

# Bentonite Modification with Manganese Oxides and Its Characterization

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## Abstract

The paper describes the preparation of new composite based on relatively cheap natural materials from domestic deposits and synthetically prepared manganese oxides. At first the natural bentonite was simple chemically modified by natrification. In general, bentonite is a rock with dominant presence of clay minerals from the smectite group, mainly montmorillonite. The properties of bentonite result from the crystal structure of this group. The particles of montmorillonite have negative charges on their faces due to isomorphic substitutions in structure. The natrification salt  $\text{Na}_2\text{CO}_3$  is used almost exclusively thanks to its financial accessibility. The significant changes of surface properties after the modification of bentonite were observed. Natrification increased the surface area of bentonite. Then the manganese oxides were precipitated on the surface of activated sodium bentonite particles. The structural changes of bentonite, before and after its modification, were studied by X-ray diffraction analysis and FTIR spectroscopy. The morphology of the bentonites was observed by scanning electron microscopy. X-ray diffraction analysis demonstrated that the structural changes in the bentonite after natrification, the related exchange of  $\text{Ca}^{2+}$  cation for  $\text{Na}^+$  in the inter-layer space of the montmorillonite structure. Manganese oxide ( $\text{MnO}_2$ ) with regular birnessite layer structure was present in all of the bentonite samples of modified manganese.

Keywords: bentonite, natrification, manganese oxide

## Introduction

The bentonite is a natural clay mineral that is found in many places of the world. Any clay of volcanic origin that contains montmorillonite is referred to as bentonite. It belongs to the 2:1 clay family, the basic structural unit of which is composed of two tetrahedrally coordinated sheets of silicon ions surrounding a sandwiched octahedrally coordinated sheet of aluminum ions. The isomorphous substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral layer and  $\text{Mg}^{2+}$  or  $\text{Fe}^{3+}$  for  $\text{Al}^{3+}$  in the octahedral layer results in a net negative surface charge on the clay. Compared with other clay types, it has excellent adsorption properties and possesses adsorption sites available within its interlayer space as well as on the outer surface and edges (Eren et al., 2008a; Eren et al., 2009b; Fusová et al., 2011a, 2011b, 2011c). Adsorption of metal ions onto montmorillonite appears to involve two distinct mechanisms: (i) an ion exchange reaction at permanent-charge sites, and (ii) formation of complexes with the surface hydroxyl groups. A composite adsorbent, manganese oxide-coated bentonite was proposed and studied in this research. The reason for choosing manganese oxides is that relative to Fe or Al

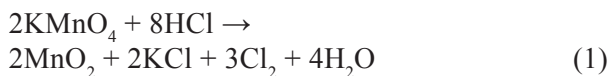
oxides, manganese oxides have a higher affinity for many heavy metals (Fan et al., 2005; Eren et al., 2009, Raclavská 2011). Bentonite, which has a high surface area, should provide an efficient surface for the manganese oxide. At the same time, the manganese oxides can improve the heavy-metal adsorption capacity of bentonite.

## Material and Methods

The bentonite used in this study originated from the Slovak deposit Stará Kremnička – Jelšovský potok. This natural bentonite (B) contains almost monomineral fraction of montmorillonite (> 90 %) with the particles size below 20  $\mu\text{m}$  (Jesenák and Hlavatý, 2000). The particular amount of natural bentonite was converted to its monoionic sodium form. The natrified bentonite (NaB) was prepared from the slurry, which contained the activating agent ( $\text{Na}_2\text{CO}_3$ ) and distilled water to which the bentonite was added.

The stabilization took 24 hours at ambient temperature. The final product was dried at 60°C and then it was mashed manually. Subsequently, the manganese oxide – natural bentonite composite (Mn-B), manganese oxide – natrified bentonite

composite (Mn-NaB) and reference sample of manganese oxides (Ref-Mn) were prepared according to the method developed by (Cole et al., 1947), represented by the reaction (1):



The Mn-B and Mn-NaB were prepared in a weight ratio 1:1 (bentonite: manganese oxides). Ref-Mn was prepared without the addition of bentonites. The process of precipitation included the following steps: Potassium permanganate was dissolved in distilled water in a beaker and kept in a water bath at 90°C for 15 min. Bentonite was added into the purple solution and this suspension was mixed gently for 10 min. After that 2M HCl was slow added dropwise to the suspension and heated in a water bath at 90°C. After the titration, the mixture was stirred further 30 min. The final product was cooled at the air and washed several times using double distilled water, dried in an

oven at 100°C for 24 hours and stored. X-Ray diffraction data were obtained by a diffractometer Bruker D8 Advance (40 kV, 40 mA), working with the CuK $\alpha$  radiation. The JCPDS (Joint Committee for Powder Diffraction Data - International Centre for Diffraction Data) database was used to analyze the diffraction peaks. The infrared spectra were obtained using the KBr disc technique using Nicolet 6700 FTIR spectrometer. For each sample 64 scans were measured in the 4000–400 cm<sup>-1</sup> spectral range in the abs mode with a resolution of 4 cm<sup>-1</sup>. The overview morphologies and sizes of the particles were obtained by a field emission scanning electron microscope TESCAN MIRA 3 FE SEM with an accelerating voltage of 20 kV. The samples were examined at several magnifications.

### Results and discussion

The X-ray diffraction analysis of natural bentonite (B) confirmed montmorillonite as dominant mineral phase (Fig. 1a). The activation of bentonite by sodium cations caused structural changes of natural bentonite (Fig. 1b). It affected mainly

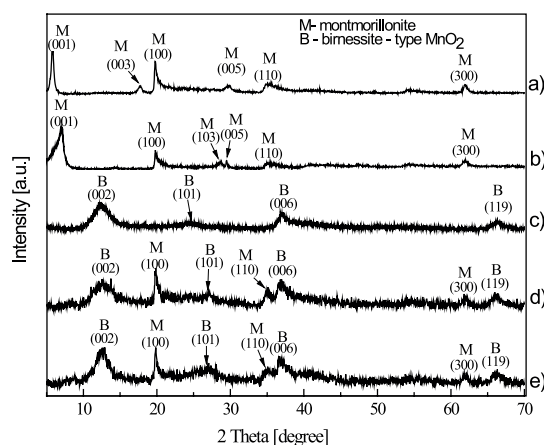


Fig. 1. X-ray diffraction patterns of the B (a), NaB (b), Ref-Mn (c), Mn-B (d) and Mn-NaB (e)

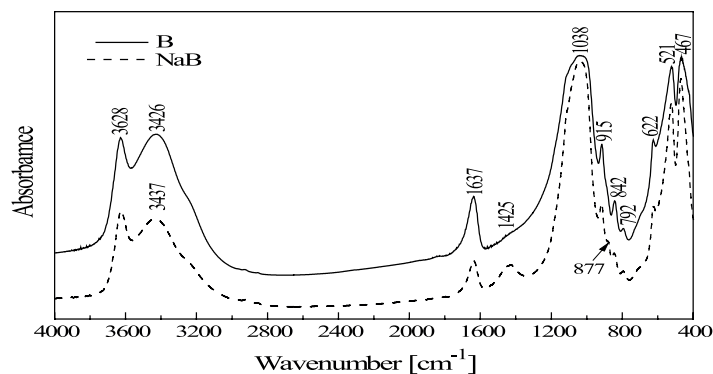


Fig. 2. Infrared spectra of B and NaB

Tab. 1. Absorption bands of bentonite infrared spectra

Absorption bands	Bentonite - standard Jelšový potok (Vaculíková, 2008)	B	NaB
OH stretching of structural hydroxyl groups	3625	3628	3627
OH stretching of water	3427	3426	3437
OH deformation of water	1637	1637	1638
traces of carbonates	-	-	1425
Si-O stretching (longitudinal mode)	1114	-	-
Si-O stretching	1037	1038	1040
AlAlOH deformation	914	915	917
traces of carbonates	-	-	877
AlMgOH deformation	842	842	844
SiO stretching of quartz and silica	792	792	791
Si-O	700	-	-
coupled Al-O and Si-O, out-of-plane	623	622	622
Al-O-Si deformation	521	521	523
Si-O-Si deformation	466	467	469

(001) reflection of montmorillonite. Shift of NaB peak to the right on x axis points to the cation exchange from interlayer space for cations with the smaller atomic radius. The shape of the diffraction pattern NaB refers the refinement of structure. Monovalent hydrated cations ( $\text{Na}^+$ ) are active dispersing the montmorillonite structure (Jelínek et al., 2010). The natrification also facilitates the separation of basic structural layers (Galamboš et al., 2010). All these factors, together with the presence of sodium carbonate and the free surface of the montmorillonite lead to the apparent reduction of the crystallinity after natrification.

The diffraction pattern of a reference sample of manganese oxides (Ref-Mn) is shown in Fig. 1c. Using Database The International Centre for Diffraction Data (ICDD), the diffraction pattern of Ref-Mn most closely approximates to the synthetic birnessite with the characteristic diffraction planes hkl (002), (101), (006) and (119) with empirical a chemical formula  $\text{MnO}_2$  (ref. no. 00-018-0802). Identified phase comprises a hexagonal crystal system. Precipitation of manganese oxides on bentonite caused structural changes in both composites Mn-B and Mn-NaB (Fig. 1d,e). The main (001) reflection of montmorillonite was reduced and (005) reflection disappeared. On the diffraction pattern of Mn-B and Mn-NaB can clearly identify the presence of manganese oxide - birnessite type. The positions of diffraction line

of manganese oxide - birnessite type in the modified bentonite can be influenced by the presence of various cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ) (Frías et al., 2007).

In Figure 2 are shown the absorption spectra of B and NaB. The results of the analysis of bentonite (B) were consistent with those of standard samples of bentonite deposits Jelšový potok listed in the database of rocks and minerals Institute of Geonics (Vaculíková, 2008). After natrification of bentonite (NaB) on the IR spectrum discovered traces of carbonates used natrified agent (Fig. 2). In the spectrum (NaB) can be seen to change the position of the vibration surface-bound water; shift of  $3426 \text{ cm}^{-1}$  to higher wave numbers at  $3437 \text{ cm}^{-1}$ , this change is probably due to the use natrified agent (Table 1).

The result of IR analysis of the reference sample of manganese oxides (Ref-Mn) is not exactly to standard  $\text{MnO}_2$  published in (Julien and Massot, 2003a; Julien and Massot, 2004b). However, the value of the absorption bands at  $520 \text{ cm}^{-1}$  and  $468 \text{ cm}^{-1}$  (Fig. 3) generally include bending vibrations O-metal (Mn-O). Moreover, the bands at  $3426 \text{ cm}^{-1}$  and  $1636 \text{ cm}^{-1}$  belong to the vibration of OH groups of absorbed water molecules. On spectrum of the sample Mn-NaB (Fig. 3) was not observed the traces of carbonates characteristic of the sample NaB ( $1425 \text{ cm}^{-1}$  and  $877 \text{ cm}^{-1}$ ). The presence of  $\text{MnO}_2$  in the pattern of Mn-NaB on the base of vibration bands ( $520 \text{ cm}^{-1}$  and  $468$

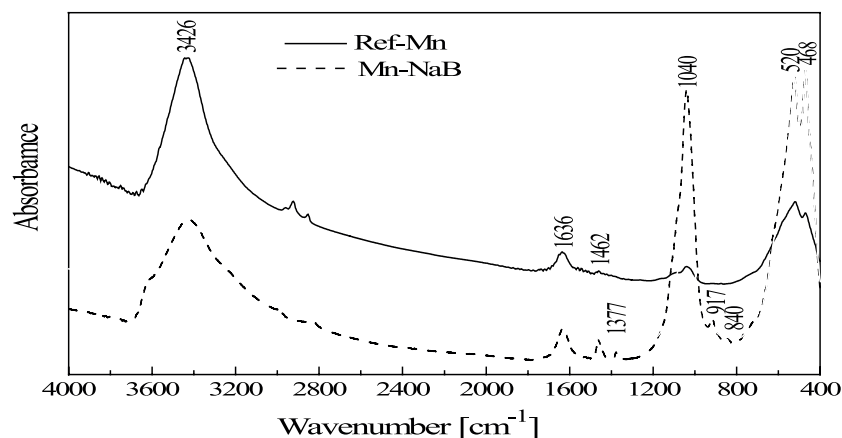
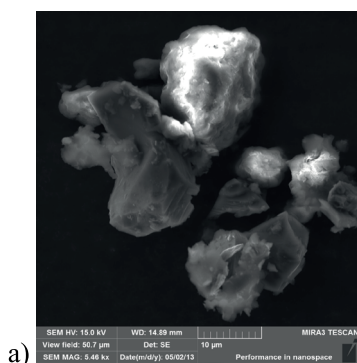
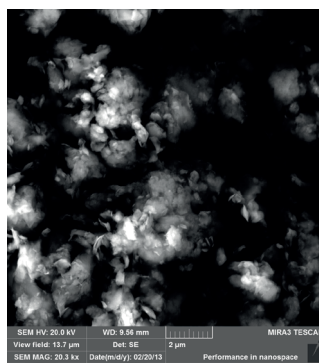


Fig. 3. Infrared spectra of Ref-Mn and Mn-NaB



a)



b)

Fig. 4. SEM images of B (a), NaB (b)

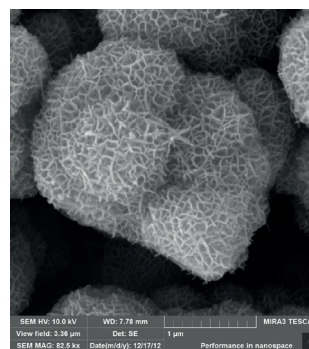


Fig. 5. SEM images of Ref-Mn

$\text{cm}^{-1}$ ) was not possible to confirm.  $\text{MnO}_2$  vibrations overlap with the bands of Si-H bonds to the clay mineral ( $523 \text{ cm}^{-1}$  and  $469 \text{ cm}^{-1}$ ). Interestingly, the intense absorption bands characteristic of the OH vibrations in the structure of montmorillonite at  $3621 \text{ cm}^{-1}$  for the sample Mn-NaB proved to be quite "minor arm", suggesting the release of water molecules from the structure of montmorillonite.

The natural bentonite (B) was characterized by particle combined in aggregates of a size of several tens  $\mu\text{m}$  (Fig 4a). The SEM image of NaB (Fig. 4b) shows that the activation of natural bentonite with sodium resulted in smaller grain sizes caused by the dispersive effect of  $\text{Na}^+$  on the bentonite structure. The SEM analysis of Ref-Mn is shown in Fig. 5. It is characterized the morphology of "sea urchin", which was formed by a thin nanowall sheets oxide with a thickness of several tens of nanometers (Zhu et al., 2008). These "nanowall sheets" were linked together, arranged randomly,

pointing to the centre, perpendicular to the sample surface forming a network. Figure 6a and 6b are listed samples of Mn-B and Mn-NaB. The spherical formations of manganese oxides cover the surface of the bentonite particles.

### Conclusion

The X-ray diffraction analysis demonstrated the structural changes after natriification of bentonite. The analysis of synthetically prepared reference sample of manganese oxides, showed manganese oxide ( $\text{MnO}_2$ ) with regular birnessite layer structure and hexagonal crystal system. This type of structure  $\text{MnO}_2$  was present in all samples modified with manganese. The study of the Mn-B and Mn-NaB morphology showed the manganese oxides covering the small particles of bentonite. The attachment of manganese oxides on sodium bentonite surfaces altered their structural and surface properties i.e.: the surface areas, the zeta potential values and their morphology.

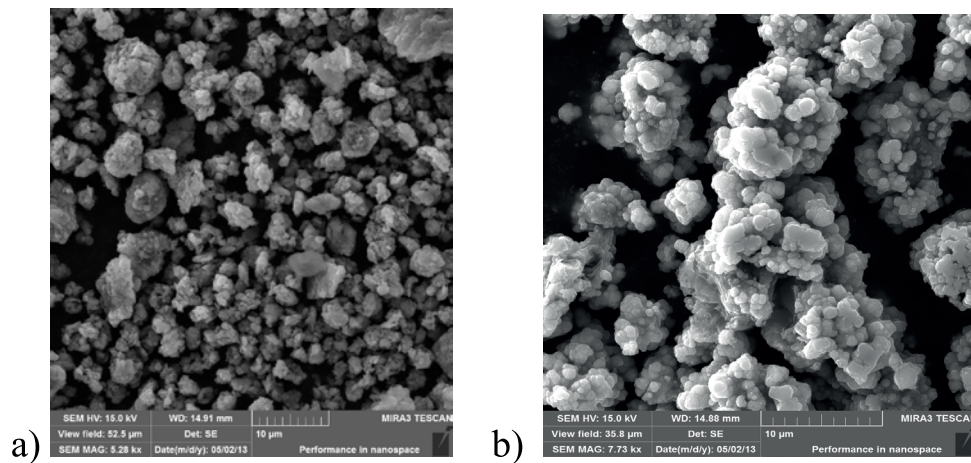


Fig. 6. SEM images of Mn-B (a), Mn-NaB (b)

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## Literatura – References

1. COLE, W.F. et al. "An X-Ray Diffraction Study of Manganese Dioxide." *Journal of the Electrochemical Society* 92(1)/1947: 133-158.
2. EREN, E. et al. "Removal of copper ions by modified Unye clay Turkey." *Journal of Hazardous Materials* 159/2008a: 235–244.
3. EREN, E. et al. "Removal of lead ions by acid activated and manganese oxide-coated bentonite." *Journal of Hazardous Materials* 161/2009b: 677–685.
4. FAN, H.-J. et al. "Copper and cadmium removal by Mn oxide-coated granular activated carbon." *Separation and Purification Technology*, 45/2005: 61–67.
5. FRÍAS, D. et al. "Synthesis and characterization of cryptomelane – and birnessite – type oxides: Precursor effect." *Materials Characterization*, 58(8–9)/2007: 776–781.
6. FUSOVÁ, L. et al. "The investigation on Pb<sup>2+</sup> and Cu<sup>2+</sup> ions on bentonite." *Inżynieria Mineralna* 7(1)/2011a: 11–18.
7. FUSOVÁ, L., et al. "Utilization of Bentonite and Its Modification for Sorption." *Środkowo-pomorskie towarzystwo naukowe ochrony Środowiska: Rocznik Ochrona Środowiska* 2011b: 163–172.
8. FUSOVÁ, L. "Bentonite and its modified derivatives as adsorbents of lead." *11th International Multidisciplinary Scientific GeoConference SGEM 2011. Sofia (Bulgaria): STEF92 Technology Ltd., 2011c:199–206.*
9. GALAMBOŠ, M. et al. "Adsorption of cesium and strontium on natrified bentonites." *Journal of Radioanalytical and Nuclear Chemistry* 283(3)/2010: 803–813.
10. JELÍNEK, P. "Iontová výměna u montmorillonitických jílnů a její důsledky." *XII. Konferencja Odlewnicza Technical: Zbornik příspěvkov. Nowa Sól: Technical Sp. zo.o. Nowa Sól* 2010:119–126.
11. JESENÁK, K. and HLA VATÝ V. "Laboratory device for sedimentation of fine bentonite fraction." *Scripta Fac. Sci. Nat. Univ. Masaryk. Brun. Geology* 28–29/2000: 33–36.
12. JULIEN, C.M. and MASSOT, M. "Lattice vibrations of materials for lithium rechargeable batteries I. Lithium manganese oxide spinel." *Materials Science and Engineering B*, 97(3)/2003a: 217–230.
13. JULIEN, C.M. and MASSOT, M. "Vibrational spectroscopy of electrode materials for rechargeable lithium batteries III. Oxide Frameworks, International Workshop «Advanced Techniques for Energy Sources Investigation and Testing»": *Proceedings*, Bulgaria: Institute of Electrochemistry and Energy Systems, Sofia, 2004b: 1–17.
14. NOÉMI, M. NAGY et al. "Study of the change in the properties of Mn-bentonite by aging." *Journal of Colloid and Interface Science* 278/2004: 166–172.
15. RACLAVSKÁ, H. et al. "Potential reduction in nutrient leachability from sewage sludge applied in land reclamation." *Inżynieria Mineralna* 2(28)/2011: 47–61.
16. VACULÍKOVÁ, L. *Nové možnosti identifikace jílových minerálů a slíd v sedimentárních horninách metodou infračervené spektroskopie s Fourierovou transformací: Závěrečná správa k post - doktorskému grantovému projektu GAČR*, Ostrava, 105/03/D079, 2008.
17. Zhue, H. et al. "Birnessite-type MnO<sub>2</sub> Nanowalls and Their Magnetic Properties." *Journal of Physical Chemistry C* 112(44)/2008: 17089–17094.