

## Study of the treated and magnetically modified bentonite as possible sorbents of heavy metals

Ján Vereš<sup>1</sup> and Zuzana Orolínová

*Bentonite with its unique structural properties is a valuable material for environmental application. Its sorption properties are usually improved by the different ways of modification. In this work, the special sedimentation method was used for the treatment of the natural bentonite to obtain monomineral fraction of montmorillonite. The modification by iron oxide particles was used with the aim to prepare the magnetic sorbent with enhanced sorption properties of treated bentonite. The removal of nickel from aqueous solutions by the natural, treated and magnetically modified bentonite was studied in batch adsorption-equilibrium experiments. The experimental data were fitted with Langmuir and Freundlich isotherms. The sorption capacities of the natural, treated and modified bentonite were compared.*

**Key words:** bentonite, modified bentonite, adsorption, adsorption isotherm.

### Introduction

Heavy metals contamination occurs in aqueous waste streams of many industries, such as metal plating facilities, mining operations, tanneries etc. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders and environmental problems. Treatment processes for metals contaminated waste streams include chemical precipitation, ion exchange, membrane separations (ultrafiltration, reverse osmosis, electrodialysis) and adsorption. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have a potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. The cost is an important parameter for the comparison of sorbent materials. Adsorption is considered to be the simplest and most cost-effective technique. The removal of heavy metal ions from industrial wastewaters using different adsorbents is currently of great interest (Bailey et al., 1999).

Some naturally occurring clay minerals may serve as cost-effective sorbents for the removal of heavy metals. While their sorption capacity is usually less than those of synthetic sorbents, these materials could provide an inexpensive substitute for the treatment of heavy metal waste waters. To enhance the sorption capacity, the clays are modified in various ways (Vengris et al., 2001).

Magnetic nanoparticles and their composites are suitable in water treatment for the coagulation of sewage or for the complete elimination of contaminants from drinking water sources such as heavy metals (Szabó et al., 2007) and can be subsequently removed from the medium by a simple magnetic process (Oliveira et al., 2003).

The bentonite samples from different regions show different behaviour in ion-exchange processes. The ion exchange process in bentonites is influenced by several factors such as concentration and nature of cations and anions, pH value and crystal structure of the bentonite.

In this work, the natural bentonite was first treated by the sedimentation method. Then the treated bentonite was used to prepare the bentonite/iron oxide composite. The structural study of these materials and their sorption capacity of nickel in comparison to the natural bentonite are discussed here.

### Experimental

#### Materials and chemicals

The natural bentonite originated from the deposit of locality Stará Kremnička (Slovakia), which crystallochemical formula is  $[\text{Si}_{7.95} \text{Al}_{0.05}] [\text{Al}_{3.03} \text{Fe}_{0.22} \text{Mg}_{0.75}] \text{O}_{20} (\text{OH})_4 (\text{Ca}_{0.42} \text{Mg}_{0.04} \text{Na}_{0.01} \text{K}_{0.01})$  (Jesenák et al., 1997). The sample was isolated from the 4 % water suspension of bentonite and treated by the special sedimentation method with the aim to obtain the monomineral fraction of montmorillonite with the particle size below 20  $\mu\text{m}$  (Jesenák et al. 2000).

---

<sup>1</sup> Ing. Ján Vereš, Ing. Zuzana Orolínová, Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 043 53, Košice, Slovak Republic, [veres@saske.sk](mailto:veres@saske.sk)  
(Recenzovaná a revidovaná verzia dodaná 24. 3. 2009)

The treated bentonite was modified by iron oxide particles by the method of coprecipitation from the solution of ferric and ferrous salts. The bentonite/iron oxide weight ratio was 3:1 and the temperature of the synthesis was 85 °C. The composite sample was denoted C85. Inorganic chemicals were supplied as analytical reagents and deionized water was used. Solution of nickel was prepared by using nitrate salt,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

### Methods

Powder X-ray diffraction (XRD) patterns were collected using a Philips PW1820 (Germany). The JCPDS PDF database was used for the phase identification. Mössbauer spectroscopy measurements were carried out with a  $^{57}\text{Co}/\text{Rh}$   $\gamma$ -ray source (Germany) at the room temperature. The velocity scale was calibrated relative to  $^{57}\text{Fe}$  in Rh. Recoil spectral analysis software was used for the quantitative evaluation of the Mössbauer spectra. The sorption of nickel from model aqueous solutions by the natural, treated and magnetically modified bentonite was carried out using batch-type equilibrium experiments in a rotary shaker for 24 hours at constant ambient temperature (25 °C). Sorption experiments were realized at pH = 5.5 and the initial total metal ion concentration range was 1 - 1000 mg/L and sorbent concentration was 2 g/L. The quantity of elements in solution has been determined both before the introduction of sorbent and after the equilibrium time of 24 hours by atomic absorption spectroscopy (AAS using a Varian 240 RS/2402). Sorption isotherms have been fitted with Langmuir and Freundlich equation.

The amount of adsorbed metal was calculated using the equation

$$q_{eq} = \frac{c_0 - c_{eq}}{c_s} \quad , \quad (1)$$

where  $c_0$  and  $c_{eq}$  [ $\text{mg} \cdot \text{l}^{-1}$ ] are the concentrations of the metal ion in initial and final solutions and  $c_s$  [ $\text{g} \cdot \text{l}^{-1}$ ] is the sorbent concentration.

### Results and discussions

XRD analysis and Mössbauer spectrum of treated and magnetically modified bentonite.

The XRD analysis of the treated bentonite showed the presence of montmorillonite phase, Fig. 1. The diffractions of iron oxide were observed in composite sample C85. It was difficult to differentiate between magnetite and maghemite phase because of strongly overlapping of diffractions. Therefore the Mössbauer spectroscopy was used to characterize the iron oxide in composite.

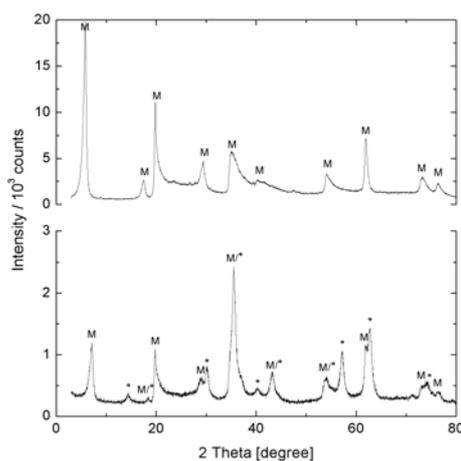


Fig. 1. XRD pattern of treated bentonite and composite C85 (M – montmorillonite, \* - iron oxide).

The Mössbauer spectrum of the treated bentonite consists of two spectral components with hyperfine parameters: isomer shifts  $IS_1 = 0,28 \text{ mm} \cdot \text{s}^{-1}$ ,  $IS_2 = 0,23 \text{ mm} \cdot \text{s}^{-1}$ ; quadrupole splittings  $QS_1 = 1,39 \text{ mm} \cdot \text{s}^{-1}$ ,  $QS_2 = 0,52 \text{ mm} \cdot \text{s}^{-1}$ ; relative intensities  $I_1 = 33,7 \%$ ,  $I_2 = 66,3 \%$ , Fig. 2a. It can be stated that iron cations in the treated bentonite are trivalent. The bentonite/iron oxide composite spectrum is complex consisting of the paramagnetic doublet and one sextet. Fitted parameters for C85 sample, Fig. 2b, indicate the  $\text{Fe}^{3+}$  in

magnetite (RA = 81.4 %; average hyperfine magnetic field,  $B^{\text{Oct}} = 38.5 \text{ T}$ , IS =  $0.25 \text{ mm}\cdot\text{s}^{-1}$ , RA = 50.9 %,  $B_{\text{hf}}^{\text{Oct}} = 46.6 \text{ T}$ , IS =  $0.13 \text{ mm}\cdot\text{s}^{-1}$ , RA = 30.5 %) and two paramagnetic positions of  $\text{Fe}^{3+}$  in bentonite. Only the presence of  $\gamma\text{-Fe}_2\text{O}_3$  phase was confirmed in composite.

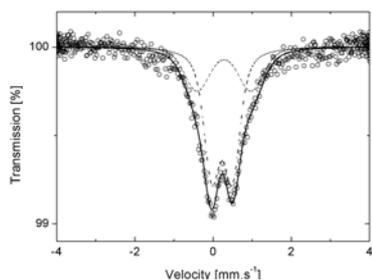


Fig. 2a. Fitted Mössbauer spectrum of treated bentonite.

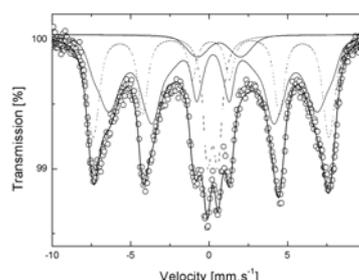


Fig. 2b. Fitted Mössbauer spectrum of composite sample.

### Adsorption isotherms

The adsorption of  $\text{Ni}^{2+}$  onto different sorbents as a function of its concentration was studied at  $25 \text{ }^\circ\text{C}$  by varying the metal concentration from 1 to  $1000 \text{ mg}\cdot\text{l}^{-1}$  while keeping all other parameters constant. The adsorption isotherms, which are the most suitable to fitting the adsorption processes on sorbents are shown on Fig. 3. The isotherm analyses showed different adsorption behaviour for  $\text{Ni}^{2+}$ . Fig. 3. presents that the sorption capacity of sorbents was not depend even by the highest initial concentration of metal ion in solution, adsorption still shows an increasing trend at higher equilibrium concentrations.

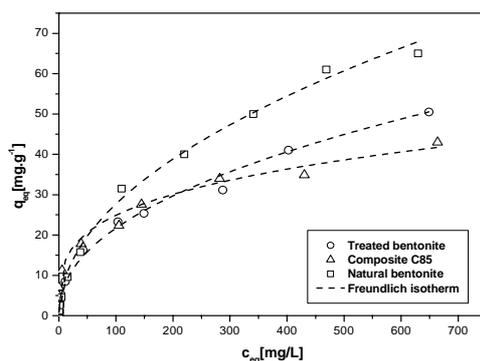


Fig. 3. Adsorption isotherms of  $\text{Ni}^{2+}$  on natural bentonite, treated and composite C85.

Fig. 4. shows adsorption capacity on selected sorbents in low concentration range. The best sorption capacity in low range of concentrations which is characteristic for environmental weight, was obtained in the following order: composite C85 > treated bentonite > natural bentonite.

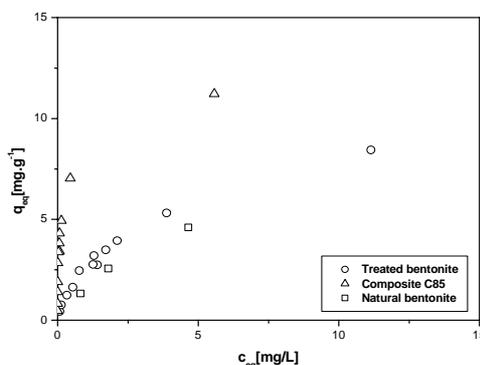


Fig. 4. Adsorption of  $\text{Ni}^{2+}$  in low range of concentrations.

### Conclusion

Magnetic modification seems to be a perspective way of enhancing the sorption properties of natural or treated bentonite and should offer an easy separation of sorbent from the medium (Bourlinos et al., 2003). The treated and magnetically modified bentonite were prepared and characterized with aim to compare their sorption properties with natural bentonite. The present study showed that the composite C85 and treated bentonite were effective in removing  $\text{Ni}^{2+}$  ions from aqueous solutions compared to the commercial bentonite from the locality Stará Kremnička. The results showed that the composite C85 in low concentration range of  $\text{Ni}^{2+}$  was the most effective in adsorption process and should be used as possible sorbent of heavy metals for environmental purposes.

Acknowledgement: *The authors are thankful for financial support of VEGA grant 2/0119/09 and APVV grant 0728-07 and APVV-51-035505.*

### References

- [1] Bailey, S. E, Olin, T.J., Bricka, R.M., Adrian, D.D.: A review of potentially low-cost sorbents for heavy metals, *Wat. Res.* 33, 2469-2479, 1999.
- [2] Vengris, T., Binkienė, R., Sveikauskaitė, A.: Nickel, copper and zinc removal from waste water by a modified clay sorbent, *Appl. Clay Sci.* 18, 183-190, 2001.
- [3] Szabó, T., Bakandritsos, A., Tzitzios, V., Papp, S., Kőrösi, L., Galbác, G., Musabekov, K., Bolatova, D., Petridis, D., Dékány, I.: Magnetic iron oxide/clay composites: effect of the layer silicate support on the microstructure and phase formation of magnetic nanoparticles, *Nanotechnology* 18, 285602-285610, 2007.
- [4] Oliveira, L.C.A., Rios, R.V.R.A., Fabris, J.D., Sapag, K., Garg, V.K., Lago, R.M.: Clay – iron oxide magnetic composites for the adsorption of contaminants in water, *Appl. Clay Sci.* 22, 169-177, 2003.
- [5] Jesenák, K., Kuchta, L., Guller, L., Fúsková, J.: Physico-chemical properties of bentonite „Stará Kremnička – Jelšovský potok“, *Mineralia Slovaca* 29, 439-442, 1997.
- [6] Jesenák, K., Hlavatý, V.: Laboratory Device for Sedimentation of Fine Bentonite Fractions, *Scripta Fac. Sci. Nat. Univ. Masaryk Brun.*, 28-29, 33-36, 2000.
- [7] Bourlinos, A.B., Zboril, R., Petridis, D.: [A simple route towards magnetically modified zeolites](#) *Microporous Mesoporous Mater.* 58, 155-162, 2003.