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Heavy metals immobilization in the sediments by sorption on the natural materials

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Abstract

The article deals with the possibility to apply the natural sorbents zeolite and bentonite, compares their sorption capacity and selects the suitable sorbents for the sorption of cadmium, chromium and lead in the contaminated sediments from the locality water reservoir Ružín I. These areas are well–known for their mining and metallurgical activities lasting several centuries. The heavy metals from the source of pollution are transported by the river water and accumulated in sediments. These metals may come directly from the weathering process of rocks, where the soil-forming process influences their concentration and distribution. The results obtained during the determination of the influence of sorbents on the sorption of Cd, Cr and Pb have demonstrated that on the sorption of cadmium and chromium the bentonite has the most significant sorption capability from three used sorbents in the order: Bentovet K (bentonite from Hliník nad Hronom, product of the firm GENES, a. s.) > zeolite from Nižný Hrabovec > zeolite from Majerovce for all samples S1 – S5. The results for the sorption of lead are in the order: zeolite Nižný Hrabovec > Bentovet K > zeolite from Majerovce.

Key words: cadmium, chromium, lead, bottom sediments, immobilization, natural sorbents

Introduction

Sediments play an important role in aquatic systems, both as a medium where contaminants can be stored and as a source of these contaminants to the overlying water and to biota. Due to their ability to sequester metals, the sediments are a good indicator of the water quality and record the effects of anthropogenic emissions (Baudo in Quevauviller, 1990). Cadmium is a natural, usually minor constituent of the surface and groundwater. It may exist in the water as the hydrated ion, in inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids. Cadmium may enter aquatic systems through weathering and erosion of soils and the bedrock, atmospheric deposition, direct discharge from industrial operations, leakage from the landfills and the contaminated sites, and the dispersive use of the sludge and fertilizers in agriculture. Particulate matter may rapidly adsorb much of the cadmium entering the fresh waters from the industrial sources, and thus sediment may be a significant place of storage for the cadmium emitted to the aquatic environment (WHO 1992). Some data show that recent sediments in lakes and streams range from 0.2 to 0.9 ppm in contrast to the levels of generally less than 0.1 ppm cited above for fresh waters (Cook et al., 1995). Although Cr is an essential nutrient for human (Iyengar et al., 1989), there is no doubt that Cr^{VI} compounds are both acutely and chronically toxic (Rinehart, 1989). The dose threshold effect for this element has not been yet determined accurately enough to allow regulations to be defined. However some risk assessment analysis is currently being undertaken. Cr^{III} is less toxic than some other elements (Hg, Cd, Pb, Ni and Zn) to mammalian and aquatic organism, probably due to the low solubility of this element in its trivalent form (Moore et al., 1984). Cr^{III} compounds also have a very low mobility in soils and are thus relatively unavailable to plants (Adriano, 1986). Compared to Cr^{VI}, the toxicity of Cr^{III} is not significant. Lead is a highly toxic metal found in small amounts in the earth´s crust. Because of its abundance, low cost, and physical properties, lead and lead compounds have been used in a wide variety of products including paint, ceramics, pipes, solders, gasoline, batteries, and cosmetics. Today, the most common sources of lead exposure are lead-based paint in older homes, contaminated soil, household dust, drinking water and lead crystal. The region of the Central Spiš was classified as a loaded region, where the water reservoir Ružín I is also situated. Mining operations with the subsequent processing of complex metals and copper ores left negative effects in this region. The region has three general industrial sources of contamination, Rudňany, Krompachy and Spišská Nová Ves. Water reservoir Ružín I, situated on the river Hornád, is shown in Fig. 1. It assumes that the main sources of the contamination are the river-basin of the Hornád river and its biggest tributary the Hnilec river. The most part of depositions lie in the branches of the reservoir, where the rivers flow into the free maximal headwater level of the reservoir and deposit eroded materials and pollutants. The bottom sediments of the water reservoir are contaminated by heavy metals as Cu, Pb, Ni, Zn, Cd, Cr, As and Hg (Bobro, 1996). Sediment is evaluated as a complicated, dynamic, chemical and

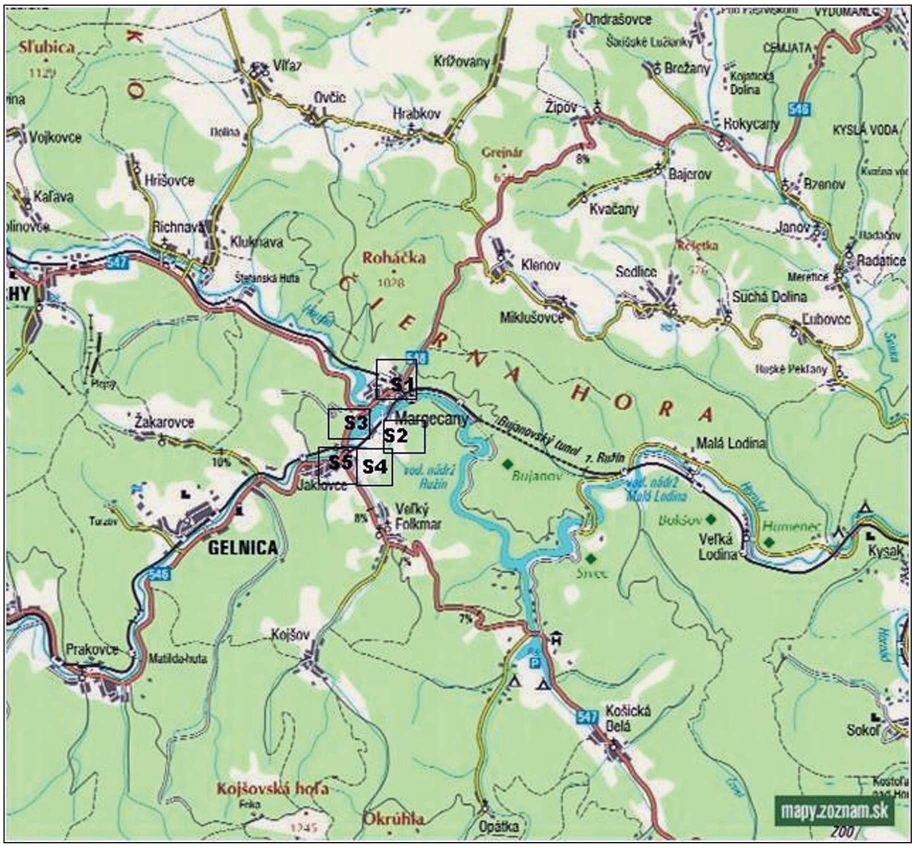


Fig. 1. The location of the sampling of sediments S1 – S5 from the water reservoir Ružín I (www.mapy.zoznam.sk).

biological reactive system including matter, which comes from the erosion and sedimentation processes. The mobility and redistribution of heavy metals are influenced by the character of interaction (pH, redox potential, sorption/desorption, precipitation, precipitation-dissolution, the rise of organic and inorganic complexes, etc.; Borovec, 2008). Soil pH is one of parameters that affect significantly to the share of bioavailable forms of metals. Increased proportions of mobile fractions of metals in the Central Spiš region were detected in samples taken from soils with acidic pH (Takáč et al., 2009). Madrid et al. (2008) found from the results for zeolite of Sevilla soils that this material is not suitable to decrease metal (Cu, Zn and Pb) in these soils. Then, the overall effect would only be an increase in metal exchangeability.

Adsorption is the most efficient and economical physico-chemical method for the immobilization of heavy metals from the wastewater and contaminated soils. The efficiency of heavy metals immobilization from the wastewaters depends on the quality of used sorbents. The sorption velocity is influenced by pH of environment, the sorption into soil increases at a lower pH value. One of the possibilities of the heavy metals immobilization is the application of sorbents as natural zeolites, bentonites, active coal and the others.

The aim of presented work was the research of the influence of the sorbents zeolite (from Nižný Hrabovec and Majerovce), bentovet K on a decrease of cadmium, chromium and lead contents in contaminated sediments from the water reservoir Ružín I from the Hnilec river branch.

Natural zeolites have a solid structure formed by the polyoxides of silicon and aluminium, with a large adsorption surface; they are hydrophilic, polar, microporous and thermal resistive (Foldešová et al., 2007). Bentonite is a natural clay, soft and oozy in the wet state. It consists of montmorillonite, a mineral with a multi-layer structure having a high ion exchange capacity and adsorptive ability.

Materials and methods

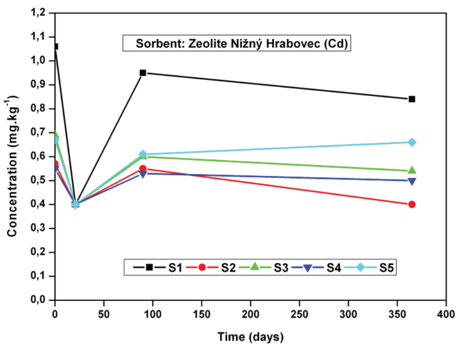
The used method consisted from the static sorption of cadmium, chromium and lead ions on 3 types of sorbents carried out on 5 samples of sediments, which were taken from the Hnilec river branch of the water reservoir Ružín I in 2007. The samples of bottom sediments were sampled into the glass bottles by sample device "Multisampler".

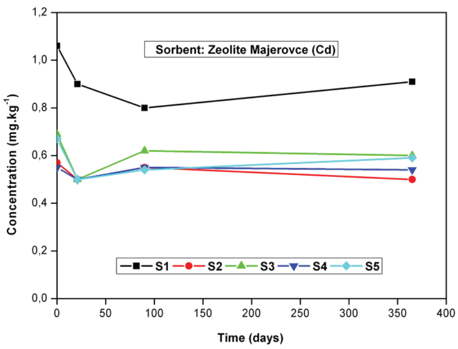
The samples were dried at room temperature, then quarted and sieved under 0.1 mm. The sorbents zeolite Nižný Hrabovec (fraction 50 μm), zeolite Majerovce (fraction 1 mm) and Bentovet K (bentonite from Hliník nad Hronom, product of the firm GENES, a. s. – 50 μm) were applied for the ion sorption in the quantity of 5 wt.%, to be precise 1 g of sediment were added to 0.05 % of sorbent and 10 ml of distilled water. All components were stirred and the time dependence of cadmium, chromium and lead ions static sorption in the interval of 21, 90 and 365 days

Tab. 1
The values of the quality factors of sediments and of sorbents from the chosen localities of the Hnilec river basin sampled in 2007

Localities	pH	Redox potential (mV)	Total conc. of sediment ($mg \cdot kg^{-1}$) Cd	Cr	Pb	CEC ($mol \cdot kg^{-1}$)	Sorbents ($mol \cdot kg^{-1}$)	CEC
S1 Estuary Hornád-Hnilec	7.87	262	1.06	1.8	38.6	0.015	zeolite N. H.	0.805
S2 Hnilec branch Rybár house	7.55	259	0.57	1.5	45.6	0.84	zeolite Majerovce	0.455
S3 Hnilec branch Vápenka	7.03	256	0.69	1.5	36	0.101	Bentovet K	0.590
S4 Kojšov stream	7.25	287	0.55	1.4	50.8	0.058		
S5 Hnilec branch Backwater	7.52	257	0.67	2.2	48.2	0.044		

(CEC) Cation exchange capacity NH_4^+ according to ČSN 72 1076





Figs. 2 – 3. The kinetic dependence of cadmium adsorption on zeolites ZNH, ZM in the samples of the sediments S1 – S5 in the leachates of 2M HNO_3 after 21, 90 and 365-day sorption.

was observed. According to the Supplement No. 2 of the Law No. 220/2004 S. c. about the protection and application of agricultural soils, the quantity of sorbed Cd, Cr, Pb on sorbents was examined in the leachates of 2M HNO_3 by the atomic absorption spectroscopy method (AAS), Pb was detected by the flame technique and Cd, Cr by the graphite furnace AAS (Varian, Australia). The authors stated that the content of metals determined with 2M HNO_3 is a more effectual in the risk assessment of metals in the environment than the total content. Bioavailability of metals plays a key role in the risk assessment for the metal contaminated sites such as the highly industrialized areas

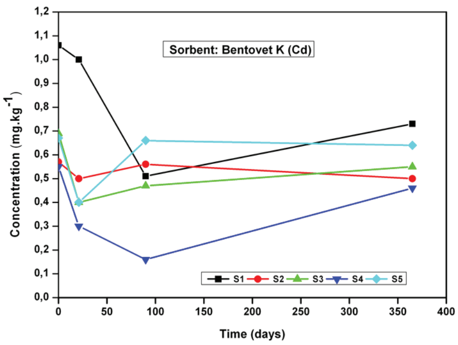


Fig. 4. The kinetic dependence of cadmium adsorption on Bentovet K in the samples of the sediments S1 – S5 in the leachates of 2M HNO_3 after 21, 90 and 365-day sorption.

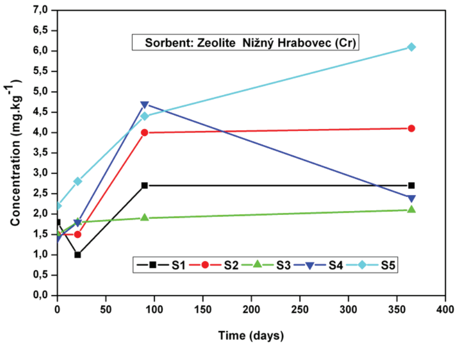
under the former and present impacts of the ore mining and smelting industry (Takáč et al., 2009).

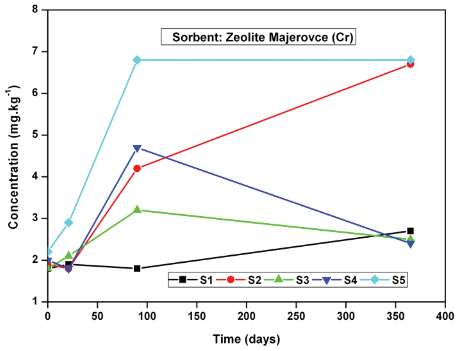
The initial sediments and sorbents properties

Qualitative mineralogical analysis of the bottom sediment of the water reservoir Ružín I was carried out by the *X-ray diffraction analysis*. *Sediments S1 – S5* contained quartz, sericite, plagioclase as major minerals >15 % and chlorite as a minor mineral 3 – 15 %. These minerals are the bases for the occurrence of heavy metals. Qualitative mineralogical analysis of sorbents confirmed that zeolite from Nižný Hrabovec and Majerovce contained >15 % clinoptilolite and cristobalite as major minerals and 3 – 15 % of plagioclase, quartz and dolomite as minor minerals. Bentovet K contained more than >15 % of smectite as major mineral and 3 – 15 % of sericite, plagioclase, magnesite and talc as minor minerals. Specific surface of tested sediments was determined to 5.2490 – 8.2713 $m^2 \cdot g^{-1}$.

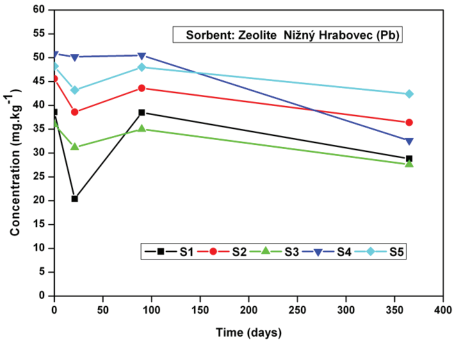
Results and discussion

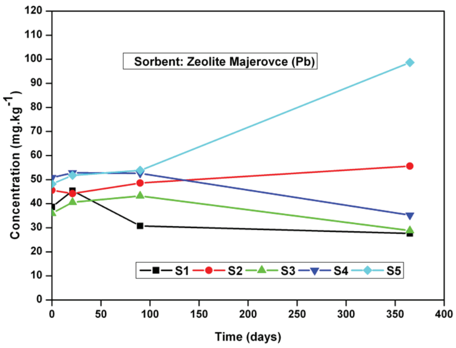
Static sorption experiment used in the interval of 21, 90 and 365 days was followed. The results of the influence





Figs. 5 – 6. The kinetic dependence of chromium adsorption on zeolite in the samples of the sediments S1 – S5 in the leachates of 2M HNO_3 after 21, 90 and 365-day sorption.





Figs. 8 – 9. The kinetic dependence of lead adsorption on zeolites in the samples of the sediments S1 – S5 in the leachates of 2M HNO_3 after 21, 90 and 365-day sorption.

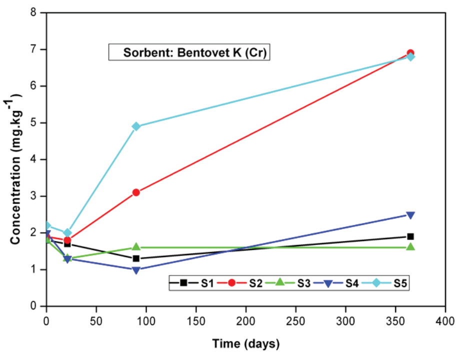


Fig. 7. The kinetic dependence of chromium adsorption on Bentovet K in the samples of the sediments S1 – S5 in the leachates of 2M HNO_3 after 21, 90 and 365-day sorption.

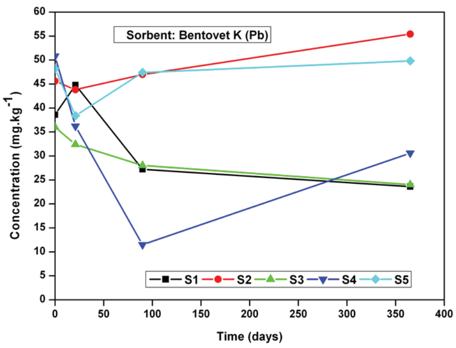


Fig. 10. The kinetic dependence of lead adsorption on Bentovet K in the samples of the sediments S1 – S5 in the leachates of 2M HNO_3 after 21, 90 and 365-day sorption.

of the sorbents (zeolites from Nižný Hrabovec (ZNH) and Majerovce (ZM), bentovet K (BK) on a decrease of Cd, Cr, Pb concentrations in the sediment samples S1 – S5 from the water reservoir Ružín I, from the Hnilec river branch, are shown in Figs. 2 – 10.

The influence of sorbents on the sorption of Cd in the leachate of sediment from the locality S1 is shown in Tabs. 2, 3 and 4. It is obvious that the highest decrease of the concentration of Cd was confirmed in 21-day sorption by the zeolite ZNH (from 1.06 mg · kg^{-1} to 0.4 mg · kg^{-1}). The concentration of Cd by the application of Bentovet K (BK) after 90 days decreased from 1.06 mg · kg^{-1} to 0.51 mg · kg^{-1}. The results of the sorption of samples S2 – S5 shown in Tab. 1 have confirmed that the highest decrease of Cd concentration in the leachates was reached by the zeolite sorbents ZNH after 365-day static sorption. After the application of zeolite ZM (S1 – S5), the reduction of Cd concentration after 21, 90, 365 days was minimal. The highest decrease of the concentration of Cd was reached after 90-day sorption of Bentovet K on sample S4 (from 0.55 mg · kg^{-1} to 0.16 mg · kg^{-1}).

As is shown in Tabs. 5, 6 and 7 the influence of sorbents on the sorption of Cr in the leachate of sediment from the locality S1 – S5 did not cause any important changes in Cr concentration. Its sorption efficiency was not significantly proved.

Tab. 2
Summary analysis of sediments from the sediment VDR1 (S1 – S5): Proportion decrease on the content of Cd, Cr, Pb in the leachates of 2M HNO_3 after 21, 90 and 365-day sorption

Sediments/(days)		**sorbent: Zeolite NH**			**sorbent: Zeolite M**			**sorbent: Bentovet K**		
		Cd	**Cr**	**Pb**	**Cd**	**Cr**	**Pb**	**Cd**	**Cr**	**Pb**
S1	21	37.7	**55.5**	52.8	84.9	x	x	**94.4**	94.5	x
	90	**89.6**	x	**100**	75.5	**100**	**79.8**	48.1	72.2	**70.5**
	365	46.7	x	74.6	**85.8**	x	71.5	68.9	**100**	61.1
S2	21	70.2	**100**	94.6	87.7	x	**96.9**	87.7	**100**	**96**
	90	**96.5**	x	**95.6**	**87.7**	x	X	**98.2**	X	X
	365	26.7	x	79.8	87.7	x	X	**87.7**	X	X
S3	21	57.9	x	86.7	72.5	x	X	57.9	86.7	**90**
	90	**86.9**	x	**97.2**	**89.8**	x	X	68.1	**100**	77.8
	365	36	x	76.7	86.9	x	**80**	**79.7**	**100**	66.7
S4	21	72.7	**x**	**98.8**	90.9	x	X	54.5	92.8	**71.2**
	90	**96.6**	**x**	**98.8**	0	x	X	29.1	71.4	22.6
	365	36	**x**	64.2	**98.2**	x	**69.3**	**83.6**	X	60.2
S5	21	59.7	**x**	89.6	74.6	x	x	59.7	90.9	79.7
	90	**91**	**x**	**98.4**	80.6	x	x	**98.5**	x	**98.3**
	365	30	**x**	87.9	**88**	x	x	89.5	x	x

Proportion decrease in the content of metals (%)

x – the content of metals in the leachates was overdrawn on the total content of metals of sediments, zeolite NH: zeolite from Nižný Hrabovec, ZM: zeolite from Majerovce, Bentovet K

The influence of sorbents on the sorption of Pb from S1 – S5 localities is shown in Tabs. 8, 9 and 10. The maximum lead concentration decrease was after 21-day sorption by zeolite NH (from 38.6 mg · kg^{-1} to 20.4 mg · kg^{-1}) measured on sample S1. In the case of zeolite sorbent ZM, its sorption efficiency was not significantly proved. The decrease of lead concentration on the Bentovet K from 50.8 mg · kg^{-1} to 11.5 mg · kg^{-1} occurred in 90-day interval measured on sample S4. The sorption experiments on samples S2 – S5 did not cause any important changes in lead concentration.

A summary of the results for these experiments is given in Tab. 2.

The most significant sorption effect of *zeolite Nižný Hrabovec* was observed for the lead and cadmium sorption after 90 days. Generally, the highest decrease of cadmium, lead and chromium concentration in all leachates of sediments was determined for *Bentovet K*. The sorption capacity was not so strong in the case of *zeolite Majerovce* for lead and chromium, the highest decrease of concentration was reached for cadmium (85.8 – 89.8 %) after 365-day sorption. Following the results of the kinetic dependencies of cadmium adsorption of Bentovet K, it can be assumed that the highest decrease of Cd concentration occurred during 90 days for samples S2, S5 and of lead in the case of zeolite from Nižný Hrabovec. The decrease was in the range from 95.6 to 100 %, after 90-day sorption for the samples S1 – S5.

Conclusion

The results obtained during the determination of the influence of sorbents on the Cd, Cr and Pb sorption have confirmed that the sorption of cadmium and chromium on *Bentovet K* has the most significant sorption capability from three used sorbents in the order: Bentovet K (*bentonite from Hliník nad Hronom, product of the firm GENES, a. s.)* > *zeolite from Nižný Hrabovec* > *zeolite from Majerovce* for all samples S1 – S5. The results for sorption of lead are in the order: *zeolite Nižný Hrabovec* > *Bentovet K* > *zeolite from Majerovce*. The kinetic dependence of cadmium, chromium and lead adsorption on each sediment has shown that long sorption experiments have not proved the bond stability of metals ions in sediments. Until now, it is not possible to recommend some of used sorbents for the immobilization of cadmium, chromium and lead in contaminated bottom sediments of the water reservoir Ružín I in the Hnilec river branch.

Reservoir sediments may be classified as complicated dynamic system. Their chemical and biological reactivity cause the difficulties in finding of the optimal method for the immobilization of heavy metals in the bottom sediments.

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