

**SORPTION KINETICS OF SELECTED HEAVY METALS
ADSORPTION TO NATURAL AND Fe(III) MODIFIED ZEOLITE TUFF
CONTAINING CLINOPTILOLITE MINERAL**

Maroš SIROTIK, Marek LIPOVSKÝ, Alica BARTOŠOVÁ

RNDr. Maroš Sirotiak, PhD., Ing. Marek Lipovský, Ing. Alica Bartošová, PhD.
Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in
Trnava, Institute of Safety, Environment and Quality, Paulínska 16, 917 24 Trnava, Slovak Republic
e-mail: maros.sirotiak@stuba.sk, marek.lipovsky@stuba.sk, alica.bartosova@stuba.sk

Abstract

In the research described in this paper, studied was sorption capacity of natural and ferric modification of zeolite tuff containing mineral clinoptilolite from the Nižný Hrabovec deposit to remove potentially toxic metals (ionic forms of chromium, nickel, copper and aluminium) from their water solutions. We reported that the Fe (III) zeolite has an enhanced ability to sorption of Cu (II), and a slight improvement occurs in the case of Cr (VI) and Ni (II). On the other hand, the deterioration was observed in the case of Al (III) adsorption.

Key words

sorption, zeolite, clinoptilolite; Fe(III) clinoptilolite; chromium; nickel; copper; aluminium

INTRODUCTION

Removal of heavy metals (potential toxic elements) from aqueous effluents can be accomplished by chemical precipitation, ion exchange, adsorption, membrane separation as well as electro dialysis (1). Of all various water-treatment techniques, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness (2, 3, 4). One of the advanced adsorbent materials is a natural zeolite (5).

Zeolites are crystalline aluminosilicates with interconnected microporosity (defined as pores in the range or 2 nm or smaller), zeolitic materials have a negatively-charged framework caused by the substitution of Si atoms by Al atoms within the structure, which are usually balanced with extra-framework cations or protons. The most abundant natural zeolite on earth is clinoptilolite which belongs to the zeolite family heulandite, and is characterised as having Si/Al > 4 ratio (6). Generally, the electroneutrality in clinoptilolite is maintained by Na (I), K (I) and Ca (II) ions. Due to its low cost and high availability, clinoptilolite has been heavily utilised in the removal of selected ions (7). However, due to the microporous characteristics of

zeolites, sorption performance is limited because of low diffusion rates (8). Therefore, different treatments of natural zeolites are used. Mechanical treatment of natural zeolites consists of crushing, grinding, screening, drying and eventually dust pelletization. Another procedure is thermal activation (for example clinoptilolite at 400 to 450 °C) or special chemical treatment (using acids, bases, inorganic salts), which improves the catalytic and absorption characteristic of natural zeolites (9). Chemical and thermal treatment may result in the diffusion of cations, and thus effect the location of cations and cell size. The objective is to create a modified form by substitution of the original exchangeable cations to specific ions. The following works may be mentioned as an example,:

Mehmet Burcin et al. (10) studied the adsorption of cadmium on the modified Turkish clinoptilolite. Chemical modification of zeolite was carried out with Na_2CO_3 . The influence of the experimental conditions for the adsorption were examined separately in the following conditions: temperature 25, 45, and 60 °C; ratio of adsorbent / adsorbate was 1/50, 1/100, 1/200 g/mL; concentrations 0.5, 1.0 and 2.0 mol/dm³; contact time 1, 2, 4, 6, 8 and 24 hours. Best results were obtained when the adsorption temperature was 45 °C and sorption time 2 h. The optimum concentration of the solution was 1 mol/dm³, and the ratio of the adsorbate / adsorbent showing the best results with the value of 1/100 g/mL.

Sirotiak and Šutriepka (11) compared the adsorption capacity of modified clinoptilolite (organic and lead form) from the Nižný Hrabovec deposit (Slovakia) and the Hector deposit (USA) with a particle size from 0.2 to 0.6, and the possibility of their use in the removal of toxic metals anionic form - arsenic and chromium in the processes of water purification and treatment. Experiments were carried out in a dynamic mode test (column experiments). Organic form was prepared as follows: 100 mL of octadecylamine solution in a 0.2 mol/L, after acidification to pH = 3 with conc. hydrochloric acid at 80 °C were mixed with 20 g of the adsorbent. After 24 hours of stirring, the solid was filtered off and dried at 60 °C to a constant weight. Inorganic modification of clinoptilolite was prepared by interaction with the lead acetate aqueous solution - 5 % solution of $\text{Pb}(\text{CH}_3\text{COO})_2$ was mixed with 20 g of zeolite and 48 h with vigorous shaking, the solid was filtered off, washed with a sufficient amount of distilled water (to remove physically bound salt of lead acetate on the surface of the adsorbent), and dried at 107 °C to constant weight. Natural clinoptilolite represents a promising starting point in improving the adsorption properties of this material. The main advantage is the increased adsorption capacity of adsorption arsenate and chromate, the possibility of regeneration by sodium chlorate aqueous solution, and thus the possibility of recycling the captured material from treated solutions.

Isaías De la Rosa Gómez et al. (12) used silver form of Mexican clinoptilolite as an antimicrobial agent for the *Escherichia coli* disinfection. At the beginning of the experiment, a sodium form of clinoptilolite was prepared. Clinoptilolite was treated with 1 mol/dm³ NaCl at 90 °C for 24 hours and then washed with deionized water until negative test for chloride. The samples were dried at 85 °C for 5 hours. The sodium form of clinoptilolite was then used to prepare the silver form of clinoptilolite. The Na-clinoptilolite was taken up in 0.1 mol/dm³ AgNO_3 and stirred for 12 hrs in the dark bottle. The solid was centrifuged, washed and dried. These experimental conditions provide the maximum amount of silver incorporated into natural zeolite. It was found that in the process of disinfection of the waste water plays an important role in particle size, amount of silver in the modified zeolite, the nature and type of the zeolite-containing aqueous medium of *E. coli*. The use of silver modification of clinoptilolite for sorption of arsenates was also investigated by Sirotiak (13) Selected modification was based on the low solubility of silver arsenate salts, thus assuming the strong binding of arsenates - chemisorption.

Jelena Pavlovic et al. (14) investigated the surface modification of the natural clinoptilolite from Miner (Vranjska Banja, Republic of Serbia) for its potential use for removing nitrates from water. Preparation of manganese and magnesium exchanged zeolite was as follows: 10 g of clinoptilolite was mixed in a glass beaker with 10 mL of 2.5 mol/dm³ MnCl₂·4H₂O or MgCl₂·H₂O and 1.0 mL of 1 mol/dm³ NaOH. The suspension was heated to 150 °C for 5 hours. Subsequently, the solid was separated by filtration and calcined at 500 °C for 1 hour. After cooling to room temperature, they were kept in a desiccator. Preparation of the ferric form of zeolite was carried out as follows: 10 g of clinoptilolite was mixed with 50 mL of 0.1 mol/dm³ FeCl₃ solution in acetate buffer (pH = 3.6). After 1 hour was added 45 mL of 4 % NaOH, the suspension was stirred and finally was added to 25 mL of 4 % NaCl solution. The suspension is again stirred for one hour at 50 °C, separated by filtration, dried at 105 °C and calcined at 500 °C for 1 hour. All of the modified forms of the zeolite is suitable for the adsorption of nitrate.

Dimirkou and Doula (15) investigated the efficiency of removal of Zn (II) and Mn (II) from drinking water by natural clinoptilolite and its ferric form prepared by mixing 20 g of clinoptilolite, 100 mL of a freshly prepared solution of Fe(NO₃)₃·9H₂O at a concentration 1 mol/dm³ and 180 mL of 5 mol/dm³ KOH solution. The suspension was diluted to 2 liters with twice distilled water and in a closed polyethylene vessel was stored at 70 °C for 60 hours. After the expiration of the period, the precipitate was centrifuged, washed and finally dried. Under the experimental conditions to the natural clinoptilolite has maximum adsorbed amount of Mn (II) 7.69 mg/g, whereas the ferric form of clinoptilolite of 27.1 mg/g. In the case of Zn (II) was adsorption 71.3 mg/g and 97.8 mg/g. The authors concluded that the system could be used to cleaning the contaminated groundwater and wastewater. Similarly prepared ferric form of zeolite was used, for example by Aleksandra Daković et al. (16) for the adsorption of toxic metal Cu (II), Zn (II) and Ni (II), Maria K. Doula (17) for the adsorption of Cu (II), or Šiljeg et al. (18) for the adsorption of As (III) and As (V).

In this paper, we deal with similarly prepared by Fe (III) modification of clinoptilolite from the Slovak deposit of Nižný Hrabovec for removing chromium, nickel, copper and aluminium from their aqueous solutions.

MATERIALS AND METHODS

All of the experiments were performed with water solutions prepared from p.a. chemicals. Stock solutions of Al (III), Cu (II), Ni (II) and Cr (VI) were prepared using Al(NO₃)₃·9H₂O, Cu(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O and K₂CO₄, respectively. As adsorbent was used zeolite tuff from Nižný Hrabovec deposit containing 82 – 84 % of clinoptilolite, 9 % of cristobalite, 2 – 3 % clayey mica and traces of quartz. Grain size of the material was 0.3 - 0.8 mm, specific weight 2.39 g/cm³, bulk density 0.84 g/cm³, porosity 64.8 % effective pore diameter 0.4 nm and specific surface 36 m²/g. (19) The Fe-clinoptilolite system was prepared by mixing 20.0 g of clinoptilolite, 100 mL of freshly prepared 1 mol/dm³ Fe(NO₃)₃ solution, and 180 mL of 5 mol/dm³ KOH solution in a 2 L polyethylene flask. The addition of KOH solution was rapid and with stirring. The suspension was diluted to 2 L with twice-distilled water and was held in a closed polyethylene flask at 70 °C for 60 h. After the appropriate period the reaction vessel was removed from the oven, and the precipitate was centrifuged, washed (until free of nitrate ions) and finally dried.

Experimental determination of kinetic addition was carried out in the following manner: 1 g of tested sample was weighed into closable tubes (natural clinoptilolite or Fe (III) - clinoptilolite), the sample was then quenched in 5 mL of the modelled solution at concentrations of metals 10 and 100 mg/L. The tubes were sealed and placed into orbital shaker with constant

shaking (so that to prevent the sorbent from settling and keep it in a fluidized condition) for 0.25; 0.5; 1; 3; 6 and in modelling solution Ni (II) 8 and 24 hours. After that time, the suspension was centrifuged at 5000 rpm for 5 min. The determinations of metals concentrations in clear solutions before and after experiment were performed by spectrophotometric methods reported in previous papers (20). All experiments were carried out in triplicate. Adsorption amount of adsorbed metal (mg/g) in the equilibrium is given by the formula:

$$a_{eq} = \frac{(C_0 - C_{eq}) \times V}{m},$$

where C_0 (mg/L) is the initial concentration of the metal in the modelled solution, C_{eq} (mg/L) is the equilibrium concentration of the metal in the solution, V (L) is the volume of the modelled solution, m (g) is the weight of the adsorbent. To evaluate the results of the sorption kinetics, software SigmaPlot 11.0 was used, where we used the function model pseudo-first order for mathematical evaluation of measured results.

RESULTS AND DISCUSSIONS

By studying the dependence of the adsorption capacity of the natural clinoptilolite and ferric form at a constant concentration and volume of the input of the modelled solution we observe the following results:

- Chromium – initial concentration 10 mg/L. After 6 h, natural clinoptilolite shows the adsorption 0.0108 mg/g and ferric modification of clinoptilolite 0.0106 mg/g. The time required to equilibrate varied in the range about 6 hours. The solution of Cr (VI) at a concentration of 10 mg/L exhibited better adsorption to the natural clinoptilolite in the early stage, after time their adsorption levelled.
- Chromium – initial concentration 100 mg/L. After 6 h, natural clinoptilolite shows the adsorption 0.2482 mg/g and ferric modification of clinoptilolite 0.2541 mg/g. The time required to adsorption equilibrium for natural clinoptilolite was about 1 hour and for ferric form of clinoptilolite from about 3 hours. As in the previous case, natural zeolite initially showed a better progress, then when it settled.

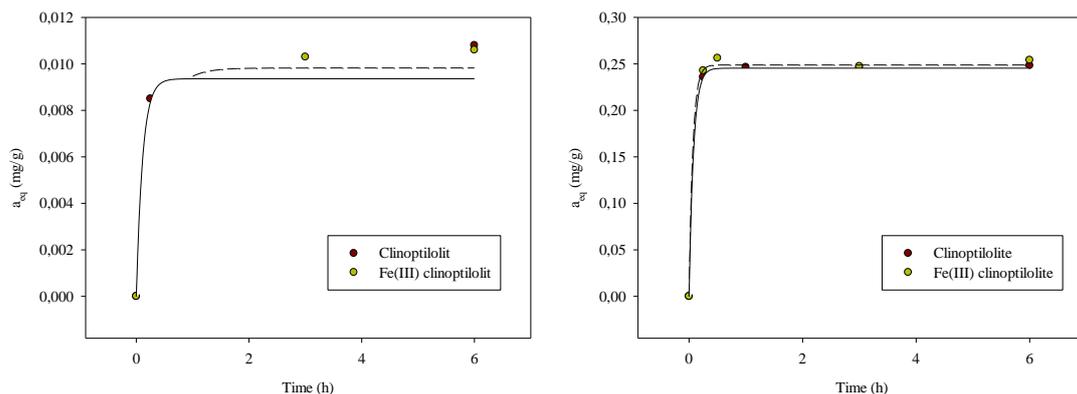


Fig. 1 Kinetics of zeolites adsorption in modelling solution with concentration Cr (VI) 10 and 100 mg/L

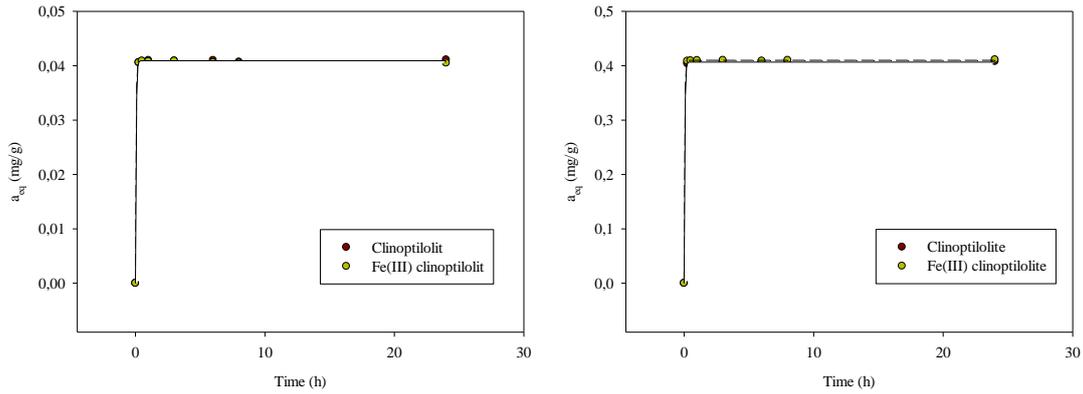


Fig. 2 Kinetics of zeolites adsorption in modelling solution with concentration Ni (II) 10 and 100 mg/L

- Nickel – initial concentration 10 mg/L. After 6 h, natural clinoptilolite shows the adsorption 0.0411 mg/g and ferric modification of clinoptilolite 0.0405 mg/g. The time necessary to equilibrate the adsorbent occurs by both the 15 min. The Ni (II) solution with a concentration of 10 mg/L for both sorbents showed the same adsorption effects throughout the duration of the experiment.
- Nickel – initial concentration 100 mg/L. After 24 h, natural clinoptilolite shows the adsorption 0.4079 mg/g and ferric modification of clinoptilolite 0.4112 mg/g. The time required to equilibrate in both adsorbents is since 15 min and similar pattern as before.

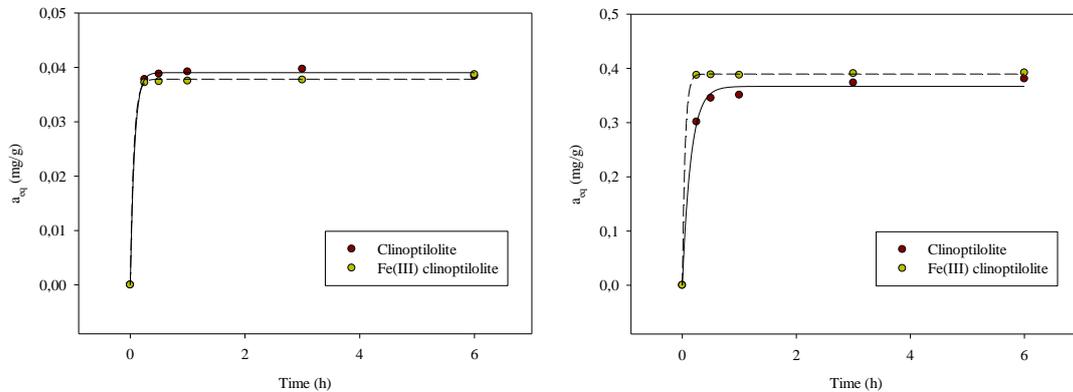


Fig. 3 Kinetics of zeolites adsorption in modelling solution with concentration Cu (II) 10 and 100 mg/L

- Copper – initial concentration 10 mg/L. After 6 h, natural clinoptilolite shows the adsorption 0.0384 mg/g and ferric modification of clinoptilolite 0.0387 mg/g. The time required to equilibrate was in both adsorbents about 15 min. Fe clinoptilolite has a higher adsorption than its natural form.
- Copper – initial concentration 100 mg/L. After 6 h, natural clinoptilolite shows the adsorption 0.3920 mg/g. The time required to equilibrate in both adsorbents was about 1 hour. Fe(III) clinoptilolite has a significantly higher adsorption than its natural form.

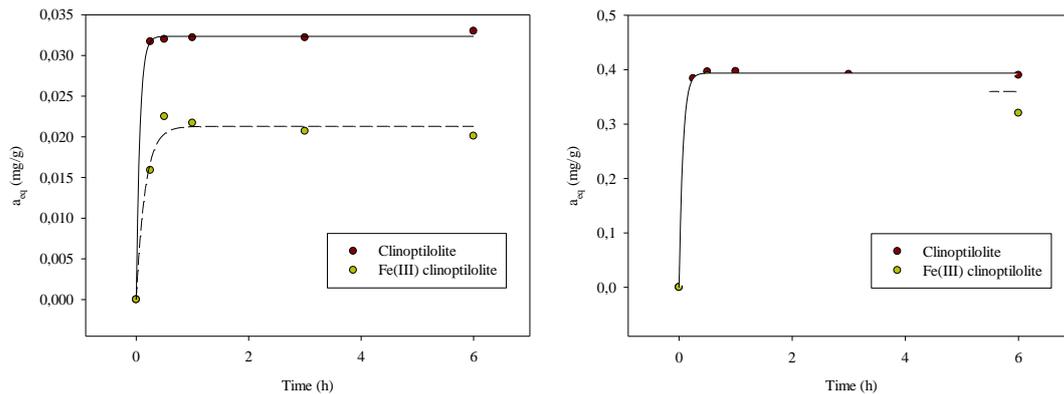


Fig. 3 Kinetics of zeolites adsorption in modelling solution with concentration Al (III) 10 and 100 mg/L

- Aluminium – initial concentration 10 mg/L. After 6 h, natural clinoptilolite shows the adsorption 0.0330 mg/g and ferric modification of clinoptilolite 0.0201 mg/g. The time required to equilibrate was in both adsorbents about 1 hour. Fe(III) clinoptilolite has worse adsorption than its natural form.
- Aluminium – initial concentration 100 mg/L. After 6 h, natural clinoptilolite shows the adsorption 0.3900 mg/g and ferric modification of clinoptilolite 0.3202 mg/g. The time required to equilibrate in both adsorbents was about 1 hour. As in the previous case, Fe(III) clinoptilolite has worse adsorption than its natural form.

CONCLUSION

In the dependence of the adsorption behaviour and capacity of the natural clinoptilolite and ferric form of clinoptilolite at initial concentration 10 mg/L, a relatively small difference between these two adsorbents has been reported. The time to equilibrate adsorption at a ratio of 1 g of adsorbent and 5 ml of the metal solution was in the range of 30 minutes for copper and nickel, 1 h at 6 hrs aluminium and chromium. At initial concentration 100 mg/L, the adsorption characteristics were considerably better, especially for Cu (II). Conversely, deteriorated was occurred in the case of Al (III). The time to equilibrate absorption at same ratio of adsorbent and volume of metal solution was in the range of about 30 minutes and one hour of nickel in chromium, copper and aluminium.

References:

1. WANG, L. K. HUNG, Y. T, LO, H. H and YAPIJAKIS, C. 2004. *Handbook of Industrial and Hazardous Wastes Treatment*. Vol. 1 Marcel Dekker Inc. 1329 p. ISBN: 0-8247-4114-5
2. AHMARUZZAMAN, M. 2011. Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. In: *Advances in Colloid and Interface Science*, **166**(1–2), pp. 36 – 59.
3. KURNIAWAN, T. A., CHAN, G. Z. S., LO, W and BABEL, S. 2006 Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of The Total Environment*, **366**(2–3), pp. 409 – 426.
4. BAILEY, S. E., OLIN, T. J., BRICKA, R. M. and ADRIAN, D.D. 1999. *A review of potentially low-cost sorbents for heavy metals*. *Water Rescure*, 33, pp. 2469–2479.
5. WANG, S. and PENG, Y. 2010. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal*, **156**(1) p. 11 – 24.

6. BARATA-RODRIGUESA, P. M, MAYS, T.J. and MOGGRIDGE, G. D. 2003. Structured carbon adsorbents from clay, zeolite and mesoporous aluminosilicate templates. *Carbon*, **41**(12), pp. 2231 – 2246.
7. SMIKLAS, I., DIMOVI, S. and PLEA, I. 2007. Removal of Cs⁺, Sr²⁺ and Co²⁺ from aqueous solutions by adsorption on natural clinoptilolite. *Applied Clay Science*, **35**, 12, pp. 139–144.
8. HUA, Z.L., ZHOU, J. and SHI, J.L. 2011: Recent advances in hierarchically structured zeolites: synthesis and material performances. *Chemical Communications*, **47**, pp. 10536–10547.
9. RYBÁR, P. 1999. *Utilization and protection of earth resources*. Košice: Elfa, 103 p. ISBN 8088964334
10. BURÇIN, M., et al. 2013. Cadmium Adsorption on Modified Turkish Clinoptilolite. *International Journal of Chemical, Environmental & Biological Sciences*, **51**(5), pp. 727-731. ISSN 2320-4079
11. SIROTIK, M. and ŠUTRIEPA, M. 2002. Sorption of anionic forms of As and Cr on the modified clinoptilolite. In: *Proceedings of Geochémia 2002*, pp. 51-52. ISBN 80-88974-42-9
12. ROSA-GÓMEZ, I., et al. 2010. Silver-Modified Mexican Clinoptilolite-Rich Tuffs With Various Particle Sizes as Antimicrobial Agents Against Escherichia coli. *Journal of Mexican Chemical Society*, **54**(3), pp. 139-142. ISSN 1870-249X
13. SIROTIK, M. 2000. Arsenate sorption on modified clays. In: *Proceedings of Geochémia 2000*, pp. 69-71. ISBN 80-88974-23-2
14. PAVLOVIC, J., et al. 2013. Surface modification of the natural clinoptilolite for its potential use for the nitrate removal from water media. In: *Proceedings of the 5th Serbian-Croatian-Slovenian Symposium on Zeolites*. ISBN 978-86-82139-41-6
15. DIMIRKOU, A. and DOULAB, M. 2008. Use of clinoptilolite and an Fe-overexchanged clinoptilolite in Zn²⁺ and Mn²⁺ removal from drinking water. *Desalination*, **224**(1-3), p. 280-292. ISSN: 0011-9164
16. DAKOVIĆ, A., et al. 2009. Adsorption of toxic metals by iron (III) modified clinoptilolites. In: *Proceedings of 2nd Slovenian-Croatian Symposium on Zeolites*. ISBN 978-953-55373-1-1
17. DOULA, M. 2007. Synthesis of a clinoptilolite–Fe system with high Cu sorption capacity. *Chemosphere*, **67**(4), p. 731–740. ISSN 0045-6535
18. ŠILJEG, M., CERJAN STEFANOVIĆ, Š., MAZAJ, M., NOVAK TUŠAR, N., ARČON, I., KOVAČ, J., MARGETA, K., KAUČIČ, V. and ZABUKOVEC LOGAR N. 2009. Structure investigation of As(III-) and As(V-) species bound to Fe-modified clinoptilolite tuffs. *Microporous and Mesoporous Materials*, **118**(1–3) 1, pp. 408-415
19. ŠAMAJOVÁ, E. and KRAUS, I. 1978. *Mineral composition and genesis of clay materials, zeolite and perlite*. Manuscript - Partial research report. Geological Survey of Comenius University Bratislava, 291 p.
20. SIROTIK, M. BARTOŠOVÁ, A. and BLINOVÁ, L. 2014. UV-VIS spectrophotometric determinations of selected elements in modelled aqueous solutions. *Journal of Environmental Protection, Safety, Education and Management*, **1**(2014). ISSN 1339-5270

Reviewers:

prof. Ing. Maroš Soldán, PhD.
 doc. Ing. Jana Müllerová, PhD.