

*Original Scientific paper*  
*UDC 553.61:[ 669.775:579.6*  
*DOI: 10.7251/afts.2018.1019.045D*  
*COBISS.RS-ID 7712280*

## STUDY OF Cu(II) ADSORPTION BY BENTONITE AND FOLLOWING REGENERATION BY BIOLEACHING

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### ABSTRACT

The natural bentonite and bentonite/iron oxide composite were used as sorbents of Cu(II). Their sorption properties were examined under the different conditions such as pH of the solution, initial metal ion concentration. The bentonite removed 71 % Cu(II) while composite 90 %. Their maximum adsorption capacities were 34.1 and 44.4 mg Cu(II) g<sup>-1</sup>, respectively. The chemical regeneration of composite sorbent by organic acids (oxalic, citric) led to partial Cu(II) dissolution. The hydrochloric acid caused its structural destruction. For the bacterial regeneration, the sorbents were inoculated with heterotrophic indigenous bacteria. After 10 days the bacteria released approximately 80 % of loaded Cu(II), leaving the sorbents stable. Longer treatment and higher concentration of metal cations caused the reverse sorption of Cu(II) by bacteria. The regenerated sorbent was successfully repeatedly used for the Cu(II) adsorption.

Keywords: *bentonite, Cu(II) adsorption, chemical leaching, bioleaching*

### INTRODUCTION

Due to the rapid increase in global industrial activities, the heavy metal pollution became serious. The hazardous heavy metal pollution of wastewater is one of the most important environmental problems in the world. A wide range of treatment technologies such as chemical precipitation, coagulation-flocculation, flotation, ion exchange, adsorption and membrane filtration have been developed for heavy metal removal. Adsorption by low-cost sorbents and biosorbents is considered as an effective and economic method for wastewater treatment. Naturally occurring clays and clay minerals are of paramount importance in the field of environmental and waste management. Bentonite is composed mainly of montmorillonite, the most common mineral of the smectite group [1-3]. The adsorption properties of bentonites are determined by their chemical and mineralogical composition, also, various ways of modifications and treatments to enhance them were studied. Surface decoration of the aluminosilicate minerals with magnetic nanoparticles had led to a new class of composite materials, which could be also used for the environmental purposes as adsorbents of the organic and inorganic compounds and metal ions [4-6].

There are few significant deposits of bentonite in East part of Slovakia (Kuzmice, Fintice, Lastovce) as well as in Central Slovakia (Stará Kremnička — Jelšový potok and Lieskovec). These bentonites are used for industrial purposes, and their geological, geotechnical and sorption properties are still studied by Slovak researchers for their wider utilization [7-15].

In spite of cumulation of sorbents after their use, relatively small number of studies was devoted to their regeneration. The recovery of bounded metal cations, regeneration and reuse of the sorbent makes the sorbent interesting from the economical point of view. The adsorbed ions can be removed by conventional methods, what are usually non economical, or cause the sorbents destruction. In a few articles the clinoptilolite regeneration was studied. The natural zeolite was used for Zn(II) and Pb(II) adsorption from the aqueous solutions, MBR permeate and from the primary treated wastewater. Then the effect of desorbing solutions (HNO<sub>3</sub>, KCl, NaCl and NH<sub>4</sub>Cl) on the metals recovery was studied. Also, several adsorption/desorption cycles were conducted. The highest desorption performance was achieved using 1 M KCl for zinc and 3 M KCl for lead. Regeneration effect for lead reduced within the first three cycles to 80-85 % and to less than 50 % after nine regeneration cycles. The recovery of zinc was lower than 50 % after four cycles, what was attributed to the lower amount of adsorbed zinc ions on zeolite in comparison to lead ions [16].

The clinoptilolite was also investigated as a possible regenerable sorbent for acid rock drainage. NaCl, NaCO<sub>3</sub>, NaHCO<sub>3</sub>, NaOH, NaOAc and Na<sub>2</sub>EDTA were tested as possible extractants from clinoptilolite samples spiked with Zn(II) and Cu(II) The rank of desorption effectiveness was EDTA > NaCl > NaNO<sub>3</sub> > NaOAc > NaHCO<sub>3</sub> > Na<sub>2</sub>CO<sub>3</sub> > NaOH > Ca(OH)<sub>2</sub> and desorption of Zn(II) and Cu(II) was found to be dependent on pH, with an optimum range from 2.5 to 4.0. For cyclic adsorption/desorption, adsorption remained satisfactory for six to nine regenerations with EDTA and NaCl, respectively [17]. The influence of the pretreatment on the clinoptilolite sorption properties and on its regeneration was studied by Gedik et al. Four different chemicals (NaCl, KCl, CaCl<sub>2</sub> and HCl) were tested for their performance in both pretreating clinoptilolite for higher Cd removal capacity, and regenerating it to sustain or improve Cd removal capacity. Successive Cd removal and regeneration cycles were conducted in continuous mode using duplicate glass columns. In order to optimize pretreatment of clinoptilolite bed to achieve the most favorable Cd removal capacity, the effect of total volume, pH and water quality of pretreatment solution (1 M NaCl) was also investigated. Five exhaustion and regeneration cycles were conducted and clinoptilolite exhibited a 36% higher removal capacity in the last three runs when compared to the first two runs [18].

Polymer-clay composites were designed to adsorb selenium from water. The chitosan-clay composite and Al-oxide columns were regenerated by rinsing with NaCl and NaOH to release the adsorbed sulphate and selenium. Increasing the pH (rinsing with NaOH) released 65 and 44% of the adsorbed sulfur and selenium, respectively. Desorption by rinsing with NaCl was lower reaching 42 and 11% for sulfur and selenium, respectively. The performance of the composite to re-adsorb selenium was tested on a composite rinsed with NaOH. The regenerated composite re-adsorbed 50 % more selenium than was its released amount. The amount of sulfur re-adsorbed by the regenerated composite increased only 10 %. The NaOH solution did not promote the anion desorption from the Al-oxide filters. By using NaCl solution 15 and 33% of the selenium and sulfur was desorbed, respectively. The regenerated filter re-adsorbed more than twice the amount of selenium that was released. These preliminary results indicate that the regeneration improved selenium removal by the composite and by the Al-oxide [19]. Zhu et al. described in their review the regeneration of spent organoclays [20].

The recovery of bound cadmium and the subsequent reuse of biosorbents - alga *Ecklonia maxima* and the waste product from the manufacture of Kelpak were investigated by Stirk and van Staden. Acids (HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) and the chloride salts (NaCl and CaCl<sub>2</sub>) were more effective at desorbing cadmium ions than the carbonate salts (NaHCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>) and the chelator Na<sub>2</sub>EDTA. The sorbent derived from ground *Ecklonia maxima* could be used for more than four adsorption-desorption cycles whereas the sorbent derived from the Kelpak Waste could only be used effectively for up to three adsorption-desorption cycles [21]. The thermal regeneration of montmorillonite – Cu(II)/Fe(III) oxides after the humic acid adsorption was studied by Peng et al. The temperature to achieve good regeneration efficiency were determined to be 300 °C and the regenerated adsorbent was still magnetic and approximately had as high specific saturation magnetization and good adsorption capacities as the as-prepared adsorbent [22].

In the most methods, either chemical agents (e.g., extraction agents, oxidation agents) or auxiliary (e.g., light, heat) have to be added, which make the regeneration process effective and/or rapid, but the costs of the processes are relatively high. In the bioregeneration method, the microbes can grow

without the addition of expensive chemical agents or auxiliary, which can make the regeneration cheaper significantly. In addition, the bioregeneration method can be performed in situ. However, the processing time is always longer.

There are a massive presence of Cu(II) contaminated soils in the eastern part of Slovakia. As the main aim of the work was to conduct the introductory experiments of sorbents bioregeneration, the bacteria present in these soils were isolated and used for the experiments. Therefore, the sorption of Cu(II) from the model solution onto natural bentonite and bentonite/iron oxide composite was studied. The dependence on pH of the solution, initial metal ion concentration was tested. The desorption of bounded Cu(II) was performed by chemical, as well as by biological methods and compared.

## EXPERIMENTAL

### Sorbents and their properties

Natural bentonite, containing montmorillonite with crystallochemical formula  $[\text{Si}_{7.95}\text{Al}_{0.05}][\text{Al}_{3.03}\text{Fe}_{0.22}\text{Mg}_{0.75}]\text{O}_{20}(\text{OH})_4(\text{Ca}_{0.42}\text{Mg}_{0.04}\text{Na}_{0.01}\text{K}_{0.01})$ , originated from the Slovak deposit Jelšový potok [23]. The sample used for the investigation was isolated from the 4 % water suspension of bentonite and treated by sedimentation method with the aim to obtain almost monomineral fraction with the particle size below 20  $\mu\text{m}$ .

The composite material was prepared by the method of precipitation of the iron oxide onto the bentonite surface, according to the method described previously [24]. The bentonite/iron oxide weight ratio in composite was 1:1.

### Sorbents characterization

The powder X-ray diffraction (XRD) patterns of natural bentonite and composite material were recorded using a Philips PW1820 diffractometer (The Netherlands) equipped with a  $\text{CuK}\alpha$  radiation (40 kV, 40 mA). The data were analysed using Philips Software, X'PertHigh Score with PDF-2 Database.

Textural properties of sorbents were determined from the adsorption and desorption isotherms measured with the ASAP 2400 apparatus (Micrometrics, USA) with the method of physical adsorption of nitrogen at 77 K. The experimental data were processed by the BET (Brunauer, Emmett, Teller) isotherm in the range of relative pressure 0.05–0.2  $p/p_0$ . The value of total pore volume  $V_a$  was estimated from the maximum adsorption at relative pressure close to the saturation pressure. [25].

### Sorption experiments

All chemicals used in this study were of analytical grade and solutions were prepared using the double distilled water. The stock solutions (1000  $\text{mg L}^{-1}$  and 100  $\text{mg L}^{-1}$ ) of Cu(II) were prepared by dissolving the solid  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in distilled water. Then they were diluted to obtain standard solutions containing 10 – 500  $\text{mg Cu(II) L}^{-1}$ . The diluted NaOH and HCl were used to adjust the pH of the solutions. The sorption measurements were made by a batch technique at the ambient temperature using the rotary shaker (30 rpm). Through the study, the pH varied from 2 to 9, initial Cu(II) concentration in model solutions from 10 to 500  $\text{mg L}^{-1}$ . A known amount of sorbent was added into the plastic tubes containing 15 ml of Cu(II) solution of known concentration and pH. The suspensions were shaken for 24 hours to reach equilibrium and then consequently filtered using the filter paper. The supernatant solutions were analyzed by the atomic absorption spectrometry (AAS, Varian 240 RS/2400).

The adsorbed amount of Cu(II) per unit mass was calculated by the following equation (1):

$$q_e = (C_0 - C_e) * V / m_s, \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentration ( $\text{mg L}^{-1}$ ),  $V$  is volume of the solution (L),  $m_s$  is the mass of the sorbent (g).

The effect of metal ion removal (%MR) was calculated using the equation (2):

$$\%MR = (C_0 - C_e)/C_0 * 100 \quad (2)$$

The linearized Langmuir and Freundlich models were used for the analyses of the adsorption isotherms [26]. Also, the effect of the sorbents was calculated from the equilibrium adsorption isotherms.

### Chemical and bacterial regeneration of composite

The efficiency of using organic acids appearing in bacterial metabolites (citric and oxalic) as well as an inorganic hydrochloric acid was studied in regeneration of composite sample and was compared with the bacterial regeneration. For the bioleaching experiments K and R bacteria were used denoting the source of soils and sediments contaminated by Cu(II), from where they were isolated Fig.1. (K – contaminated soil near the metallurgical factory Kovohuty Krompachy, Slovakia and R – sediment loaded with Cu(II) from the river Hornád, locality near the Ružín dam, Slovakia). As the dominant bacteria the strains of Bacillus sp. were identified in both isolates. For some extra bioregeneration experiments with abiotic controls, the K bacteria and pure strain of Bacillus cereus were selected. The experiments were realized in test tubes containing the same ratio of powdered sample and a liquid medium as during the Cu(II) sorption.

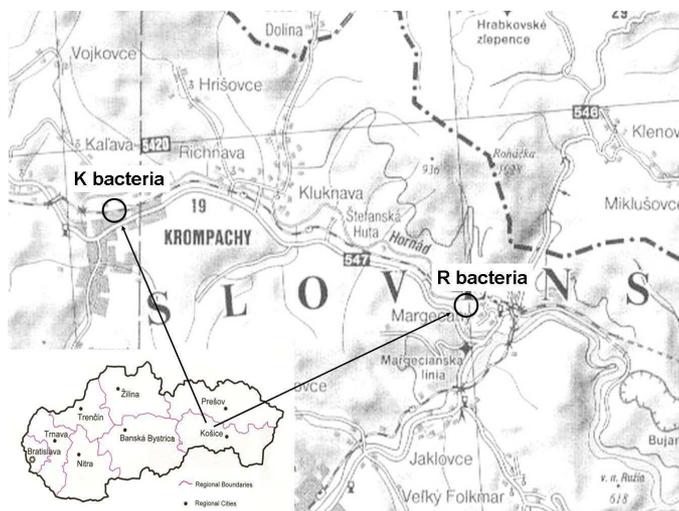


Figure 1 Map with marked locations of bacteria isolation

## RESULTS AND DISCUSSIONS

### Sorbents characterization

The dominant phase in natural sample determined from the XRD analysis was montmorillonite, Fig. 2. Diffraction signals of montmorillonite in composite sample decreased in intensity due to presence of precipitated iron oxides on the bentonite surface. Probably, the shift of basal spacing of montmorillonite -  $d(001)$  from 1.5 nm to 1.23 nm is caused by exchange of cations present in the interlayer space of natural montmorillonite during the bentonite modification in water environment [27]. Except the Fe oxidized phase goethite phase ( $\alpha$ -FeOOH) was observed in composite sample, too. In our previous study the Mössbauer spectroscopy was used to determine the present iron oxide phase in the composite sample [28-29]. The analyses showed the presence of maghemite, as well as goethite in the composite sample, what corresponds with the result obtained from the XRD analysis.

The textural properties of composite were analyzed by low temperature nitrogen adsorption method and compared with natural bentonite. The value of specific surface area of natural bentonite increased after the precipitation of iron oxide particles on its surface almost twice, Table 1. Also, similar

increase of total pore volume was detected, possibly in consequence of iron oxide agglomeration on the bentonite surface.

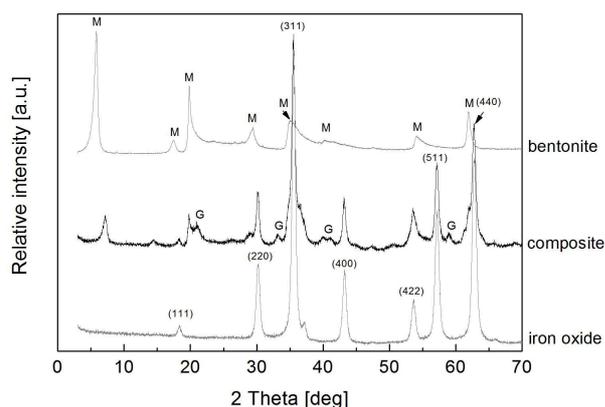


Figure 2 XRD pattern of natural bentonite, composite and synthesized iron oxide without the bearer (M – montmorillonite, G – goethite)

Table 1 Textural parameters of natural bentonite and composite

| Sample    | $S_{\text{BET}}$<br>[ $\text{m}^2 \text{g}^{-1}$ ] | $V_a$<br>[ $\text{cm}^3 \text{g}^{-1}$ ] |
|-----------|--|--|
| bentonite | 39.4   | 0.096                                    |
| composite | 73.7   | 0.216                                    |

### Sorption experiments

The pH of the solution influences the sorption of metal ions by sorbent. The uptake of metal ions by natural and modified bentonite slightly increased in the pH range from 3.0 to 6.0, higher adsorbed amounts was observed for natural bentonite, Fig. 3. Generally, when the pH value is higher than 5.5, soluble Cu(II) ions begin to precipitate as metal hydroxides because of the increasing concentration of OH<sup>-</sup> ions in solution. From this reason, almost no Cu(II) ions were detected in the solution in the range of pH 7.0 – 9.0 by the spectrometry measurement. These values were not considered for the data evaluation due to observable precipitation of Cu(II) ions in the solution. Also the dissolution of Fe(III) from the composite was studied. The precipitated iron oxide particles on the bentonite surface were stable in the solutions with pH > 4. On the basis of these results, for the next adsorption experiments the pH value 5 was selected.

In the initial stages of the adsorption, the amount of Cu(II) cations adsorbed at the equilibrium increased rapidly with the increasing initial cations concentration, then increased slowly, Fig. 4. Higher metal uptake was observed for the composite in the whole studied concentration range. Adsorption isotherm is an empirical relationship used to predict how much solute can be adsorbed by sorbent. The adsorption isotherm is defined as a graphical representation showing the relationship between the amount adsorbed by a unit weight of sorbent and the amount of adsorbate remaining in a test medium at equilibrium. The distribution of metal ions between the liquid and solid phase can be described by several isotherm models, the well-known are Langmuir and Freundlich, Figs. 5, 6.

The Langmuir model, often applied by various workers for the adsorption of variety of compounds, properly fitted the experimental data in the studied range of the initial concentrations. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface. Once a site is filled, no further sorption can take place at that site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved.

Its linear form is represented by Eq. (3):

$$C_e/q_e = 1/Q_0 \cdot b + C_e/Q_0, \quad (3)$$

where  $C_e$  and  $q_e$  are equilibrium solute concentration and equilibrium adsorption capacity, respectively,  $Q_0$  is Langmuir constant representing maximum adsorption capacity (amount of adsorbed metal ions per 1 gram of sorbent) and  $b$  is adsorption equilibrium constant relates to the energy of adsorption. Their values were obtained from the slope and interception of the plot, Fig. 7 and are presented in Table 2. The Freundlich isotherm is introduced as an empirical model. Its linear form is represented by Eq. (4):

$$\log q_e = \log K_f + 1/n \log C_e, \quad (4)$$

where  $K_f$  and  $n$  are Freundlich constants which correspond to adsorption capacity and adsorption intensity, respectively.

Freundlich equilibrium constants were determined from the plot of  $\log q_e$  versus  $\log C_e$  from Fig. 8, on the basis of the linear form of Freundlich equation. The  $n$  value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if  $n = 1$ , then adsorption is linear; if  $n < 1$ , then adsorption is a chemical process; if  $n > 1$ , then adsorption is a physical process. The value in Freundlich equation was found to be 3.2–4.9, Table 3. The situation is most common and may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent-adsorbate interaction with increasing surface density and the values of within the range of 1–10 represent good adsorption.

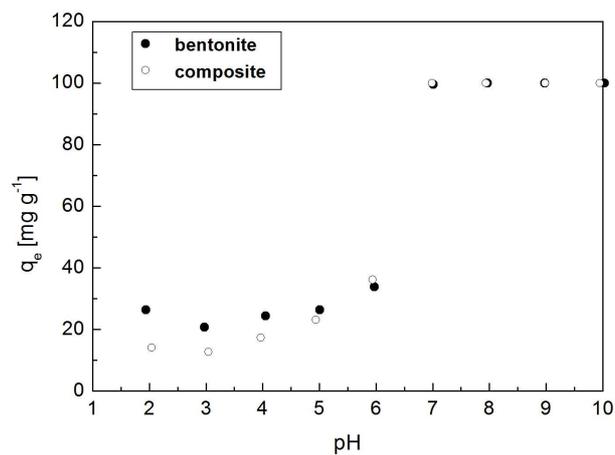


Figure 3 Dependence of sorption capacity of studied sorbents on the pH of the solution ( $C_0 = 100 \text{ mg Cu(II) L}^{-1}$ ,  $m_s = 1 \text{ g L}^{-1}$ , pH range 2 – 10,  $t = 24 \text{ hrs}$ )

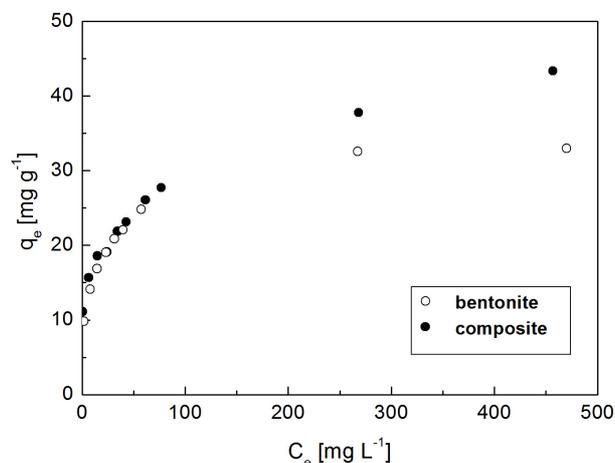


Figure 4 Adsorption of Cu(II) onto natural bentonite and composite in dependence of initial metal ion concentration ( $C_0 = 10 - 500 \text{ mg Cu(II) L}^{-1}$ ,  $m_s = 1 \text{ g L}^{-1}$ , pH = 5,  $t = 24 \text{ hrs}$ )

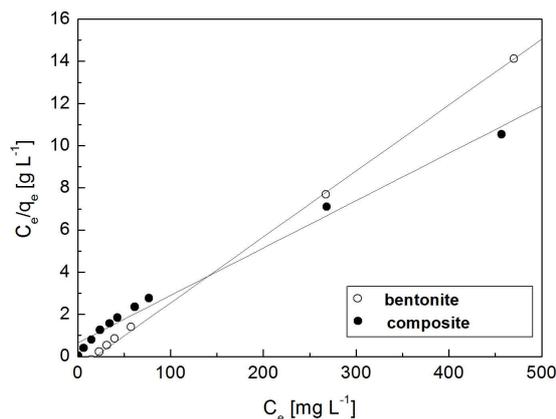


Figure 5 Linearized Langmuir model applied to the obtained adsorption isotherms of Cu(II) onto natural bentonite and composite ( $C_0 = 10 - 500 \text{ mg Cu(II) L}^{-1}$ ,  $m_s = 1 \text{ g L}^{-1}$ ,  $\text{pH} = 5$ ,  $t = 24 \text{ hrs}$ )

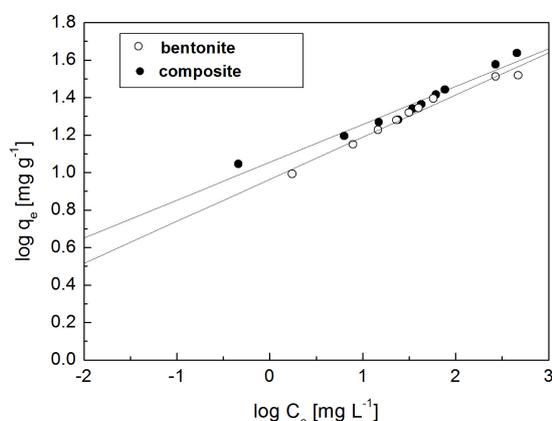


Figure 6 Linearized Freundlich model applied to the obtained adsorption isotherms of Cu(II) onto natural bentonite and composite ( $C_0 = 10 - 500 \text{ mg Cu(II) L}^{-1}$ ,  $m_s = 1 \text{ g L}^{-1}$ ,  $\text{pH} = 5$ ,  $t = 24 \text{ hrs}$ )

Table 2 Langmuir and Freundlich parameters for Cu(II) sorption onto bentonite and composite

| Sample    | Langmuir                 |                        |        | Freundlich              |        |        |
|-----------|--------------------------|------------------------|--------|-------------------------|--------|--------|
|           | $Q_0 [\text{mg g}^{-1}]$ | $b [\text{L mg}^{-1}]$ | $R^2$  | $K_f [\text{L g}^{-1}]$ | $1/n$  | $R^2$  |
| bentonite | 34.1                     | 0.064                  | 0.9988 | 2.624                   | 0.2247 | 0.9772 |
| composite | 44.4                     | 0.034                  | 0.9878 | 2.871                   | 0.2022 | 0.9588 |

In both cases, linear plots were obtained, which reveal the applicability of these isotherms on the ongoing adsorption process. However, comparing the correlation coefficients, Table 2, the Langmuir model better characterized the sorption process. Higher value of maximum adsorption capacity,  $44.4 \text{ mg Cu(II) g}^{-1}$ , was obtained for the composite sorbent.

Table 3 compares the maximum sorption capacities of Cu(II) for different natural and modified bentonites and smectites reported in research studies. Among the natural materials the highest value of maximum adsorption capacity showed the bentonite used in this study. Comparing the natural samples originated from the same locality Jelšovský potok, the sample with particle size under  $200 \mu\text{m}$  reached lower adsorption capacity of Cu(II) than the Na-saturated fraction with particle size under  $2 \mu\text{m}$  [34]. The equal value was also obtained by Víglašová et al. [35]. The highest maximum adsorption capacity proved the natural sample contained almost monomineral fraction of montmorillonite (this study). The magnetic modification enabled to enhance the bentonite adsorption capacity, comparable

with capacity published for acid activated bentonite [30]. Additionally magnetic sorbents could be separated from the medium after the adsorption process in high gradient magnetic field [36].

Table 3 Comparison of adsorption capacity of Cu(II)

| Adsorbent                  | $Q_0$ [mg g <sup>-1</sup> ] | Reference     |
|----------------------------|-----------------------------|---------------|
| Raw bentonite              | 32.17                       | [30]          |
| Acid activated bentonite   | 42.41                       |               |
| Natural Ca-bentonite       | 32.26                       | [31]          |
| Na-bentonite               | 17.88                       | [32]          |
| Natural bentonite          | 11.34                       | [33]          |
| Bentonite Jelšový potok    | 23.75                       | [34]          |
| Bentonite Lieskovec        | 7.27                        |               |
| Na-bentonite Jelšový potok | 28.33                       |               |
| Bentonite Jelšový potok    | 28.63                       | [35]          |
| Bentonite Lieskovec        | 15.94                       |               |
| Illite/smectite            | 4.44                        |               |
| bentonite                  | 34.10                       | In this study |
| composite                  | 44.40                       | In this study |

The next goal of this work was the bioregeneration of the sorbents. For this purpose much higher amounts of studied samples are needed. For the subsequent bioremediation 10 grams of sorbents per liter were used for Cu(II) adsorption. The initial metal ion concentration of the solution was 100 mg Cu(II) L<sup>-1</sup> and pH 5. Under these experimental conditions the bentonite and composite removed from the solution 71 % and 90 % Cu(II), respectively.

### Chemical regeneration of composite

The treating of the composite with oxalic, citric and hydrochloric acids was proved and considered. After 2 days the oxalic acid dissolved 24 % of adsorbed Cu(II), the citric acid 34 % and the hydrochloric acid 95 %. Unfortunately, together with Cu(II) also high amount of Fe(III) was liberated from the composite surface (253 mg L<sup>-1</sup>, 81 mg L<sup>-1</sup> and 333 mg L<sup>-1</sup>, respectively).

### Bacterial regeneration of the sorbent by R and K bacteria and *Bacillus cereus* sp.

The results published previously by Dankova et al. [37] confirmed the success of sorbent regeneration by selected bacteria. In the beginning of bioregeneration there was no significant difference in the activity of R and K bacteria, although after 7 days slight variations in their activity were observed, Fig 7. During the bacterial treatment almost 82 % of Cu(II) was released from the bentonite and 78 % from the composite. Revealing the effect of bacteria on Fe(III) release, the same bacterial treatment was applied also to the composite without adsorbed Cu(II).

The dissolution of Fe(III) from the composite loaded with Cu(II) turned to obvious when the precipitation of Cu(II) was observed. It is supposable that after finishing Cu(II) dissolution, the bacteria started to release Fe(III) ions from the composite. Although the liberation of Fe(III) from the composite without adsorbed Cu(II) in the case of both (R and K) bacteria was much higher than from the composite loaded with Cu(II), Fig. 8.

During the experiments focused on the comparison of the activity of K bacteria (presenting a mixture of bacterial strains of *Bacillus* sp.) and a selected bacterial strain (*Bacillus cereus*), no significant difference was observed, Fig. 9. On the basis of these results it can be concluded, that the isolation of selected species for bioregeneration purposes is not essential.

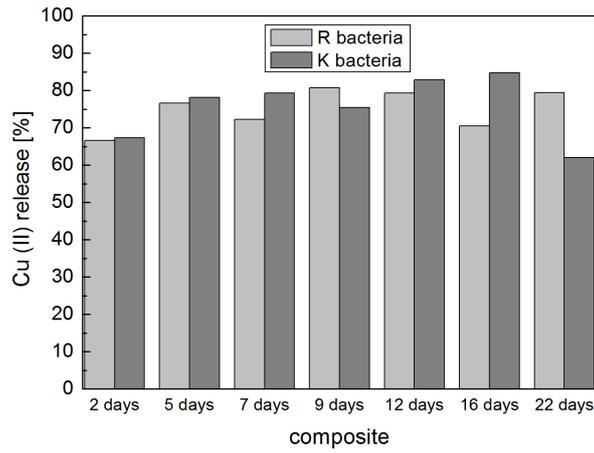


Figure 7 The effect of R and K bacteria on Cu (II) release from the composite material

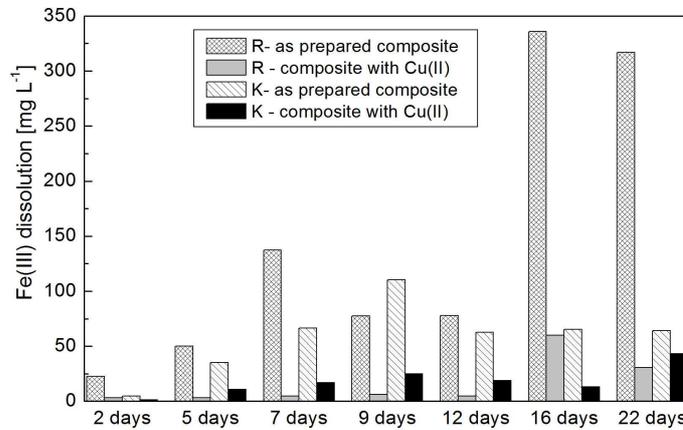


Figure 8 The effect of R and K bacteria on Fe(III) dissolution from the as-prepared composite and from the composite after the Cu (II) adsorption

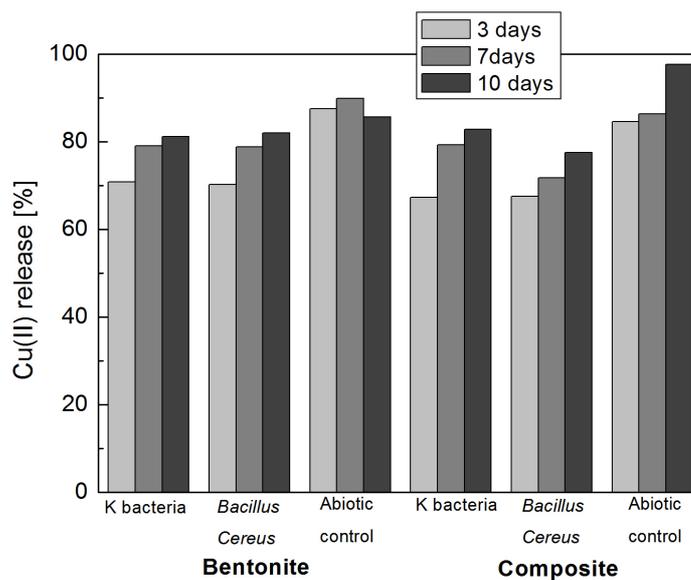


Figure 9 The effect of K bacteria and the strain Bacillus cereus on sorbent regeneration during the selected days in comparison with abiotic control

## Abiotic control

The abiotic controls were made in parallel with the regeneration experiments. Unlike in abiotic controls, the sorbents were treated by the same medium used for the bioleaching but without bacteria. According to the comparison of Cu(II) release, in abiotic controls higher amounts of dissolved Cu(II) were measured as for solutions with K bacteria and strain *Bacillus cereus*, Fig. 9. That is probably caused by presence of strong chelators and leachates used for medium preparation. To verify the effect of bacteria on the Cu(II) release, the same experiments were repeated with media containing only the bacteria (without chelators and leachates). The measurements were made after 2 and 5 days. For both of sorbents, the bacterial efficiency decreased after 5 days of bioleaching. It should be mentioned that bacteria need also the chelators for their activity. Therefore the conditions and optimization of this process should be more studied. Also, probably the reverse sorption of dissolved Cu(II) by bacteria in the medium takes place. The same phenomenon was observed during the bioleaching of contaminated soils and sediments by heterotrophic bacteria [38].

## CONCLUSION

The natural bentonite and bentonite/iron oxide composite were used as Cu(II) sorbents. The modified bentonite showed better sorption properties than natural. It was shown and proved, that modification of natural clay by iron oxide particles improves its sorption properties. The removal of Cu(II) was studied due to the following introductory experiments of sorbents regeneration by the heterotrophic indigenous bacteria isolated from the soils and sediments loaded by Cu(II). The results from the bioleaching were compared with the chemical methods, those were not appropriate for sorbent regeneration; except of Cu(II), high amount of Fe(III) was dissolved from the composite surface in a short period of time. The bacterial treatment was very effective in Cu(II) release from the bentonite and composite surface. No significant difference in activity of K bacteria and bacterial strain of *Bacillus cereus* was observed. The bioregenerated sorbent, used repeatedly for the adsorption, reached lower value of adsorption capacity than as-prepared, but was still sufficient for removal of heavy metal ions from the solutions.

Utilization of bacteria for the regeneration of sorbent represents an ecological method, easy applicable for in-situ processes [39]. Therefore our study will continue with the aim to specify the conditions supporting the bioregeneration. Also, the as-prepared composite material was treated by R and K bacteria to study the Fe(III) dissolution from the composite and following was used for another sorption experiments. The bacteria transformed presence Fe particles to active forms, which participated in adsorption process [40]. Nor only the sorbent regeneration by bacteria is interesting from the environmental and economical point of view. But also the adhesion of heterotrophic indigenous bacteria onto the sorbent surface and bioleaching as improvement of sorption properties of materials could be applicable as low-cost and ecological methods for wastewaters treatment.

### List of symbols

|                  |   |
|------------------|---|
| $S_{\text{BET}}$ | specific surface area [ $\text{m}^2 \text{g}^{-1}$ ]                              |
| $V_a$            | total pore volume [ $\text{cm}^3 \text{g}^{-1}$ ]                                 |
| $C_0$            | initial metal ion concentration [ $\text{mg L}^{-1}$ ]                            |
| $m_s$            | sorbent concentration [ $\text{g L}^{-1}$ ]                                       |
| $C_e$            | equilibrium metal ion concentration [ $\text{mg L}^{-1}$ ]                        |
| $q_e$            | amount of metals adsorbed at equilibrium [ $\text{mg g}^{-1}$ ]                   |
| $Q_0$            | Langmuir constant representing maximum adsorption capacity [ $\text{mg g}^{-1}$ ] |
| $b$              | Langmuir sorption equilibrium constant [ $\text{L mg}^{-1}$ ]                     |
| $K_f$            | Freundlich constant corresponds to adsorption capacity [ $\text{L g}^{-1}$ ]      |
| $1/n$            | Freundlich constant corresponds to adsorption intensity [-]                       |
| $R^2$            | coefficient of determination [-]  |

Acknowledgement: The authors are thankful for financial support of VEGA grant 2/0049/15.

(Received June 2018, accepted September 2018)

## REFERENCES

- [1] Fu, F., Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management*, vol. 92, pp.407-418.
- [2] Sousa, F.W., Sousa, M.J., Oliveira, I.R.N., Oliveira, A.G., Cavalcante, R.M., Fechine, P.B.A., Neto, V.O.S., Keukeleire, D., Nascimento, R.F. (2009). Evaluation of a low-cost adsorbent for removal of toxic metal ions from wastewater of an electroplating factory. *Journal of Environmental Management*, vol. 90, pp.3340-3344.
- [3] Sen Gupta, S., Bhattacharyya, K.G. (2012). Adsorption of heavy metals on kaolinite and montmorillonite: A review. *Physical Chemistry Chemical Physics*, vol. 14, pp. 6698-6723.
- [4] Wang, Ch., Juang, L.C., Lee, C.K., Hsu, T.C., Lee, J.F., Chao, H.P. (2004). Effects of exchanged surfactant cations on the pore structure and adsorption characteristics of montmorillonite. *Journal of Colloid Interface Science*, vol. 280, pp. 27-35.
- [5] Hua, J. (2015). Synthesis and characterization of bentonite based inorgano-organo-composites and their performances for removing arsenic from water. *Applied Clay Science*, vol. 114, pp. 239-246.
- [6] Hashemian, S., Saffari, H., Ragabion, S. (2015). Adsorption of cobalt(II) from aqueous solutions by Fe<sub>3</sub>O<sub>4</sub>/bentonite nanocomposite. *Water, Air and Soil Pollution*, vol. 226, pp. 2212-2221.
- [7] Galamboš, M., Rosskopfová, O., Kufčáková, J., Rajec, P. (2011). Utilization of Slovak bentonites in deposition of high-level radioactive waste and spent nuclear fuel. *Journal of Radioanalytical and Nuclear Chemistry*, vol. 288, pp.765-777.
- [8] Galamboš, M., Daňo, M., Rosskopfová, O., Šeršeň, F., Kufčáková, J., Adamcová, R., Rajec, P. (2012). "Effect of gamma-irradiation on adsorption properties of Slovak bentonites. *Journal of Radioanalytical and Nuclear Chemistry*, vol. 292, pp. 481-492.
- [9] Galamboš, M., Magula, M., Daňo, M., Osacký, M., Rosskopfová, O., Rajec, P. (2012). Comparative study of cesium adsorption on dioctahedral and trioctahedral smectites. *Journal of Radioanalytical and Nuclear Chemistry*, vol. 293, pp. 829-837.
- [10] Galamboš, M., Osacký, M., Rosskopfová, O., Krajňák, A., Rajec, P. (2012). Comparative study of strontium adsorption on dioctahedral and trioctahedral smectites. *Journal of Radioanalytical and Nuclear Chemistry*, vol. 293, pp. 889-897.
- [11] Galamboš, M., Krajňák, A., Rosskopfová, O., Viglašová, E., Adamcová, R., Rajec, P. (2013). Adsorption equilibrium and kinetic studies of strontium on Mg-bentonite, Fe-bentonite and illite/smectite. *Journal of Radioanalytical and Nuclear Chemistry*, vol. 298, pp. 1031-1040.
- [12] Rosskopfová, O., Pivarčiová, L., Krajňák, A., Galamboš, M., Rajec, P. (2016). Adsorption of nickel on illite/smectite Dolná Ves. *Journal of Radioanalytical and Nuclear Chemistry*, vol. 307, pp. 179-185.
- [13] Andrejkovičová, S., Pentrák, M., Jankovič, L., Komadel, P. (2010). Sorption of heavy metal cations on rhyolitic and andesitic bentonites from Central Slovakia. *Geologica Carpathica*, vol. 61, pp. 163-171.
- [14] Pivarčiová, L., Krajňák, A., Rosskopfová, O., Galamboš, M., Rajec, P. (2015). Adsorption of nickel on andesitic bentonite Lieskovec. *Journal of Radioanalytical and Nuclear Chemistry*, vol. 304, pp. 851-858.
- [15] Krajňák, A., Pivarčiová, L., Rosskopfová, O., Galamboš, M., Rajec, P. (2015). Adsorption of nickel on rhyolitic Slovak bentonites. *Journal of Radioanalytical and Nuclear Chemistry*, vol. 304, pp. 587-593.
- [16] Katsou, E., Malamis, S., Tzanoudaki, M., Haralambous, K.J., Loizidou, M. (2011). Regeneration of natural zeolite polluted by lead and zinc in wastewater treatment systems. *Journal of Hazardous Materials*, vol. 189, pp. 773-786.
- [17] Li, L.Y., Chen, M., Grace, J.R., Tazaki, K., Shiraki, K., Asada, R., Watanabe, H. (2007). Remediation of acid rock drainage by regenerable natural clinoptilolite. *Water Air and Soil Pollution*, vol. 180, pp. 11-27.
- [18] Gedik, K., Imamoglu, I. (2008). Removal of cadmium from aqueous solutions using clinoptilolite: Influence of pretreatment and regeneration. *Journal of Hazardous Materials*, vol. 155, pp. 385-392.
- [19] Bleiman, N., Mishael, Y.G. (2010). Selenium removal from drinking water by adsorption to chitosan-clay composites and oxides: Batch and columns tests. *Journal of Hazardous Materials*, vol. 183, pp. 590-595.
- [20] Zhu, R., Zhu, J., Ge, F., Yuan, P. (2009). Regeneration of spent organoclays after the sorption of organic pollutants: A review. *Journal of Environmental Management*, vol. 90, pp. 3212-3216.
- [21] Stirk, W.A., Van Staden, J. (2002). Desorption of cadmium and the reuse of brown seaweed derived products as biosorbents. *Botanica Marina*, vol. 45, pp. 9-16.
- [22] Peng, X., Luan, Z., Zhang, H. (2006). Montmorillonite-Cu(II)/Fe(III) oxides magnetic material as adsorbent for removal of humic acid and its thermal regeneration. *Chemosphere*, vol. 63, pp. 300-306.
- [23] Jesenák, K., Kuchta, L., Guller, L., Fúsková, J. (1997). Physico-chemical Properties of Bentonite "Stará Kremnička - Jelšový potok": I. Particle Size Distribution. *Mineralia Slovaca*, vol. 29, pp. 439-442.
- [24] Mockovčiaková, A., Matik, M., Orolínová, Z., Hudec, P., Kmecová, E. (2008). Structural characteristics of modified natural zeolite. *Journal of Porous Materials*, vol. 15, pp. 559-564.
- [25] Sing, K. (2001). The use of nitrogen adsorption for the characterization of porous materials. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 187-188, pp. 3-9.

- [26] Ho, Y.S., Chiu, W.T., Wang, Ch.Ch. (2005). Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. *Bioresource Technology*, vol. 96, pp. 1285-1291.
- [27] Sposito, G., Skipper, N.T., Sutton, R., Park, S.H., Soper, A.K., Greathouse, J.A. (1999). Surface geochemistry of the clay minerals. *Proceedings of the National Academy of Sciences of the United States of America*, vol. 96, pp. 3358-3364.
- [28] Orolínová, Z., Mockovčiaková, A. (2009). Structural study of bentonite/iron oxide composites. *Materials Chemistry and Physics*, vol. 114, pp. 956-961.
- [29] Danková, Z., fedorová, E., Bekényiová, A. (2017). Bentonite/iron oxide magnetic composites: Characterization and application as Pb(II) adsorbents. *Archives for Technical Sciences*, vol. 16, pp. 65-75.
- [30] Eren, E., Afsin, B. (2008). An investigation of Cu(II) adsorption by raw and acid-activated bentonite: A combined potentiometric, thermodynamic, XRD, IR, DTA study. *Journal of Hazardous Materials*, vol. 151, pp. 682-691.
- [31] Bourliva, A., Michailidis K., Sikalidis, C., Filippidis, A., Betsiou, M. (2015). Adsorption of Cd(II), Cu(II), Ni(II) and Pb(II) onto natural bentonite: study in mono- and multi-metal systems. *Environmental Earth Sciences*, vol. 73, pp. 5435-5444.
- [32] Zhi-rong, L., Shao-qi, Z. (2010). Adsorption of copper and nickel on Na-bentonite. *Process Safety and Environmental Protection*, vol. 88, pp. 62-66.
- [33] Melichová, Z., Hromada, L. (2013). Adsorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> ions from aqueous solution on natural bentonite. *Polish Journal of Environmental Studies*, vol. 22, pp. 457-464.
- [34] Brtáňová, A., Melichová, Z., Komadel, P. (2012). Sorption of Cu<sup>2+</sup> from aqueous solutions by Slovak bentonites. *Ceramics – Silikaty*, vol. 56, pp. 55-60.
- [35] Viglašová, E., Daňo, M., Galamboš, M., Krajňák, A., Rosskopfová, O., Rajec, P. (2017). Investigation of Cu(II) adsorption on Slovak bentonites and illite/smectite for agricultural applications. *Journal of Radioanalytical and Nuclear Chemistry*, vol. 314, pp. 2425-2435.
- [36] Štefušová, K., Václavíková, M., Lovás, M., Hredzák, S. (2012). Use of magnetic filtration in waste water treatment. *Acta Montanistica Slovaca*, vol. 1, pp. 81-84.
- [37] Danková, Z., Štyriaková I., Mockovčiaková, A., Štyriak, I., Orolínová M. (2013). Bioleaching as possible method of sorbent regeneration. *Bioengineering and Bioscience: Agriculture & Life Sciences*, vol. 1, pp. 31-36.
- [38] Štyriaková, D., Štyriaková, I., Štyriak, I., Šuba, J., Danková, Z., Gešperová, D. (2015). Inhibition effect of heterotrophic microorganisms on Cu and Zn cations mobilization from contaminated soil and sediment. *Procedia Earth and Planetary Science*, vol. 15, pp. 866-871.
- [39] Štyriaková, I., Jablonovská, K., Mockovčiaková, A., Bekényiová, A., Štyriak, I., Kraus, I., Osacký, M., Lovás, M. (2010). Dissolution of iron from quartz sands by basin bioleaching under static in-situ condition. *Hydrometallurgy*, vol. 104, pp. 443-447.
- [40] Doušová, B., Koloušek, D., Štyriaková, I., Lhotka, M., Machovič, V., Danková, Z., Štyriak, I., Duchková, E. (2016). Bioleaching effect on adsorption activity of Fe-rich clays. *Book of Abstracts, 8<sup>th</sup> Mid-European Clay Conference*, July 4-8, 2016, Košice, Slovakia, p.60, ISBN 978-80-972288-0-4.