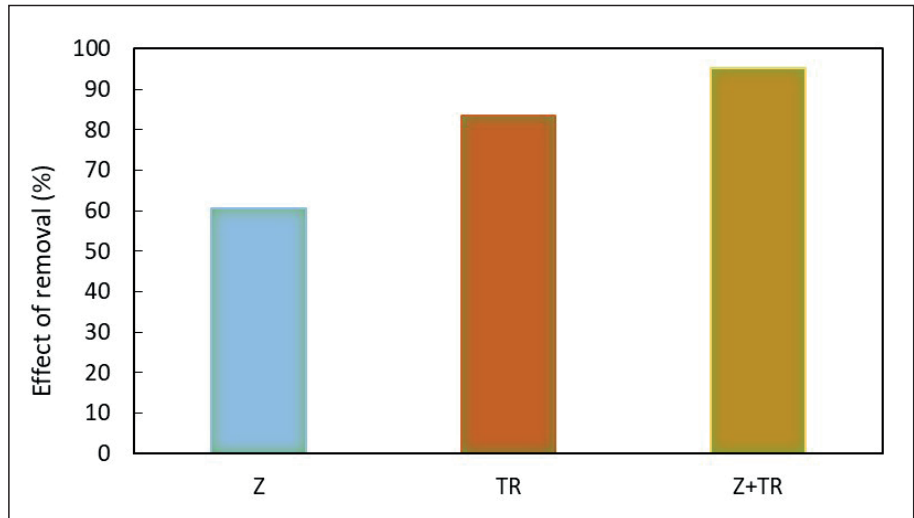


Fig. 13. Effect of As removal from the pit water by selected adsorbents.

Tab. 4

Kinetic parameters of pseudo-second-order model for the in-situ adsorption of As onto studied adsorbents.

Adsorbent	k [$\text{g} \cdot \mu\text{g}^{-1} \cdot \text{min}^{-1}$]	q_e [$\mu\text{g} \cdot \text{g}^{-1}$] cal.	q_e [$\mu\text{g} \cdot \text{g}^{-1}$] exp.	R ²
Zeolite	0.0009	20.2	19.5	0.9982
Terra rossa	0.0036	30.2	32.0	1
Zeolite + terra rossa	0.0022	29.3	31.0	0.9999

Also as in laboratory, in-situ As adsorption was fast for both adsorbents as well as for their mixture. The adsorption capacity for TR and Z + TR was higher in comparison to zeolite. After 90 minutes of adsorption the effectivity of zeolite decreased. The kinetic curves obtained for terra rossa and combined adsorbent were similar, slight higher adsorption capacity was shown by TR (Fig. 15). After 24 hours of experiment the effect of As elimination increased for all studied materials.

The kinetic parameters, Table 4, calculated from the applied PSO kinetic model (Fig. 16), pointed again at the external surface adsorption.

From the selected adsorbents, the most effective in As elimination, in spite of results of laboratory experiments, was TR. Slightly lower efficiency was obtained for



Fig. 14. In-situ batch adsorption experiment.

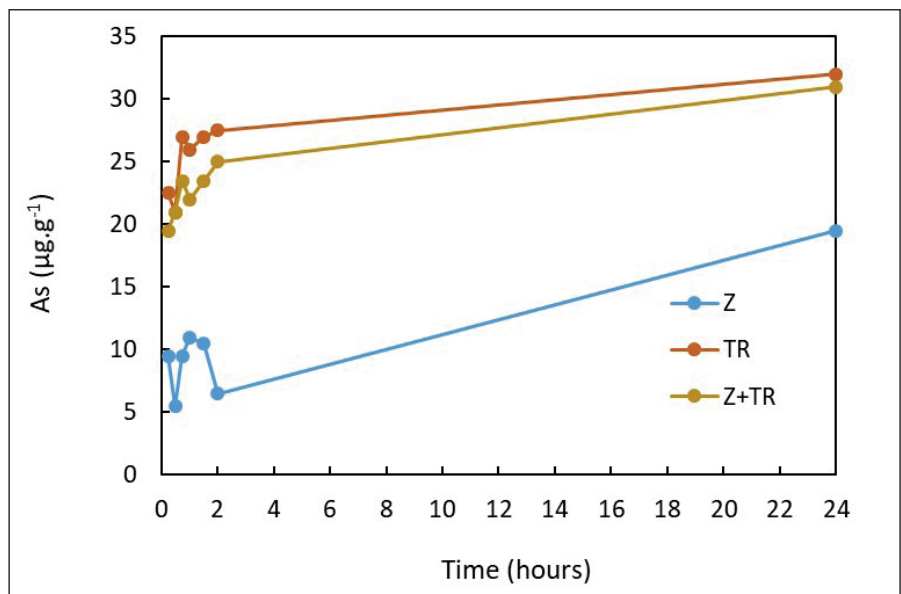


Fig. 15. Dependence of As adsorption on time in in-situ batch conditions.

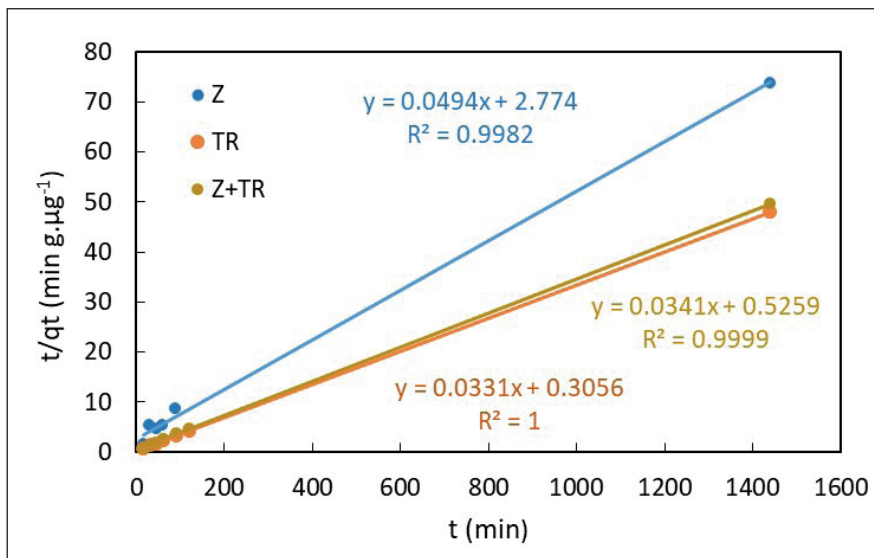


Fig. 16. Pseudo-second-order kinetic plots for the adsorption of As onto studied adsorbents.

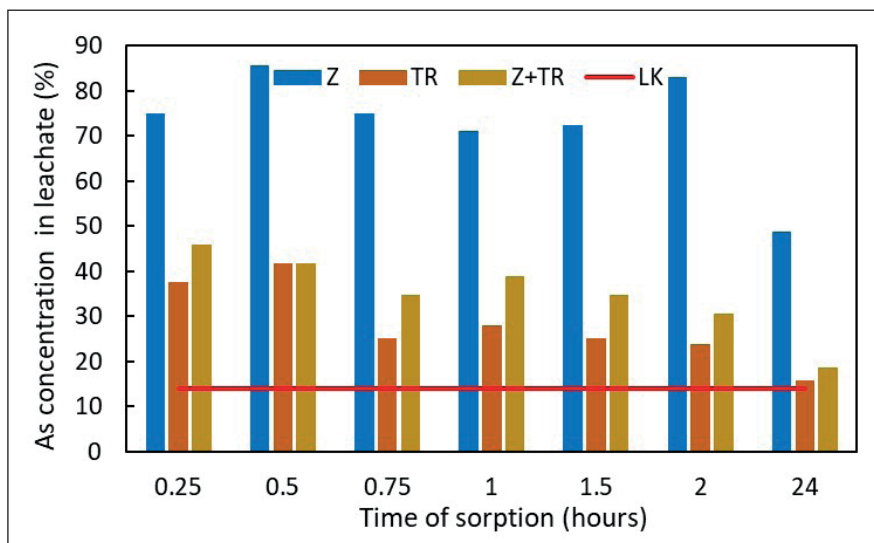


Fig. 17. Decrease of As concentration in leachates after in-situ adsorption in selected time periods in comparison with limited value of As concentration for irrigation waters.

TR + Z. During two hours of experiment non adsorbent was able to decrease the As concentration on the required value, even if it was more than 50 % lower for suspensions with TR and Z + TR (Fig. 17). The highest removal effect of all adsorbents was observed after 24 hours of experiment, where the As concentration in suspension with TR was the lowest and very close to required value. In regard to natural and weathering conditions, the obtained results were good input for realization of column experiments.

The column experiments were performed in laboratory conditions. The columns were filled with layers of zeolite and terra rossa (Fig. 18)

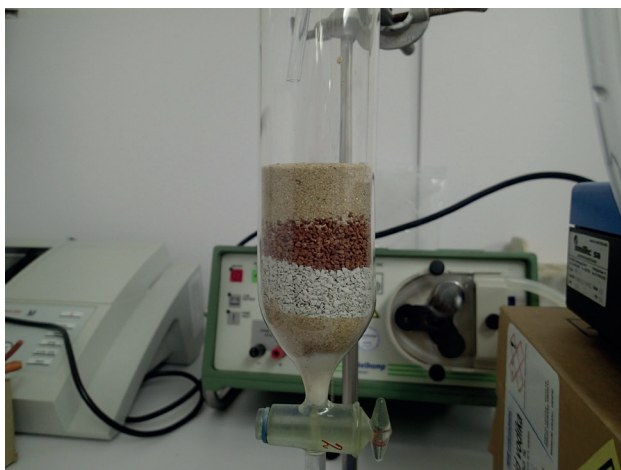


Fig. 18. Sorption column filled with zeolite and terra rossa in layers.



Fig. 19. Parallel test of As elimination in columns with mixture of adsorbents in laboratory conditions.

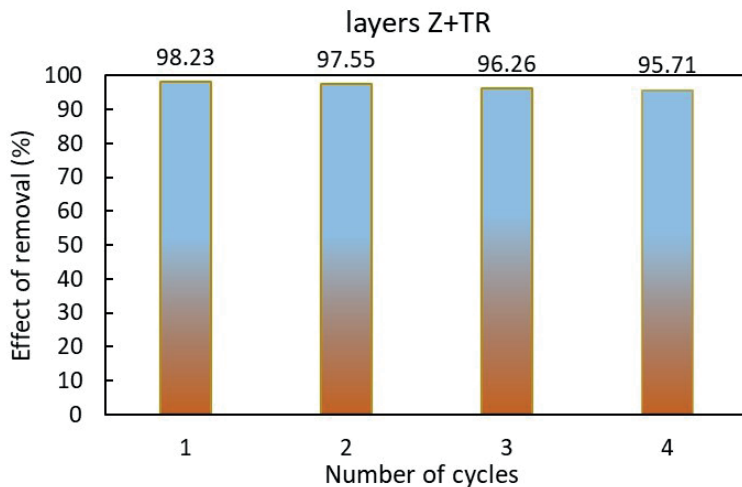


Fig. 20. Effect of As removal by column filled by zeolite and terra rossa layers, 4 cycles of experiment.

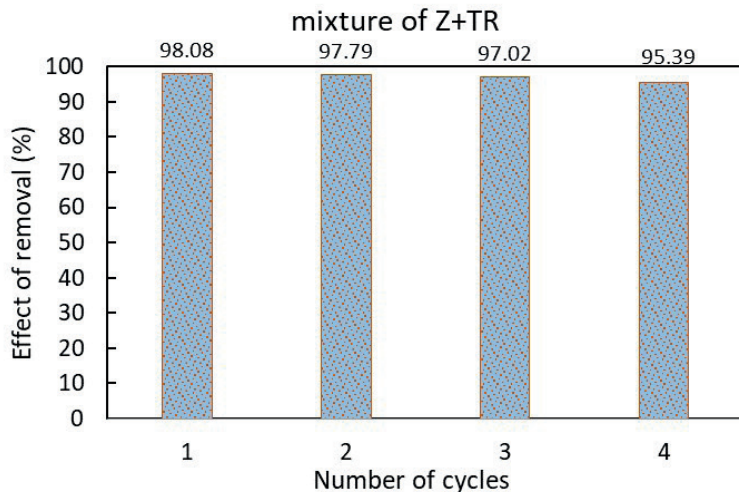


Fig. 21. Effect of As removal by column filled by mixture of zeolite and terra rossa, 4 cycles of experiment.

in second one, with their mixture (Fig. 19). As a permeable layer, quartz sand was used. The As elimination was studied in four cycles for both types of columns to prove their sorption capacity for longer utilization.

The first percolation of pit water led to almost 100 % of As elimination for both types of used columns (Figs. 20–21). After the fourth cycle the effectivity of columns decreased to approximately 95 %, no depending on the columns filling. Slight decrease in effectivity signified that the columns were not saturated yet and could be used for more adsorption cycles again (without need of exchange of the filling or its regeneration).

These results are positive for future columns applications directly on the studied locality. In next experiments, bigger columns of higher adsorbents amounts will be tested in-situ with the aim to suggest the method for pit water

cleaning and its following use for plants irrigating in local gardens.

4 Conclusion

The introductory experiments on selected locality of Zlatá Idka-Rieka, Slovakia, loaded by arsenic after previous mining activity confirm presence of high content of As in the lake sediment caused by the outflow of pit water. As is easy mobile depending on the chemical bonds with non-stable Fe (Fe, Mn) oxides/hydroxides creating surface coatings on the grains of minerals and soil present in the lake of pit water. From this reason it is also potential toxic for local population through contamination of vegetables or contaminated coarse dust inhalation.

Laboratory batch adsorption experiments and following in-situ experiments showed high effect of terra rossa in As removal. In spite of high efficiency, the required concentration value was not reached in solutions after adsorption (it was slightly higher), probably also due to not very favourable climate conditions during the in-situ testing. Also higher adsorbent doses should lead to expected results for As concentration.

Laboratory column experiments verified the repeated usage of adsorption columns with slight decreasing removal effect, not depended on the adsorbents bedding (layers or mixture), what is promising result for future in-situ testing of As elimination from the pit water in dynamic regime.

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Štúdium kontaminovaných sedimentov a eliminácie As z podzemnej banskej vody na lokalite Zlatá Idka-Rieka

Cieľom štúdie bolo charakterizovať sediment z jazierka tvoreného vytekajúcou banskou vodou na lokalite Zlatá Idka-Rieka z hľadiska mobility a bioprístupnosti potenciálne toxických prvkov nachádzajúcich sa v sedimente a experimentálne overiť možnosti in-situ odstránenia/eliminácie obsahu As z vytekajúcej podzemnej banskej vody zo štôlne Hauser.

Vzorka sedimentu (označená H1) na granulometrickú analýzu a magnetickú separáciu bola podrobená zrnitostnému rozboru za mokra, sušená a analyzovaná. Frakciu väčšiu ako 2 mm tvoril len organický materiál (listy, šišky, konáriky). Granulometrická analýza potvrdila prítomnosť častíc menších ako 1 mm a poukázala na širokú distribúciu veľkosti častíc v rozsahu 1 až 500 µm, s maximom na distribučnej krivke v prípade frakcie 63 µm. Vzorka sa potom spracovala na kalovom magnetickom separátore a jej produkty boli podrobené rtg. analýze. Okrem hlavnej minerálnej fázy, kremeňa, obe frakcie sedimentu (magnetická aj nemagnetická) obsahovali muskovit a plagioklas, v prípade magnetickej frakcie aj chlorit. Röntgenovou analýzou sa však prítomnosť predpokladaných oxidov železa (kryštalických fáz) nepotvrdila.

Vzorka hnedočerveného nánosov, jemných usadenín z horninových povrchov, po ktorých banská voda vyteká do jazierka, sa analyzovala na rastrovacom elektrónovom mikroskope. Bodová EDX analýza preukázala prítomnosť Fe a O (41,6 hm. % a 40,1 hm. %), ako aj výrazne vyšší obsah As a Mn.

Chemické analýzy sedimentu poukázali na zvýšenú koncentráciu Cr a Pb, ktorých hodnoty prekročovali intervenčné kritérium (IT) pre obytné zóny, a zvýšenú koncentráciu As a Sb, ktorých hodnoty prekročovali IT pre priemysel v zmysle prílohy č. 12 smernice Ministerstva životného prostredia Slovenskej republiky z 28. januára 2015 č. 1/2015-7. Preto sa v ďalšom kroku testovala mobilita kontaminantov obsiahnutých vo vzorke sedimentu v prípade potenciálnej acidifikácie nánosov sedimentu v okolí výpustu banskej vody kyslými zrážkami v laboratórnych podmienkach (Metóda U.S. EPA 1312).

Mobilita potenciálne toxických prvkov po lúhovaní vzorky sedimentu simulovaným kyslým dažďom nebola veľmi výrazná a pohybovala sa v rozsahu 0,02 až 0,38 %. Najviac mobilným prvkom sa javil Mn, najmenej Ba. Aj napriek nižšej mobilite Fe a As (0,03 a 0,04 %) ich

koncentrácia vo výluhu po teste aj vzhľadom na ich vstupnú koncentráciu v sedimente predstavovala relatívne vysoké hodnoty. Mobilita As závisí aj od pevnosti väzieb As, ako aj samotnej stability Fe (Fe, Mn) oxyhydroxidov a hydroxidov, čo korešponduje aj s výsledkami EDX analýz.

Výluhy po teste bioprístupnosti (SBET metóda) s využitím kyseliny chlorovodíkovej obsahovali vysokú koncentráciu Fe ($223 \text{ mg} \cdot \text{l}^{-1}$), Mn ($165 \text{ mg} \cdot \text{l}^{-1}$) a As ($11,1 \text{ mg} \cdot \text{l}^{-1}$) a nižšiu koncentráciu Zn, Pb, Ba a Cu. Výrazne kyslé prostredie viedlo k uvoľneniu vysokej koncentrácie Fe, Mn a As do výluhu. Stabilitu precipitátov Fe a Mn oxidov s As ovplyvňuje zmena pH vody v jazierku, ale aj sezónne poveternostné podmienky. As sa tak stáva ľahko mobilným a môže byť potenciálne toxický pre miestnych obyvateľov, ktorí sú vystavení jeho expozícii vo forme kontaminovanej pôdy využívanaj na pestovanie zeleniny, ale aj priamemu vdychovaniu kontaminantu vo forme prachových častíc.

Na adsorpčné experimenty boli zvolené prírodné adsorbenty zeolit (Majerovce, označ. Z), terra rosa (Včeláre, TR) a ich zmes (Z + TR). Sledoval sa vplyv času na elimináciu As z podzemnej banskej vody. Všetky experimenty sa realizovali duplicitne. Adsorpcia As na zeolit a terra rosu mala rýchly priebeh, rovnováha nastala po približne 240 minútach experimentu. Vyššia sorpčná kapacita bola pozorovaná v prípade TR. Adsorpčný proces sa riadil kinetickým modelom pseudodruhého poriadku, čo naznačuje, že ide o mechanizmus adsorpcie na externých povrchoch materiálov. V ďalšom laboratórnom experimente sa sledoval vplyv množstva adsorbentu ($10 \text{ g} \cdot \text{l}^{-1}$) na odstránenie As. Po 20 hodinách najvyššiu účinnosť (viac ako 90 %) dosiahla zmes Z + TR. Časová závislosť adsorpcie a adsorpčná kapacita použitých prírodných adsorbentov sa následne testovala priamo v teréne s cieľom znížiť koncentráciu As na limitnú hodnotu, prípustnú pre povrchovú vodu určenú na závlahy ($50 \mu\text{g} \cdot \text{l}^{-1}$ v zmysle nariadenia vlády SR č. 269/2010 Z. z., ďalej nariadenie). Vzorky suspenzií sa premiešavali na terénnej trepačke priamo na lokalite počas dvoch hodín. Výluhy po adsorpcii sa odoberali vo vybraných časových intervaloch a filtrovali na následnú chemickú analýzu. Tri suspenzie s obsahom jednotlivých

sorbentov boli po 2 hodinách miešania prinesené z terénu do laboratória a ponechané v chladničke (na zabezpečenie podmienok podobných prírodným v čase priebehu experimentu – zimné obdobie s teplotou okolo $0 \text{ }^\circ\text{C}$) a filtrovali sa až po 24 hodinách.

Podobne ako v prípade laboratórnych testov, aj adsorpcia As bola rýchla. Adsorpčná kapacita TR a Z + TR bola vyššia ako v prípade zeolitu. Po 24 hodinách experimentu sa zaznamenalo jej zvýšenie pri všetkých použitých adsorbentoch. Počas dvoch hodín experimentu in-situ sa ani napriek viac ako 50 % účinnosti odstránenia As z podzemnej banskej vody nedosiahla požadovaná hodnota koncentrácie ukazovateľa vo výluhoch. Až po 24 hodinách sa efektívnosť zmesového sorbentu Z + TR zvýšila a koncentrácia As vo výluhu len mierne prekračovala limitnú hodnotu v zmysle nariadenia. Aj napriek takýmto výsledkom boli získané poznatky veľmi dobrým vstupom na nastavenie adsorpcie v dynamických podmienkach v kolónach.

Adsorpčné experimenty sa uskutočnili v laboratórnych podmienkach v sklenených kolónach s rozmermi 5 cm (vnútorný priemer) a 18 cm (výška kolóny). Jednotlivé kolóny boli naplnené kremenným pieskom (60 g) na zabezpečenie ľahšej perkolácie podzemnej banskej vody a vrstvou zeolitu (20 g) a terra rosy (20 g), resp. ich zmesou. V jednom cykle pretieklo kolónami 150 ml banskej vody pri konštantnej prietokovej rýchlosti $2,8 \text{ ml/min}$ v priebehu 50 minút.

Po prvej perkolácii dosiahli oba typy kolón (vrstvy, zmes) takmer 100 % účinok odstránenia As. Po štvrtom prietokovom cykle klesla ich účinnosť na približne 95 %, bez závislosti od typu kolóny. Ešte stále to predstavovalo účinné zníženie koncentrácie ukazovateľa na požadovanú limitnú hodnotu v zmysle nariadenia. Uloženie adsorbentov v kolóne nemalo vplyv na množstvo odstráneného arzenu. Ani po 4 cykloch nedošlo k nasýteniu kolóny, čo umožňuje jej opätovné použitie bez potreby výmeny náplne, resp. jej regenerácie.

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