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## STUDY AND CHARACTERIZATION OF NATURAL BENTONITE MODIFIED BY MANGANESE OXIDES

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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. The natrification salt  $\text{Na}_2\text{CO}_3$  is used almost exclusively thanks to its financial accessibility. 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.

**Keywords:** *bentonite, natrification, manganese oxides*

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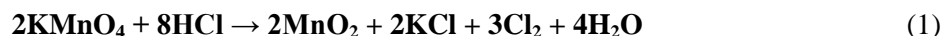
### Introduction

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). 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). 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.

### Materials 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.

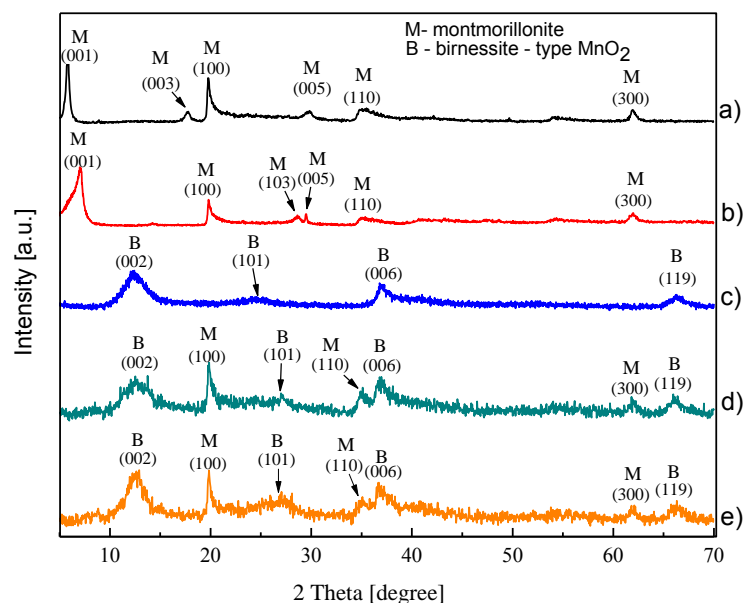
X-Ray diffraction data were obtained by a diffractometer Bruker D8 Advance (40 kV, 40 mA), working with the  $\text{CuK}\alpha$  radiation. The JCPDS (Joint Committee for Powder Diffraction Data - International Centre for Diffraction Data) database was used to analyze the diffraction peaks.

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  $\text{cm}^{-1}$  spectral range in the abs mode with a resolution of 4  $\text{cm}^{-1}$ .

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.

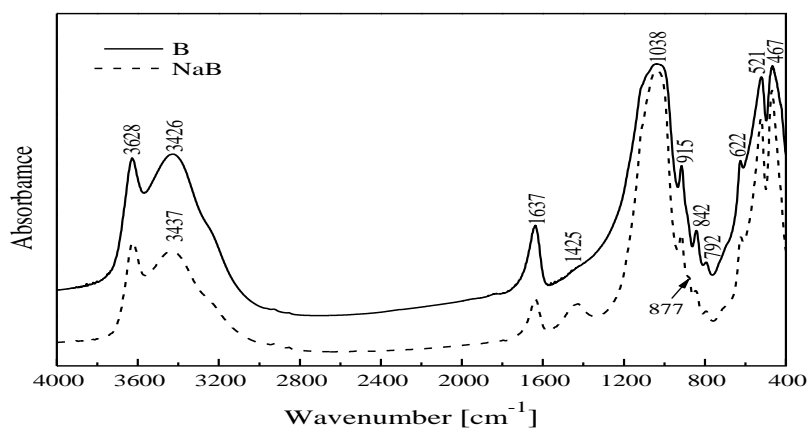
## Results and discussion

The X – ray diffraction analysis of natural bentonite (B) shows the typical and dominant montmorillonite patterns (Fig. 1a). The natrification of bentonite (NaB) has supported the separation of regular montmorillonite structural layers which leads to the decomposition of its structure and the formation of colloids. Effect of natrification can be observed by the comparison of the montmorillonite basal plane diffractions  $d_{001}$  before and after natrification (Fig. 1b). The shift of the  $d_{001}$  montmorillonite reflection to the right on the x axis points on the ion exchange in the interlayer space ( $\text{Na}^+$  for  $\text{Ca}^{2+}$ ). 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 (Figure 1).



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

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 ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ) and water molecules between the structural layers (Frias et al., 2007).



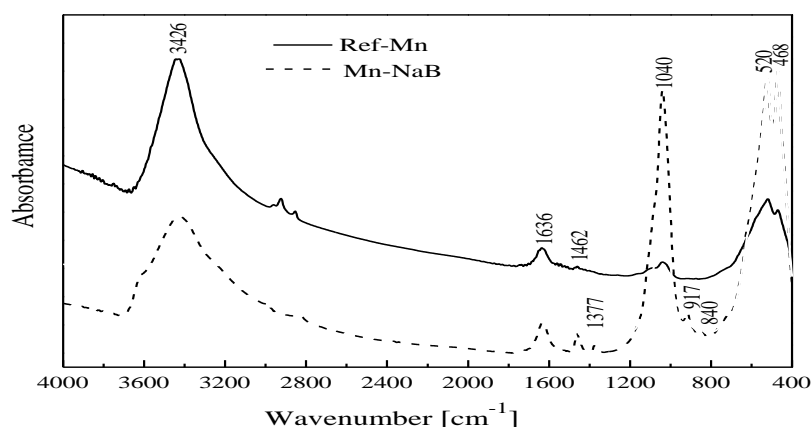
**Figure 2.** Infrared spectra of B and NaB

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 Jelšovský 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).

**Tab. 1** Absorption bands of bentonite infrared spectra

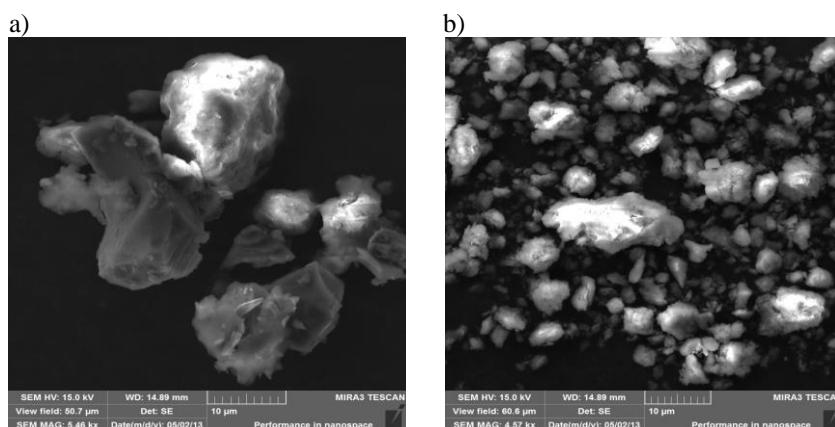
Absorption bands	Bentonite - standard Jelšovský potok [114]	B	NaB
OH stretching of structural hydroxyl groups	3625	3628	3627
OH stretching of water	3427	3426	3437
OH deformation of water	1637	1637	1638
traces of carbonates	-	-	1425
Si-O stretching (longitudinal mode)	1114	-	-
Si-O stretching	1037	1038	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

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  $468 \text{ cm}^{-1}$ ) 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.

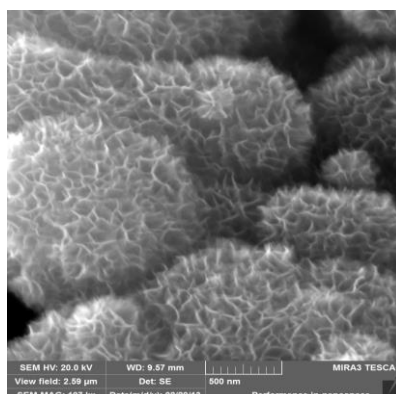
**Figure 3.** Infrared spectra of Ref-Mn and Mn-NaB

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",

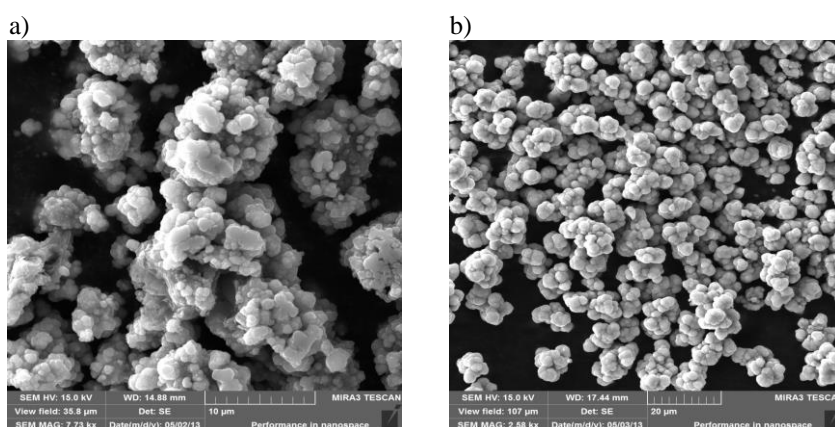
which was formed by a thin nanowall sheets oxide with a thickness of several tens of nanometers (Zhu et al., 2008). These "nanowall sheets" were linked together, arranged randomly, pointing to the center, perpendicular to the sample surface forming a network. Figure 6a and 6b are listed samples of Mn-B and Mn-NaB. The spherical formations of manganese oxides cover the surface of the bentonite particles.



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



**Figure 5.** SEM images of Ref-Mn



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

## Conclusion

The X-ray diffraction analysis demonstrated the structural changes after natrification of bentonite, related to the exchange of  $\text{Ca}^{2+}$  cation for  $\text{Na}^+$  in the inter-layer space of the montmorillonite structure. 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.

## Acknowledgements

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