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Original Research

Comparison of the Efficiency of Low-Cost Adsorbents for Heavy Metals Removal from the Monitored Polluted River of Nitra

Anna Ďuricová[1], Dagmar Samešová[1], Adam Pochyba[1], Veronika Štefanka Prepilková[2], Juraj Poništ[1]°*, Andrea Zacharová[1], Marián Schwarz[1], Peter Andráš[3], Darina Veverková[4], Michal Sečkár[1], Jarmila Schmidtová[5]

[1]Department of Environmental Engineering, Faculty of Ecology and Environmental Sciences, Technical University in Zvolen, T.G. Masaryka 24, 96001 Zvolen, Slovak Republic
[2]Fortischem a.s., M.R. Štefánika 1, 972 71 Nováky, Slovakia
[3]Department of Geography and Geology, Matej Bel University in Banská Bystrica, Tajovského 40, 974 01 Banská Bystrica, Slovak Republic
[4]Institute of Foreign Languages, Technical University in Zvolen, T.G. Masaryka 24, 960 01 Zvolen, Slovak Republic
[5]Department of Mathematics and Descriptive Geometry, Faculty of Wood Sciences and Technology, Technical University in Zvolen, T.G. Masaryka 24, 96001 Zvolen, Slovak Republic

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Abstract

Pollution of surface water by heavy metals is a major environmental problem worldwide. The aim of the study was to evaluate the effectiveness of natural adsorbents (bentonites from the Kopernica deposit) with commercial types (zeolites of different quality) in removing selected heavy metals from the polluted surface stream in the monitored area. The adsorption process of the monitored metals was evaluated in terms of adsorption capacity and percentage of metal ion removal efficiency. The surface flow in the monitored area is significantly polluted and does not achieve the necessary water quality. The results of the research point to the high adsorption capacity of bentonites for Hg, while zeolites showed this ability less and were suitable only for some of the monitored heavy metals. The adsorption of zeolite of the type ZeoCem Eco Micro 200 (type C) is suitable for metals in the direction from the most adsorbed heavy metal to the least adsorbed as follows: Sb > Hg > Cr > Cd > Cu > Zn. As showed no affinity for adsorption onto zeolite C. The research confirmed the suitability of low-cost adsorbents for the remediation of polluted water in the monitored area.

Keywords: removal of heavy metals, purification of surface water, low-cost adsorbents, pollution of watercourse

*e-mail: jurajponist1111@gmail.com
Tel.: +421-45-520 61 11
Fax: +421-45-533 00 27
°ORCID iD: 0000-0002-6399-3308

Introduction

The Nitra River has been one of the most polluted rivers in Slovakia for a long time. It occurs most often in the upper part and its tributaries. Pollution comes from large industrial enterprises, agriculture, and mining activities. Public sewerage from cities and municipalities, as well as from unsewered areas, also contributes to considerable pollution [1]. The river water and bank sediments are contaminated with heavy metals, especially Hg, Cd, and Zn. Even after the end of old mercury technologies in one enterprise, their levels remain elevated [2]. The extraction of sediments would be financially and technically very demanding, and at the same time, there is a challenge for the remediation and immobilization of these sediments. People living in the area are concerned about the pollution of the Nitra River and, together with activists, rightly demand that the riverbed be repaired and cleaned. Paradoxically, a large number of fish live in the river, but the contamination of the water prevents fishing. The results of fish analyses point to high levels of organic pollutants, benzene, vinyl chloride, and other organo-halogen compounds, but also heavy metals [3]

In general, the following can be used for the removal of metals from water: precipitation, ion exchange processes, adsorption, electrochemical processes, membrane filtration, biosorption, etc. [4]. Currently, a number of modern adsorption materials (carbon molecular sieves, carbon fabrics, and others) are being developed for adsorption, the efficiency of which is relatively high, but the disadvantage is the high cost of such adsorbents. The most tested heavy metal sorbents are iron oxides and oxide-hydroxides, activated alumina, sand coated with iron hydroxide, and activated carbon with a layer of TiO_2 or MnO_2 [5].

The use of natural sorbents (brown and black coal, iron humates, lignite, peat, bark, humic acids, algae) is advantageous due to their low price, but they mostly show low adsorption capacity. From this point of view, the use of synthetic and natural zeolites and bentonite for the adsorption of heavy metals seems promising, especially due to higher efficiency [6].

In addition to natural adsorbents, industrial wastes such as paper sludge can also be used as low-cost adsorbents [7], fly ash [8], or coal fly ash [9].

Slovakia has a large and so far unused potential of natural adsorbents (of bentonite and zeolite character). Bentonite is a clay mineral with a layered structure, the main component of which is smectite (montmorillonite). Its layers are made up of two networks of tetrahedra, predominantly SiO_4, between which there is one octahedral lattice $MO_4(OH)_2$, where M can be Al(III), Fe(III), Mg(II), or Fe(II). The adsorption capacity of bentonite is caused by a negative surface charge. This charge originates from the substitution of central atoms with atoms of lower oxidation states in tetrahedral (Al(III) for Si) and octahedral (Mg(II) for Al(III)) lattices. The ability to exchange cations in the interlayer space is directly related to this negative charge. The most common exchangeable cations are Ca(II), Mg(II), Na(I), and K(I), which are differently hydrated depending on temperature and humidity [10].

Zeolites form a large group of hydrated silicates. The crystal structure of zeolites is made up of tetrahedra SiO_4 and AlO_4, in which one central Al or Si atom is surrounded, from the vertices of the tetrahedron, by four oxygen atoms. All tetrahedra AlO_4 and SiO_4 share one oxygen atom with their neighboring tetrahedron, forming a perfect three-dimensional lattice structure [11].

There are no interconnections between two AlO_4 tetrahedra in the structure. The entrance holes of zeolites are circular or elliptical and formed by rings of 8-12 oxygen atoms (sometimes up to 18). Their effective diameters range from 0.3 nm to 1.2 nm. Cavities make up about 50% of the volume of zeolite. They can have a uniform diameter or several different types of channels in the structure. These may or may not be interconnected [12]. The negative charge of the zeolite skeleton is caused by the substitution of Al(III) for Si(IV). This difference is compensated for by weakly bound cations (+1 or +2) from the inner structure, together with water molecules. Tetrahedra of zeolite structure do not have a precisely defined arrangement of exchange cations in their cavities. Each zeolite has different levels of dislocation of aluminum and silicon in the overall arrangement of the tetrahedral structure. The symmetry reflects the geological environment during zeolite formation, which permanently affects its properties.

The novelty of this study lies in monitoring the adsorption of a wide range of heavy metals present in Nitra River samples. Current studies mostly focus on the adsorption of individual heavy metals from synthetically prepared aquatic solutions [13-15]. The study is also unique in combining watercourse pollution monitoring with an evaluation of adsorption effectiveness. Most of the research is diversified either to monitor the pollution of a watercourse [16-18] or on the adsorption of heavy metals from polluted watercourses [19-21], or synthetically prepared aquatic solutions of metal ions [22, 23]. Unlike studies testing modified adsorbents [24-27], we focused on low-cost, untreated natural adsorbents to reduce modification costs.

The study aimed to compare the effectiveness of natural adsorbents (Kopernica bentonites) with commercial zeolites of different qualities in removing selected heavy metals from a polluted surface stream. The combination of surface flow monitoring with subsequent remediation provides conditions for the practical use of adsorption processes in real field conditions.

Materials and Methods

Monitoring of Pollution of the Nitra Watercourse

Samples for analysis were collected at three intervals (August 2019, September 2019, and May 2020) from

specific locations. The samples were preserved with concentrated nitric acid (pH<2), stored at 5ºC, and analyzed within one month.

The sampling point was selected according to the expected source of pollution. Zemianske Kostoľany is located on the left bank of the Nitra River, approximately 5 km south of the town of Nováky. Two streams flow through the village, the Lazný potok stream from the Vtáčnik hill and the second stream from the Lelovská dolina valley. Both streams flow into the Nitra River. Water samples were taken from three points: two within the Nitra River and one at the tributary of Lazný Potok (Fig. 1).

Sampling points were:

1. Lazný potok near Zemianske Kostoľany – 48°40'59.18"N, 18°31'4.91"E,
2. Nitra River near Nováky – 48°41'49.70"N, 18°31'16.94"E,
3. Nitra River near Dolné Lelovce – 48°41'34.87"N, 18°31'13.97"E.

Samples were taken according to STN EN ISO 5667-3 [28].

Natural and Commercial Adsorbents

Sampling the Natural Adsorbents

Natural adsorbent – bentonite – was taken from the deposit of Kopernica. The bentonite deposit of Kopernica is situated on the southwestern edge of the Kremnické vrchy mountains, 5 km from the town of Kremnica (1 km from the deposit of K-bentonite Dolná Ves). This bentonite was formed by the alteration of the volcanic rock rhyolite.

Based on crystal-chemical characteristics, the main clay component (smectite, 80%) can be classified into the Al-Mg montmorillonite group. Its octahedral structure is mainly formed by aluminum and magnesium. Together with a deposit of Jelšový potok stream (3 km south of Kopernica), they belong to the deposits of bentonites of the highest quality in the Western Carpathians (Figs 2 and 3).

Fig. 1. Map of water sampling points.
Notes: 1st sampling point: Lazný potok stream, site – Zemianske Kostoľany, 2nd sampling point: Nitra River, site – Nováky, 3rd sampling point: Nitra River, site – Dolné Lelovce. Samples were taken three times according to STN EN ISO 5667-1: 2007. The values in the tables represent averages of the collected samples.

Sampling of Commercial Adsorbents

Four commercial types of zeolites were used for the experiment. Zeolites were obtained from the quarry Kučín in Nižný Hrabovec (Fig. 4).

Characteristics of Adsorbents

Characteristics of Natural Adsorbents

Natural adsorbent – bentonite – was characterized from the viewpoint of chemical and mineral composition (Fig. 5). Table 1 illustrates the chemical and mineral characteristics of bentonite.

Variability in montmorillonite content (50-98%) does affect adsorption performance, but the direction and magnitude of the effect depend on the specific

Fig. 2. Deposit of Kopernica for bentonite sampling.

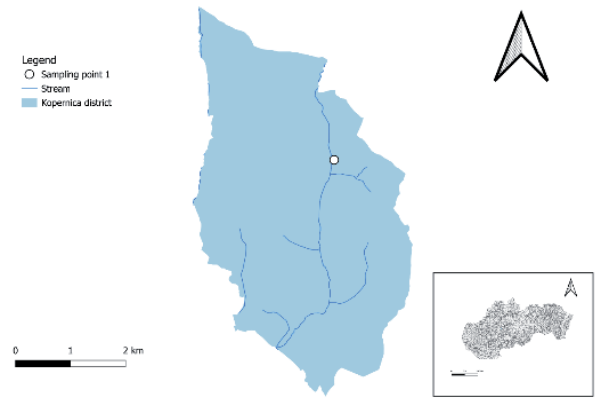

Fig. 3. Map of the sampling point (quarry) of bentonite in the village of Kopernica.

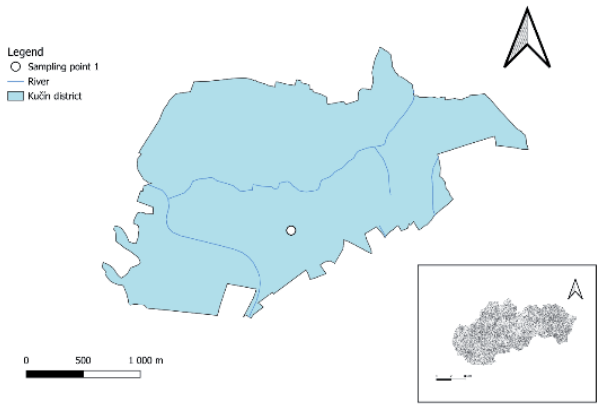

Fig. 4. Map of the sampling point (quarry) of zeolite in the village of Kučín.

Fig. 5. Spatial comparison of sites of Kopernica (bentonite) and Kučín (zeolite).

contaminant and system. Higher montmorillonite content generally enhances adsorption for many organics and some metals, but not universally for all adsorbates [29-31].

The characteristics of the used commercial adsorbents are shown in Tables 2-5. Four types of zeolites were used for the adsorption of heavy metals – two types of zeolites after crushing and sorting of the rock (A – ZeoAqua 1 – 2.5 mm; B – ZeoWater 0.5 – 1 mm), zeolite after the treatment of the rock by thermal activation (C – ZeoCem Eco Micro 200), zeolite after the treatment of the rock by micronization (D – ZeoCem Eco Micro 20) (Fig. 6.).

Thermal activation is a key process for enhancing the adsorption performance of Zeolite C, primarily by increasing surface area, optimizing pore structure, and modifying surface chemistry. This results in higher removal efficiencies for heavy metals, gases, and organics, making thermally activated zeolites highly effective and reusable adsorbents for environmental applications [32, 33].

Table 5. presents the BET surface area of the sorbents used in the study, expressed in $m^2 \cdot g^{-1}$.

Mineral composition of initial samples/materials and their changes upon thermochemical treatment are shown in Table 6.

Determination of Heavy Metals

Determination of Hg

a) by method of AAS using AMA – 254.
b) by the cold vapor technique of CV AAS.

Determination of other metals – ICP MS

Determination of general indicators of surface water quality – pH, conductivity, $N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, Cl^- and SO_4^{2-} - in compliance with the standards STN [35].

Atomic Absorption Spectrometry (AAS)

The AVANTA Σ AAS Flame Atomization Spectrometer (GBC Scientific) was used to determine the metal ions during the adsorption process. The source of radiation was a hollow cathode ray tube with a supply current of 3.00 mA. Air/acetylene with a flow rate of 11.50 dm^3/min for air

Table 1. Chemical and mineral characteristics of bentonite.

Chemical composition of bentonite		Mineral composition of bentonite	
Oxid	Content [%]	Mineral	Content [%]
SiO_2	59.02-74.6	Montmorillonite	50-98
Al_2O_3	12.07-23.67	Plagioclase	2.53
Fe_2O_3	2.01-3.2 bound to biotite	K-feldspar	1.89
CaO	0.99-1.74	Biotite	5.33
MgO	1.03-3.47	Quartz-cristobalite	13.44
TiO_2	0.13-0.24	Volcanic glass	5.13
Na_2O	0.16-0.88	loss by annealing	0.48
K_2O	0.68-1.28	–	

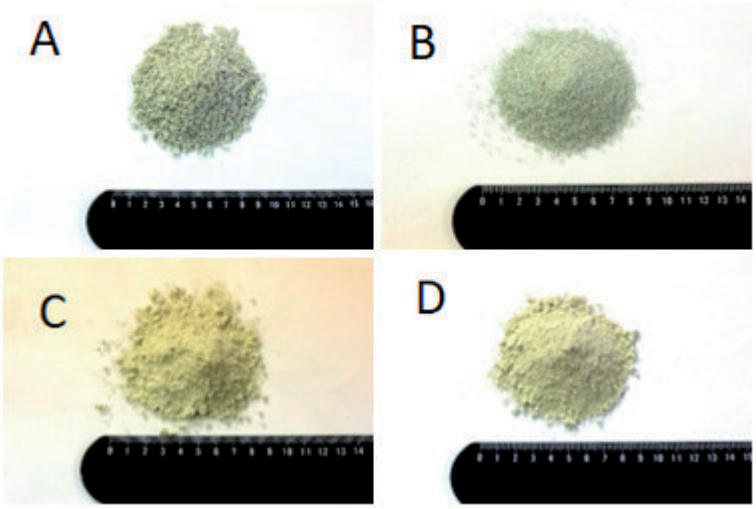

Fig. 6. A – ZeoAqua 1-2.5 mm, B – ZeoWater 0.5 – 1 mm, C – ZeoCem Eco Micro 200, D – ZeoCem Eco Micro 20 Extra Dry.

Table 2. Properties of used zeolites.

Zeolite	Abs. density ($g \cdot cm^{-3}$)	CEC ($mmol \cdot g^{-1}$)	Stability (pH)	Grain size (mm)	Humidity (%)
A	2.367	0.85	7.3 - 8	1 – 2.5	4.74
B	2.367	0.85	7.3 - 8	0.5 – 1	4.74
C	~ 2.2	0.85	7.3 - 8	0.09 – 0.2	4.21
D	~ 2.2	0.86	7.3 - 8	0.032	1.32

Table 3. Chemical composition of zeolites.

Zeolite	Si/Al (mol/mol)	Chemical composition (weight %)							
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2
A/B	4.77	68.83	12.25	1.40	3.09	0.72	3.11	0.81	0.16
C/D	4.98	70.37	11.98	1.76	3.57	0.31	-	-	-

Table 4. Heavy metal content of used zeolites.

Zeolite	Actual value ($mg \cdot kg^{-1}$)							
	Hg	Pb	Cd	As	Se	Cr	Ni	Sb
A	0.003	8.0	< 0.3	1.61	22.0	1.34	< 0.3	< 0.1
B	0.009	8.39	0.045	0.91	< 8.0	1.74	< 0.2	4.01
C	0.0254	10.88	0.017	1.01	3.57	-	--	-
D	0.01	10.0	< 0.3	0.90	< 5	< 3	-	-
Limit value (mg/kg)*	0.1	20	2.0	5	30	30	5	10

*Limit values according to the standard DIN EN16070.

and 1.10 dm^3/min for acetylene was used as a flame type. The relative errors in measurements by AAS were less than 5%. The operation of the device and the evaluation of the results were carried out using the software GBC Avanta ver. 2.0.

pH Determination

The pH parameter was determined according to STN ISO No. 10390 [36].

Table 5. BET characteristics of the sorbents used [$m^2 \cdot g^{-1}$].

Adsorbent	BET surface area ($m^2 \cdot g^{-1}$)
bentonite	43.098
A – ZeoAqua 1-2.5 mm	33.506
B – ZeoWater 0.5-1 mm	39.023
ZeoCem Eco Micro 200	52.461
ZeoCem Eco Micro 20 Extra Dry	58.603

Implementation of Heavy Metals Adsorption

The first part of the adsorption experiments with bentonite and zeolites was focused on the removal of mercury. Natural bentonite was added in different amounts: 1 g, 1.5 g, and 2 g. In the first case, different weights of bentonite were used for the experiments, in the second case 4 types of zeolites (A – ZeoAqua 1-2.5 mm, B – ZeoWater 0.5-1 mm, ZeoCem Eco Micro 200, ZeoCem Eco Micro 20 Extra Dry) of a weight of 1 g and in the third case only one type of zeolite determined from previous experiments as the most suitable in different weights. Water samples were always added in the same amount – 100 ml.

Table 6. Normalized results of quantitative X-ray powder diffraction analysis (weight %).

Adsorbent sample	Bentonite, before treatment	Zeolite, before treatment
Method	RJ	RJ
Mineral	[wt. %]	
Quartz	6	-
K-feldspar	11	< 1
Plagioclase	-	4
Biotite	2	< 1
Clinoptilolite/heulandite	-	76
Opal-CT	6	15
Arcanite	-	-
Cancrinite	-	-
Calcite	-	-
Portlandite	-	-
Hydroxylapatite	-	-
Periclase	-	-
Kaolinite	2	-
Smectite	73	3
Amorphous content	-	-
Sum	100	100

Note: RJ - RockJock - Eberl, D.D., 2003: User guide to RockJock – A programme for determining quantitative mineralogy from X-ray diffraction data. U.S. Geological Survey Open-File Report, OF 03-78, 40 p. Rie - Rietveld - Bruker AXS (2008) TOPAS V4: General profile and structure analysis software for powder diffraction data. User's Manual, Bruker AXS, Karlsruhe, Germany [34].

Adsorption was performed in closed containers for 2 h of shaking on a horizontal vibrating shaker. Consequently, the samples were centrifuged for 20 min at 5,000 rpm, filtered on MN 1640 m filters, and analyzed.

Calculations

Adsorption Capacity

From the measured concentrations, the adsorption capacity at equilibrium (q_e), the amount of metal adsorbed per unit sorbent at time t (q_t) from the solution q_e were calculated.

The adsorption capacity at equilibrium and at time t, respectively, was calculated according to Eq. (1) [37]:

$$q_e = \frac{(c_o - c_e) \cdot V}{m} \quad (1)$$

where c_o is the initial concentration of ions in solution (mg dm^{-3}), c_e is the equilibrium concentration of ions in solution or the concentration of ions in solution at time t (mg·dm^{-3}), V is the volume of solution (dm^3), m is the mass of adsorbent added (g) and q_e is amount of adsorbed heavy metal per unit sorbent mass (mg g^{-1}).

Percentage of Metal Ion Removal Efficiency

The percentage removal efficiency of metal ions from the solution was calculated according to the following Eq. (2) [37]:

$$\text{Ads.}\% = \frac{(c_o - c_e)}{c_o} * 100 \quad (2)$$

Statistical Analysis

A one-way ANOVA enables us to determine whether the variability of the outcomes is due to chance or to the effect of the investigated factor. By any words, this technique is used to estimate how the mean of a quantitative (dependent) variable changes according to the levels of a categorical variable called a factor.

If the MS effect is significantly greater than MS error, then the null hypothesis is rejected in favor of the alternative hypothesis-de facto, the given factor is responsible for differences among sample means. Subsequently, Duncan's test was applied to identify significant pairwise differences.

In all tests, 5% level of significance was used. The analyses were carried out using statistical

software STATISTICA 14, developed by TIBCO Software 14.0.0.

Results and Discussion

Pollution Monitoring of the Nitra Watercourse

Surface water samples from three points were monitored for selected heavy metals and general pollution indicators. This followed Government Regulation No. 269/2010 Coll., which sets requirements for good water status. The monitoring was focused on the presence of the most serious toxic and suspected heavy metal: mercury. Besides mercury, Cu and Zn concentrations also exceeded limit values. Hg was 1.4-9 times higher, Cu 1.2-28.3 times, and Zn 1.1-2.3 times (Table 7) [38].

Surface water quality (Table 8) showed significant exceedances of limit values. This was especially true for sample 2, near the industrial plant. All nitrogen parameters were elevated. Nitrates were highest, showing a 1.3-13-fold increase over the limit. Nitrite values were also high, 2.9-20 times above the limit. COD, an indicator of organic pollution, increased 1.2-3.8 times over the limit. Conductivity and chlorides exceeded limits in 2019, mainly in sample 2, likely due to pollution from the industrial plant.

In repeated sampling, values decreased, especially nitrogen parameters. However, sample 2 remained high, confirming above-average pollution of the Nitra River. Organic contamination rose in sample 3, indicating the need for further measurements at the same points.

Measured values from two periods confirm anthropogenic pollution from a nearby industrial source. Mercury adsorption to bentonite and zeolite occurred

Table 7. Analysis of metal samples from watercourses in the monitored area in 2019 and 2020.

Native sample	Cr [μg·dm^{-3}]	Mn [μg·dm^{-3}]	Fe [μg·dm^{-3}]	Ni [μg·dm^{-3}]	Cu [μg·dm^{-3}]	Zn [μg·dm^{-3}]	As [μg·dm^{-3}]	Cd [μg·dm^{-3}]	Pb [μg·dm^{-3}]	Sb [μg·dm^{-3}]	Hg [μg·dm^{-3}]
August 2019											
1	0.38	45	211	1.12	1.30	12.3	0.6	0.062	0.56	3.21	<0.05
2	0.20	93	252	0.46	31.09	18	5.9	0.026	3.57	1.24	0.23
3	0.15	81	142	2.22	26.08	10.6	4.1	0.014	4.96	1.52	0.07
June 2020											
1	0.21	39	187	0.13	1.60	6	1.6	0.022	0.66	0.21	<0.05
2	0.25	77	185	0.56	1.52	15	5.4	0.016	0.36	0.24	0.46
3	0.11	77	144	0.46	0.99	8	5.8	0.004	0.20	0.24	0.09
Limit value*	9	300	2000	20	1.1	7.8	7.5	0.08	7.2	25	0.05

Government Regulation No. 269/2010 Coll., setting the requirements for achieving good water status.

Table 8. Physical and chemical analysis of samples of watercourses in the monitored area in 2019 and 2020.

Native sample	pH	Conductivity (Ms m^{-1})	NH_4^+ [mg·dm^{-3}]	NO_2^- [mg·dm^{-3}]	NO_3^- [mg·dm^{-3}]	Cl^- [mg·dm^{-3}]	SO_4^{2-} [mg·dm^{-3}]	COD [mg·dm^{-3}]
August 2019								
1	7.66	69.09	0.93	0.058	6.26	3.59	46.82	28.50
2	7.11	200.8	2.12	0.085	65.19	457.75	98.37	63.32
3	7.74	16.13	0.75	0.082	8.34	117.43	71.2	112.84
June 2020								
1	7.39	29.55	0.12	0.003	4.62	3.47	4.12	0
2	7.72	111.17	0.63	0.1	8.1	176.25	55.36	41.22
3	7.22	53.92	0.88	0.4	4.16	69.92	37.86	132.82
Standard	6-8.5	110	1	0.02	5	200	250	35

*Limit values according to 269/2010 Coll – Regulation of the government of the Slovak Republic, setting the requirements for achieving good water status.

in August 2019 (Tables 8 and 9). The decrease in metal concentrations, except for Hg, was likely due to reduced industrial activity during March-April 2020 (COVID-19 quarantine).

Adsorption of Heavy Metals

The adsorption capacity of bentonite was the highest for sample 2, which was the richest in mercury. As the concentration of Hg in the sample increased, the adsorption capacity of bentonite rose, too. The most suitable amount of adsorbent in terms of adsorption capacity was 1 g. The qe value decreased as the adsorbent weight increased. The maximum value was obtained for sample 2 and a bentonite weight of 1 g, namely 0.090 μg.g^{-1} (Table 9).

The decreasing q_e values for the observed mercury at different amounts of bentonite are likely related to the competition from other metal ions in the solution, and naturally, to the increasing concentration gradient of other metals over a larger number of available adsorption sites.

The obtained results of the percentage removal of mercury confirm a high level of adsorption (75.3-97.1%). Bentonite's high affinity for Hg is primarily due to its large surface area, cation exchange capacity. Structural modifications further enhance these properties, making bentonite and its composites highly effective for mercury removal from aqueous environments [39]. Our results correspond with a study [40] reporting that natural Ca-bentonite achieved impressive Hg(II) ion removal efficiency, exceeding 94 % for all initial concentrations of this metal ion.

The most appropriate amount of added bentonite, resulting from experiments in terms of % purification, is 1.5 g/100 ml of the sample (Table 9).

Tables 10 and 11 present the statistical evaluation comparing the significance of differences in adsorption capacities depending on the addition of bentonite.

The results of the analysis of variance demonstrated that the addition of the adsorbent has a highly significant effect on the adsorption capacity of bentonite, q_e [μg·g^{-1}].

The F-test statistic reached a value of 16.33, indicating that the variability in adsorption capacity between different groups (levels of adsorbent addition) is substantially greater than the variability within these groups (random error).

A key finding is the p-value of 0.000. Since this value is well below the standard significance level of $\alpha = 0.05$ (and even $\alpha = 0.01$), we reject the null hypothesis of equal means. This confirms that changes in the amount of added adsorbent lead to statistically significant differences in the final adsorption capacity of the material. Therefore, it can be concluded that the conditions of adsorbent dosing are a critical factor affecting the performance of bentonite.

All three tested adsorbent doses (1 g, 1.5 g, and 2 g) resulted in statistically different mean adsorption capacities. There is no pair of doses that does not differ statistically. This indicates that even relatively small

Table 9. Average mercury concentration in samples before and after the adsorption by bentonite.

Original samples							
Amount of bentonite							
Native sample	–	1 g		1.5 g		2 g	
	c [μg·dm^{-3}]						
1	0.527±0.012	0.130±0.027		0.038±0.005		0.044±0.001	
2	1.069±0.035	0.102±0.002		0.063±0.002		0.058±0.003	
3	0.931±0.061	0.030±0.008		0.027±0.002		0.030±0.002	
Adsorption process							
	–	q_e [μg·g^{-1}]	%	q_e [μg·g^{-1}]	%	q_e [μg·g^{-1}]	%
1	–	0.0397	75.3	0.0326	92.8	0.0242	91.7
2	–	0.0967	90.5	0.0671	94.1	0.0506	94.6
3	–	0.0901	96.8	0.0603	97.1	0.0451	96.8

Table 10. Analysis of variance of bentonite adsorption capacity depending on the addition of the adsorbent.

Adsorption capacity	ANOVA							
	Sum of squares	Degree of freedom	Mean of squares	Sum of squares	Degree of freedom	Mean of squares	F-test	p-level
qe [μg·g^{-1}]	0.0116	2	0.0058	0.0182	51	0.0004	16.33	0.000

Table 11. Duncan's test of bentonite adsorption capacity depending on the addition of the adsorbent.

Adsorbent dose [g]	Duncan's test		
	1	1.5	2
1		0.001	0.000
1.5	0.001		0.038
2	0.000	0.038	

changes in the adsorbent dosage have a measurable and significant impact on the final adsorption capacity.

Table 12 presents the values of average mercury concentration in samples before and after adsorption by zeolites.

The adsorption capacities q_e (Table 12) show that zeolites have lower mercury adsorption than bentonites. The experiment aimed to identify the most suitable zeolite type. Zeolites showed significantly different sorption behavior compared to bentonites. Bentonite almost completely adsorbed Hg, while zeolites were less effective.

Tables 13 and 14 present the statistical evaluation comparing the significance of differences in adsorption capacities depending on the type of zeolite.

The type of zeolite has a highly significant effect on the adsorption capacity of bentonite (q_e). The choice of a specific zeolite type added to bentonite has a key and measurable impact on the resulting adsorption efficiency. The differences in adsorption capacity observed among the four zeolite types are too large to be attributed solely to random error.

Table 14. Duncan's test of bentonite adsorption capacity depending on the type of zeolite.

Type of zeolite	Duncan's test			
	A	B	C	D
A		0.056	0.000	0.008
B	0.056		0.022	0.372
C	0.000	0.022		0.125
D	0.008	0.372	0.125	

Zeolite Type C produces a clearly distinct mean adsorption capacity compared to the other variants (A, B, D), with the largest difference observed relative to Type A. Types B, D, and A (with some caution) form one statistically similar group.

Results showed much lower mercury removal in samples 1 and 3. Natural zeolites often contain impurities such as Fe^{2+}, SO_4^{2-}, quartz, other zeolites, clay minerals, feldspars, and amorphous glass. These reduce the proportion of valuable components in the raw material and limit its use in applications where high purity and uniformity are required. To overcome

Table 12. Average mercury concentration in samples before and after the adsorption by zeolites.

Original samples									
	Type of zeolite								
Native sample	-	A		B		C		D	
	c [µg·dm^{-3}]								
1	0.632±0.024	0.600±0.023		0.787±0.065		0.274±0.021		0.462±0.041	
2	0.971±0.010	0.852±0.042		0.523±0.062		0.268±0.002		0.318±0.022	
3	0.540±0.015	0.310±0.028		0.462±0.082		0.410±0.042		0.496±0.028	
Adsorption process									
	–	q_e [µg·g^{-1}]	%	q_e [µg·g^{-1}]	%	q_e [µg·g^{-1}]	%	q_e [µg·g^{-1}]	%
1	–	0.003	4.8	0.005	7.9	0.036	57.1	0.017	27.0
2	–	0.012	12.2	0.045	46.4	0.071	73.2	0.066	68.0
3	–	0.008	14.8	0.019	42.6	0.013	24.1	0.005	9.3

Table 13. Analysis of variance of bentonite adsorption capacity depending on the type of zeolite.

Adsorption capacity	ANOVA							
	Sum of squares	Degree of freedom	Mean of squares	Sum of squares	Degree of freedom	Mean of squares	F-test	p-level
qe [µg·g^{-1}]	0.0087	3	0.0029	0.0291	68	0.0004	6.74	0.000

this limitation, various modification methods – thermal, chemical, surfactant-based, or their combinations (e.g., thermal treatment, acid or alkaline treatment, surfactant modification) – can be applied to remove impurities, enhance structural properties, increase ion affinity, and broaden the range of potential applications. Thermal and chemical treatments may cause cation migration within the zeolite framework and facilitate their substitution with newly introduced cations, thereby altering cation positions and pore openings. As a result, ions can be replaced with more easily exchangeable ones under ion-exchange conditions, leading to the predominance of a single cation and the formation of an almost homoionic zeolite with improved effective exchange capacity [41]. Such modifications could enhance Hg removal efficiency to levels that comply with legal requirements.

Đozić et al. reported Hg(II) removal by bentonite at 94%, similar to our findings [40]. Fernández-Nava used granular bentonite for Hg(II) adsorption [42]. They reported a higher adsorption capacity (1.7 $mg \cdot g^{-1}$) than our results, likely due to different conditions such as input concentration, pH, adsorbent amount, and use of simulated solutions instead of native samples.

Sample 2, with the highest Hg concentration, showed the highest removal, 73.2%, using zeolite C. Zeolite B is the most positive for sample 3, but zeolite C is more suitable for higher concentrations of Hg in samples. The adsorption capacities of zeolites, as well as the % of Hg removal, were lower for zeolites than for bentonite. The highest values were recorded for zeolite C for sample 2, i.e., 0.071 $\mu g \cdot g^{-1}$.

Subsequently, adsorption was carried out on zeolite C, which showed the most suitable efficiency against Hg in the previous experiment. Analyses were performed on a sensitive instrument using the ICP MS method after previous filtration of samples. Mercury was measured using the cold vapour technique.

Table 15 provides an evaluation of the measured concentrations of heavy metals after adsorption by zeolite C in samples 1, 2, and 3 collected in June 2020. The results are expressed as the percentage of metal removal and the adsorption capacity of the zeolite (q_e, $\mu g \cdot g^{-1}$).

Original samples showed above-limit concentrations for Cu (samples 1 and 2), Zn (samples 2 and 3), and Hg (samples 2 and 3) (Table 6). Hg concentrations were similar in both monitoring stages. After adsorption to zeolite C, above-limit values remained for all three metals, indicating the insufficiency of the adsorbent used, despite positive adsorption.

The analyzed heavy metals can be divided into four groups according to the course of adsorption:

In the first group, zeolite C adsorbed metals positively at a high adsorbent-to-sample ratio (1:1000, 0.1 g adsorbent + 100 ml sample), mainly Cr and Cu, and partially Zn and Cd. Higher adsorbent masses had a negative effect on these metals. In adsorbates, we measured their increased concentration, which was reflected in negative values of metal removal percentage and adsorption capacity of metal q_e.

Chromium adsorption ranged from 18-43%. Álvarez et al. [43] reported similar removal (45%) using 1 g adsorbent per 100 ml effluent. Mthombeni et al.

Table 15. Evaluation of measured values of heavy metals concentrations after adsorption by zeolite C in samples 1, 2 and 3 – June 2020 – in the form of % metal removal and adsorption capacity of zeolite qe $\mu g \cdot g^{-1}$.

Heavy metal	Amount of zeolite											
	1/0.1g		2/0.1g		3/0.1g		1/1g		2/1g		3/1g	
	q_e	%	q_e	%	q_e	%	q_e	%	q_e	%	q_e	%
Cr	0.09	43	0.07	28	0.02	18	-0.006	-29	-0.009	-36	-0.012	-109
Mn	-8	-21	-8	-10	-5	-6	-18	-461	-14.5	-188	-13	-168
Fe	-60	-32	-59	-31	-64	-44	-102	-542	-86	-463	-82	-566
Ni	-0.15	-115	-0.06	-10	-0.08	-17	-0.093	-715	-0.074	-132	-0.078	-170
Cu	0.3	19	0.1	6.6	0.69	70	-0.145	-90	-0.136	-89	-0.14	-141
Zn	-5	-83	2	13	2	25	-2.3	-383	-1.1	-73	-1.1	-137
As	0.1	6	0.1	2	0.1	2	-0.01	-6	0.01	2	0.03	5
Cd	0.005	23	0.006	38	-0.006	-150	-0.0032	-145	-0.0027	-168	-0.0033	-825
Pb	-0.91	-138	-0.87	-242	-1.03	-515	-0.268	-406	-0.309	-858	-0.268	-1345
Sb	0.14	67	0.07	29	0.08	33	0.015	71	0.012	50	0.013	54
Hg	*	*	0.1	22	0.03	33	*	*	0.015	33	0.003	33

Note: *Below the level of determinability
Green colour – positive values
Yellow colour – highly positive values
Red colour – negative values
Blue colour – significantly indistinctive decrease/increase of adsorption
No colour – insignificant values for the evaluation

reported 99% Cr(VI) removal [44], likely due to using a magnetic natural zeolite-polymer composite or different adsorption conditions.

Cu(II) adsorption ranged from 6.6-70%. This removal was lower than that reported by Balintova et al. [45] (89%) and Pfeifer et al. [13] (98.5%), but higher than that reported by Olegario-Sanchez and Pelicano [20] (36%).

This shows that removal efficiency depends on adsorption conditions. Zeolite is suitable for Cu(II) removal from polluted water. Zinc reacted negatively to the adsorption in the 1st sample. However, during the adsorption of samples 2 and 3, its concentration decreased (sample 2 by 13% and sample 3 by 25%). Zn adsorption to zeolite C reached the highest capacity of all metals, 2 $\mu g \cdot g^{-1}$.

Ryu et al. reported similar Zn(II) removal (~30%) using zeolite in acidic mine drainage. Their study used DCMD-zeolite systems, which may improve adsorption [19]. Adsorption capacity decreased in the order: Cu > Cr > Cd.

In the second group, zeolite C adsorption increased even at higher adsorbent amounts (1 g:100 ml ratio). It is mainly the most observed heavy metal – Hg. In addition to Hg, Sb was also very positively adsorbed. The adsorption efficiency was at the level of 33% for Hg and 50-71% for Sb. Chojnacki et al. found an adsorption capacity of 0.021 in the adsorption of industrial and domestic mixed effluents using zeolite; 0.015 and 0.0061 $mg.g^{-1}$ at adsorbent doses of 0.35, 0.7, and 2.1 $g.dm^{-3}$ [46]. In our case, the same trend was observed. Increasing the zeolite dose for Hg adsorption requires monitoring, as adsorption may decrease beyond a certain limit.

The third group represents metals whose concentrations increased after adsorption: Mn, Fe, Ni, Pb. We assume that the reason may be the original concentration of these metals in zeolite, and thus, the opposite process occurred – desorption, in which these heavy metals were washed out into a more dilute solution. Negative adsorption values of some metals are likely caused by the competition of solvated ions for available sites on the adsorbent compared to smaller ions. In this context, Pb(II) stands out, with an empirical ionic radius of 180 pm, making it the largest among the studied adsorbed ions [47]. Similarly, the van der Waals radius of Ni(II), which is the largest among the studied ions, may contribute to its desorption. According to [48], chromium and nickel are less readily sorbed, likely due to the size of their hydrated ions relative to the zeolite pore dimensions, which renders the material selective toward certain cations. Based on experiments with a real surface water sample contaminated with heavy metals, the zeolite demonstrated high sorption capacities for cations in the following order: Sb > Hg > Cu > Cr > Cd > Zn. Under our experimental conditions, Mn, Fe, Ni, and Pb cations were unsuitable for adsorption. This can be attributed to competition among the metals already present in the sample at relatively high concentrations, such as Fe or Mn, as well as the specific speciation of metal compounds in the real sample.

The second reason is probably the steric barrier to the amount of metal ions present in the natural sample. It is also possible to count ions of the monitored general pollution in the samples taken. However, none of the metals showed above-limit values in the samples after adsorption, although the % removal and adsorption capacity parameters had negative values. Adsorption studies showed rapid uptake of heavy metals generally within the first 40 min, corresponding to ~80% of total removal. After this initial fast phase, the adsorption rate decreases [49]. After rapid adsorption, some metals may desorb back into the water.

As was completely non-adsorptive on zeolite C. Arsenic concentrations remained below the limit and did not change during adsorption. Rusman et al. reported high As(III) removal using 12.5 $g \cdot dm^{-3}$ zeolite with ozonation for 2 h [50]. Higher removal could be achieved by adjusting the process or modifying the adsorbent.

After adsorption using zeolite C (ratios 1:100 and 1:1000), Hg, Cu, and Zn remained above limit values. Zeolite C, though the best among the tested zeolites, could not reduce Hg below 0.05 $\mu g \cdot dm^{-3}$.

The change in pH during the adsorption process of natural samples ranges from 7.15 to 8.30 for bentonite and from 7.28 to 8.02 for zeolite. All processes fall within the limit values set by Act No. 269/2010 Coll. – Government Regulation of the Slovak Republic on the quality of surface waters. It follows that the use of natural sorbents, such as untreated bentonite and zeolite, does not affect the change in pH during adsorption. The effect of different pH levels on the adsorption behavior of bentonite and zeolite was also evaluated in our previous research [51].

Heavy metal contamination in soil and water is a critical concern due to the serious risks it poses to both ecosystems and society. Several treatment techniques – such as ion exchange, chemical precipitation, reverse osmosis, carbon adsorption, solvent extraction, and electrodialysis – are available to remove these pollutants, with ion exchange standing out for its ease of application. Nonetheless, many of these methods involve high implementation costs. As a result, there is growing interest in identifying alternative, cost-effective materials, such as natural zeolites, for the removal or stabilization of heavy metals. Zeolites stand out from other crystalline inorganic oxides due to several distinctive features: their tetrahedral framework, which creates unique properties on both the external and internal crystalline surfaces (resulting in a high surface area); the presence of metal-oxygen tetrahedra on the internal surface, which can be readily modified through processes such as cation exchange, substitution [52].

A study by Abadzic and Ryan confirms that there is a real risk of clogging with large-scale zeolite applications, especially if the released particles migrate into finer layers of materials or into a substrate with small pores. These particles can reduce substrate

permeability; if zeolite or bentonite has adsorbed toxic metals or other contaminants, their release back into the environment is possible, especially if the particles become loose or the material degrades, or physically alter sediments or soil, affecting microorganisms and plants [53].

According to Wang et al. (2006), zeolite can be regenerated using two methods: high-temperature calcination (HT) and Fenton oxidation (FR). Regeneration of natural zeolites by these two methods cannot fully restore their adsorption capacity. Regenerated samples produced by both techniques perform similarly, retaining approximately 60% of the adsorption capacity of fresh zeolite [54]. The minimization of adsorbent consumption, along with the extension of its lifespan and the enhancement of its adsorption capacity, was also confirmed by the use of pulsed column adaptation [55].

According to Kuliš Ivan, the sorbability of Hg is much higher in the presence of Fe(III)-modified zeolite. In our case, the original sample was rich in Fe, which may specifically enhance the sorption of Hg on the zeolite [56].

According to numerous authors in review articles, the adsorption of heavy metals on zeolites depends on several factors, such as the concentration of specific ions in the original solution, the speciation form of the component, competition among multiple ions, grain size, and the composition of the particular zeolite from the deposit in a given country. Moreover, many experimental studies are conducted using synthetic, laboratory-prepared aqueous solutions, which may not accurately reflect experiments with real samples containing high amounts of specific metal compounds [57]. In the future, research could focus on treating contaminated water using alternative methods, such as photocatalysis [58, 59].

Conclusions

Slovakia has significant, yet underutilized, potential in environmental raw materials. These include deposits of bentonite and zeolites, which are found in Slovakia in large quantities and quality. They do not cause environmental devastation; on the contrary, they protect all its basic components.

The results of the research indicate a high adsorption capacity of bentonites for Hg. Zeolites showed this ability to a lesser extent and were suitable only for some of the monitored heavy metals. Positively adsorbed metals: Sb – excellent adsorption with zeolite of type C: 50-71%, Hg – very good adsorption efficiency with bentonite (90%), and relatively good zeolite adsorption efficiency of 33% was determined. Cr and Cd, although below the limit in water, adsorbed well to zeolite C: 18-43% for Cr and 23-38% for Cd. Both adsorption levels were achieved using an adsorbent-to-sample volume ratio of 1:1,000. Using zeolite C, Cu was adsorbed in the range of 19-70%, while lower adsorption levels of 13-25% were observed for Zn (adsorbent dose in proportion to sample volume 1:1,000). Maximum adsorption capacities were found to be 0.69 for Cu and 2 $\mu g.g^{-1}$ for Zn.

Zeolite C adsorbs metals in the order: Sb > Hg > Cr > Cd > Cu > Zn. Unsuitable adsorption was demonstrated for heavy metals Pb, Ni, Mn, and Fe. In this case, the opposite process was observed – the leaching of ions into a solution. The reason for this is probably the incorporation of metals in the structure of zeolite and the steric ratios of ions in the samples. Arsenic was indifferent in the adsorption process.

Metals Sb and Hg, whose suitability for the use of zeolite C is the most optimal, achieve an adsorption capacity of 0.012 and 0.015 $\mu g.g^{-1}$ for the monitored sample 2 q_e.

Surface watercourses in Slovakia, specifically the Nitra River, are significantly polluted and do not meet the required water quality standards. One option for their protection is the use of readily available, rich sources of natural adsorbents.

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Conflict of Interest

The authors declare no conflict of interest.

References

1. Ministry of the Environment of the Slovak Republic. Information on the status of monitoring of geological environmental factors with reference to impending accidents and possibilities for preventing these accidents. Available online: https://rokovania.gov.sk/RVL/Material/23760/1 (accessed on 4 February 2025).
2. STANOVIČ R., KUJOVSKÝ M., VOLLMANNOVÁ A., ÁRVAY J., HARANGOZO L., BAJČAN D. Medziročné porovnanie obsahu ťažkých kovov v sedimentoch rieky Nitra. Nitra: Slovenská poľnohospodárska univerzita. **2017** [In Slovak].
3. ANDREJI J., DVOŘÁK P., FIK M. Distribution of heavy metals (Ni, Co, Pb, Cd, Hg) in tissues of European chub (*Squalius cephalus* L.) from the middle course of the Nitra River, Slovakia. Advanced Research in Life Sciences. **2** (1), 16, **2018**.
4. MELICHOVÁ Z., ĎURICOVÁ A., SAMEŠOVÁ D., NAGYOVÁ I. Hodnotenie rizík vybraných kovových prvkov vo vodách. Univerzita Mateja Bela, Fakulta prírodných vied, Banská Bystrica, Slovakia, **2017** [In Slovak].

5. ARORA R. Adsorption of heavy metals – a review. Materials Today: Proceedings. **18**, 4745, **2019**.
6. VRÎNCEANU N.O., MOTELICĂ D.M., DUMITRU M., CALCIU I., TĂNASE V., PREDA M. Assessment of using bentonite, dolomite, natural zeolite and manure for the immobilization of heavy metals in a contaminated soil: The Copșa Mică case study (Romania). CATENA. **176**, 336, **2019**.
7. CALACE N., NARDI E., PETRONIO B.M., PIETROLETTI M., TOSTI G. Metal ion removal from water by sorption on paper mill sludge. Chemosphere. **51** (8), 797, **2003**.
8. MOHAMMED N.H., ATTA M., YAACUB W.Z.W. Remediation of heavy metals by using industrial waste by products in acid mine drainage. American Journal of Environmental and Agricultural Sciences. **10** (4), 1001, **2017**.
9. LEKGOBA T., NTULI F., FALAYI T. Application of coal fly ash for treatment of wastewater containing a binary mixture of copper and nickel. Journal of Water Process Engineering. **40**, 101822, **2021**.
10. ŠURÁNEK M., MELICHOVÁ Z., THOMAS M. Removal of cadmium and cobalt from water by Slovak bentonites: efficiency, isotherms, and kinetic study. Environmental Science and Pollution Research. **31** (20), 29199, **2024**.
11. ALSAWALHA M. Overview of current and future perspectives of Saudi Arabian natural clinoptilolite zeolite: A case review. Journal of Chemistry. **2019** (1), 3153471, **2019**.
12. JESENÁK K. Environmentálna anorganická chémia. Univerzita Komenského: Bratislava, Slovakia, pp. 159, **2005** [In Slovak].
13. PFEIFER A., ŠKERGET M., ČOLNIK M. Removal of iron, copper, and lead from aqueous solutions with zeolite, bentonite, and steel slag. Separation Science and Technology. **56** (17), 2989, **2021**.
14. FLIEGER J., KAWKA J., PŁAZIŃSKI W., PANEK R., MADEJ J. Sorption of heavy metal ions of chromium, manganese, selenium, nickel, cobalt, iron from aqueous acidic solutions in batch and dynamic conditions on natural and synthetic aluminosilicate sorbents. Materials. **13** (22), **2020**.
15. BAKALÁR T., KAŇUCHOVÁ M., GIROVÁ A., PAVOLOVÁ H., HROMADA R., HAJDUOVÁ Z. Characterization of Fe(III) adsorption onto zeolite and bentonite. International Journal of Environmental Research and Public Health. **17** (16), **2020**.
16. HADŽIĆ E., BONACCI O., MILIŠIĆ H., ZVIZDIĆ D., LAZOVIĆ N. Watercourse recovery process - the role and importance of water monitoring. In Interdisciplinary Advances in Sustainable Development, TUFEK-MEMIŠEVIĆ T., ARSLANAGIĆ-KALAJDŽIĆ M., ADEMOVIĆ N., Eds., Springer International Publishing: Cham, Switzerland, 326, **2023**.
17. ALEKSANDER-KWATERCZAK U., PLENZLER D. Contamination of small urban watercourses on the example of a stream in Krakow (Poland). Environmental Earth Sciences. **78** (16), 530, **2019**.
18. MEYER A.M., KLEIN C., FÜNFROCKEN E., KAUTENBURGER R., BECK H.P. Real-time monitoring of water quality to identify pollution pathways in small and middle scale rivers. Science of The Total Environment. **651**, 2323, **2019**.
19. RYU S., NAIDU G., HASAN JOHIR M.A., CHOI Y., JEONG S., VIGNESWARAN S. Acid mine drainage treatment by integrated submerged membrane distillation–sorption system. Chemosphere. **218**, 955, **2019**.
20. OLEGARIO-SANCHEZ E., PELICANO C.M. Characterization of Philippine natural zeolite and its application for heavy metal removal from acid mine drainage (AMD). Key Engineering Materials. **737**, 407, **2017**.
21. WULANDARI E., HIDAYAT A.E., MOERSIDIK S.S. Comparison of copper adsorption effectivity in acid mine drainage using natural zeolite and synthesized zeolite. IOP Conference Series: Earth and Environmental Science. **473** (1), 012143, **2020**.
22. ŠURÁNEK M., MELICHOVÁ Z., KUREKOVÁ V., KLJAJEVIĆ L., NENADOVIĆ S. Removal of nickel from aqueous solutions by natural bentonites from Slovakia. Materials. **14** (2), **2021**.
23. AL-ABBAD E.A., AL DWAIRI R.A. Removal of nickel (II) ions from water by Jordan natural zeolite as sorbent material. Journal of Saudi Chemical Society. **25** (5), 101233, **2021**.
24. GUMEDE S., MUSONGE P. Characterisation of Mg-Al hydrotalcite and surfactant-modified bentonite nano clays for the treatment of acid mine drainage. Sustainability. **14** (15), **2022**.
25. MOKGEHLE T.M., GITARI W.M., TAVENGWA N.T. Synthesis of di-carboxylic acid functionalized zeolites from coal fly ash for Cd (II) removal from acid mine drainage using column studies approach. Journal o f Environmental Chemical Engineering. **7** (6), 103473, **2019**.
26. BUEMA G., HARJA M., LUPU N., CHIRIAC H., FORMINTE L., CIOBANU G., BUCUR D., BUCUR R.D. Adsorption performance of modified fly ash for copper ion removal from aqueous solution. Water. **13** (2), **2021**.
27. CHANGALVAEI M., NILFOROUSHAN M.R., ARABMARKADEH A., TAYEBI M. Removal of Ni and Zn heavy metal ions from industrial waste waters using modified slag of electric arc furnace. Materials Research Express. **8** (5), 055506, **2021**.
28. STN EN ISO 5667-3. Kvalita vody – Odber vzoriek – Časť 3: Konzervácia vzoriek vody a manipulácia s nimi (ISO 5667-3:2024); ÚNMŠ: Bratislava, Slovakia, **2025** [In Slovak].
29. MU'AZU N.D., BUKHARI A., MUNEF K. Effect of montmorillonite content in natural Saudi Arabian clay on its adsorptive performance for single aqueous uptake of Cu(II) and Ni(II). Journal of King Saud University – Science. **32** (1), 412, **2020**.
30. SHI L., QIU J., WANG W., DING Z., ZHANG W., LIANG J., LI P., FAN Q. Influence of cations and low molecular weight organic acids on Cs(I) adsorption on montmorillonite and vermiculite. Journal of Molecular Liquids. **402**, 124778, **2024**.
31. ZHU Z., HUANG Y., DONG L., XU W., YU M., LI Z., XIAO Y., CHENG H. Dual effects of NaCl on the high temperature adsorption of heavy metals by montmorillonite. Chemical Engineering Journal. **494**, 152661, **2024**.
32. KULDEYEV E., SEITZHANOVA M., TANIRBERGENOVA S., TAZHU K., DOSZHANOV E., MANSUROV Z., AZAT S., NURLYBAEV R., BERNDTSSON R. Modifying natural zeolites to improve heavy metal adsorption. Water. **15** (12), 2215, **2023**.
33. SAN T.Z., PARK J.H., WIN M.Z., DILSHOD U.L., OO W., YI K.B. Enhanced ammonia adsorption-desorption properties of synthesized zeolite-carbon composite with

the effect of Si/Al ratio. Separation and Purification Technology. **353** (C), 128560, **2025**.
34. EBERL D.D. User Guide to RockJock – A Program for Determining Quantitative Mineralogy from X-Ray Diffraction Data; U.S. Geological Survey: Reston, VA, USA, **2003**.
35. HORÁKOVÁ M. Analytika vody, 2nd ed.; Vysoká škola chemicko-technologická v Praze: Praha, Czech Republic, **2007** [In Slovak].
36. STN EN ISO 10390. Zemina, upravené bioodpady a kaly – Stanovenie pH (ISO 10390:2021); ÚNMŠ: Bratislava, Slovakia, **2022** [In Slovak].
37. BALINTOVA M., HOLUB M., STEVULOVA N., CIGASOVA J., TESARCIKOVA N. Sorption in acidic environment—biosorbents in comparison with commercial adsorbents. Chemical Engineering Transactions. **39**, 625, **2014**.
38. MINISTRY OF THE ENVIRONMENT OF THE SLOVAK REPUBLIC. Act No. 269/2010 Coll. on Waste; Collection of Laws of the Slovak Republic: Bratislava, Slovakia, **2010**. Available online: https://www.slov-lex.sk/pravne-predpisy/SK/ZZ/2010/269/ (accessed on 4 February 2025).
39. WANG X., YANG L., ZHANG J., WANG C., LI Q. Preparation and characterization of chitosan–poly(vinyl alcohol)/bentonite nanocomposites for adsorption of Hg(II) ions. Chemical Engineering Journal. **251**, 404, **2014**.
40. ĐOZIĆ A., ALIHODŽIĆ H., JUNUZOVIĆ H., ŠESTAN I., ZOHOROVIĆ M., AHMETOVIĆ M. Removal of As(V) and Hg(II) ions from simulated wastewater using natural and modified Ca-bentonite. International Journal of Environmental Agriculture and Biotechnology. **7**, 178, **2022**.
41. SENILA M., CADAR O. Modification of natural zeolites and their applications for heavy metal removal from polluted environments: Challenges, recent advances, and perspectives. Heliyon. **10** (3), e25303, **2024**.
42. FERNÁNDEZ-NAVA Y., ULMANU M., ANGER I., MARAÑÓN E., CASTRILLÓN L. Use of granular bentonite in the removal of mercury (II), cadmium (II) and lead (II) from aqueous solutions. Water Air Soil Pollution. **215** (1), 239, **2011**.
43. ÁLVAREZ A.M., GUERRÓN D.B., CALDERÓN C.M. Natural zeolite as a chromium VI removal agent in tannery effluents. Heliyon. **7** (9), e07974, **2021**.
44. MTHOMBENI N.H., ONYANGO M.S., AOYI O. Adsorption of hexavalent chromium onto magnetic natural zeolite-polymer composite. Journal of the Taiwan Institute of Chemical Engineers. **50**, 242, **2015**.
45. BALINTOVA M., HOLUB M., SINGOVSZKA E. Study of iron, copper and zinc removal from acidic solutions by sorption. Chemical Engineering Transactions. **28**, 175, **2012**.
46. CHOJNACKI A., CHOJNACKA K., HOFFMANN J., GÓRECKI H. The application of natural zeolites for mercury removal: from laboratory tests to industrial scale. Minerals Engineering. **17** (7), 933, **2004**.
47. Periodická Tabuľka – Ptable. Available online: https://ptable.com/?lang=sk.
48. KORINEKOVÁ M., HAVLÍK T. Odstraňovanie ťažkých kovov z roztokov sorpciou na zeolit. Acta Metallurgica Slovaca. **12**, 208, **2006** [In Slovak].
49. MOTSI T., ROWSON N.A., SIMMONS M.J.H. Adsorption of heavy metals from acid mine drainage by natural zeolite. International Journal of Mineral Processing. **92** (1), 42, **2009**.
50. RUSMANA Y., NOTODARMOJO S., HELMY Q. Arsenic removal in groundwater by integrated ozonation and adsorption by activated carbon and zeolite. IOP Conference Series: Materials Science and Engineering. **536** (1), 012073, **2019**.
51. ĎURICOVÁ A., PREPILKOVÁ V.Š., SEČKÁR M., SCHWARZ M., SAMEŠOVÁ D., MURAJDA T., ANDRÁŠ P., EŠTOKOVÁ A., HOLOŠOVÁ M.Č., PONIŠT J., ZACHAROVÁ A., SCHMIDTOVÁ J., VEVERKOVÁ D., BIROŇ A. Comparison of Cu(II) adsorption using fly ash and natural sorbents during temperature change and thermal–alkaline treatment. Materials. **18** (19), 4552, **2025**.
52. MORANTE-CARBALLO F., MONTALVÁN-BURBANO N., CARRIÓN-MERO P., JÁCOME-FRANCIS K. Worldwide research analysis on natural zeolites as environmental remediation materials. Sustainability. **13** (11), 6378, **2021**.
53. ABADZIC S.D., RYAN J.N. Particle release and permeability reduction in a natural zeolite (clinoptilolite) and sand porous medium. Environmental Science & Technology. **35** (22), 4502, **2001**.
54. WANG S., LI H., XIE S., LIU S., XU L. Physical and chemical regeneration of zeolitic adsorbents for dye removal in wastewater treatment. Chemosphere. **65** (1), 82, **2006**.
55. YIMRATTANABOVORN J., PHALAIPHAI M., NAWONG S. Pulsed-bed column adsorption for triclosan removal using macadamia nut shell activated carbon. Civil Engineering Journal. **10** (5), 1645, **2024**.
56. KULIŠ I. Sorpcija Hg(II) na Fe(III)-modificiranom zeolitu klinoptilolitu – određivanje mehanizma sorpcije. Bachelor Thesis, University of Split, Faculty of Chemistry and Technology, Division of Engineering and Chemistry, **2022** [In Slovak].
57. VELARDE L., NABAVI M.S., ESCALERA E., ANTTI M.-L., AKHTAR F. Adsorption of heavy metals on natural zeolites: A review. Chemosphere. **328**, 138508, **2023**.
58. SANTIS A., ARBELÁEZ O., CARDENAS L.A., CASTELLANOS J., VELASQUEZ P. Optimizing Cr(VI) reduction in plastic chromium plating wastewater: Particle size, irradiation, titanium dose. Emerging Science Journal. **8** (1), 17, **2024**.
59. NISAR N., SHAH R., ZADA F.M., KHAN B., AZIZ S., REHMAN N., AHMAD N., KHAN M., HANZALA, MIN H.S. Novel Ni/ZnO nanocomposites for the effective photocatalytic degradation of malachite green dye. Civil Engineering Journal. **10** (8), 2601, **2024**.