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SURFACE AND STRUCTURE STUDY OF CLAY-BASED COMPOSITES AFTER THERMAL TREATMENT

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ABSTRACT

The composite materials prepared from clay and iron oxides in different weight ratios and temperatures denoted as A85 and E20 were heated at 300 °C in reductive atmosphere and up to 650 °C in inert atmosphere. The changes in the structure, surface and pore properties were examined by XRD, N₂ adsorption method and TG, DTA method. The morphology was studied using scanning electron microscope. The heating of composites up to temperature 300 °C in the reductive atmosphere caused the transformation of the present oxide phases. The distribution curve of the heated composites is narrower and is shifted to the lower pores. The composites heated up to 650 °C in the N₂ atmosphere showed to the transformation of iron oxide phases to hematite; the composites contained less pores, became denser and due to sintering of iron oxides particles a decrease in specific surface area was observed.

Keywords: clay/iron oxide composite, thermal treatment, surface properties, pore size distribution

INTRODUCTION

Bentonites are used as industrial raw materials in many applications. The major uses are iron pelletizing, pet adsorbents, drilling fluids, bleaching of edible oils, applications in civil engineering and the foundry industry.

Due to its physical and chemical properties, i.e., large specific surface area, cation exchange capacity and adsorptive affinity for organic and inorganic ions, bentonite is a point of study in many publications, used in decontamination and disposal of high-level heavy metal wastes [1-7]. Materials whose physical properties can be varied by application of external magnetic fields belong to a specific class of smart materials [8-10].

Surface decoration of the aluminosilicate minerals with magnetic nanoparticles had led to a new class of composite materials [11], which could be also used for environmental purposes as adsorbents of organic and inorganic compounds and metal ions [12, 13] or as possible contrast agent in MRI of gastrointestinal tract [14].

The natural bentonite from locality Jelšový potok (Slovakia) has been used as a support for the magnetic particles. The clay based composite materials were prepared with weight ratio of minerals to

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iron oxide 1:1 and 5:1 at temperatures 20 and 85 °C by precipitation of magnetic particles onto mineral surface. The changes in structural and surface properties of prepared composites were studied in [15] where in composites the maghemite phase was confirmed. The iron oxides present in the composite samples prepared at temperature 20 °C were distributed between the maghemite and goethite phases and the sample contained smaller particles. It followed from the further study that the modification of clay minerals by iron oxide particles has positive influence on their sorption ability towards metal ions from aqueous solutions [16].

In this paper the thermal treatment of two composite samples were studied. As the selected composites differ in the iron oxide content, the results of heating experiments will be affected by their phase transformation. The samples were heated in two atmospheres, in reductive [17] to the temperature 300 °C and in inert up to 650 °C with the aim to investigate the changes in their surface and structural properties.

EXPERIMENTAL

The composite samples A85, prepared in weight ratio 1:1 of bentonite to iron oxide at the temperature 85 °C and E20, in ratio 5:1 at ambient temperature were used as the starting material. The samples were at first heated for 90 minutes in reductive atmosphere up to the temperature of 300 °C. After heating, the samples were cooled down in the furnace in the same atmosphere. The another experiment using N₂ atmosphere was realized for heating of composites up to the temperature of 650 °C, following the transformation of iron oxide phases.

The changes in the structure of heated samples were studied by X-ray diffraction analysis using a PW 1820 diffractometer (Phillips, Netherlands) equipped with the CuK α radiation (40 kV, 40 mA). The JCPDS PDF database was used for the phase identification.

The morphology of the sample A85 after heating was observed by the scanning electron microscope (SEM) of type JSM-6400 (JEOL Ltd., Japan)

Thermal behaviour of the composites A85 and E20 were characterized using the Derivatograph C (MOM, Hungary). The thermoanalytical measurements were conducted in the atmosphere of air in the temperature range from 20–800 °C at a heating rate of 10 min⁻¹.

The surface properties of heated samples A85 and E20 were investigated using the method of physical adsorption on apparatus Micrometrics ASAP 2400 (USA). BET (Brunauer, Emmett, and Teller) isotherm [18] was used to calculate the specific surface area; the micropore volume V_{micro} and the external surface area S_t were calculated from the t -plot method and the value of total pore volume V_a was estimated from the maximum adsorption at relative pressure close to the saturation pressure. The pore size distribution was obtained from the BJH (Barret–Joyner–Halenda) method [19].

RESULTS

The XRD measurements of the composite samples A85 and E20 are shown in Figures 1, 2. The phase analysis of the non-heated composite A85 confirmed the presence of montmorillonite phases, denoted as M, and maghemite phase with reflection on planes (220), (311), (400), (422), (511) and (440). The diffraction patterns after heating in reductive atmosphere to 300 °C did not change almost: the oxide phases reflected on the same planes. Not the same was observable after heating of the sample A85 to the temperature 650 °C in N₂ atmosphere. New phase with reflections on planes (012), (104), (110), (113), (024) (116), (122), (214) and (300) are pointing out on the transformation of the maghemite to hematite which started below this temperature [20].

The phase analysis of the non-heated composite sample E20 showed besides the montmorillonite M, also the presence of two Fe oxide phases in the sample: maghemite reflecting on planes (220), (311), (422) and (440), and goethite, denoted as G. In the sample heated in atmosphere H₂ to 300 °C a transformation of goethite phase to the hematite reflecting on (012), (104), (113), (024), (122) and (300) was observed. The heating in the atmosphere N₂ at higher temperature caused the transformation of maghemite to hematite, so additional reflections on planes (110), (116) and (214) were detected.

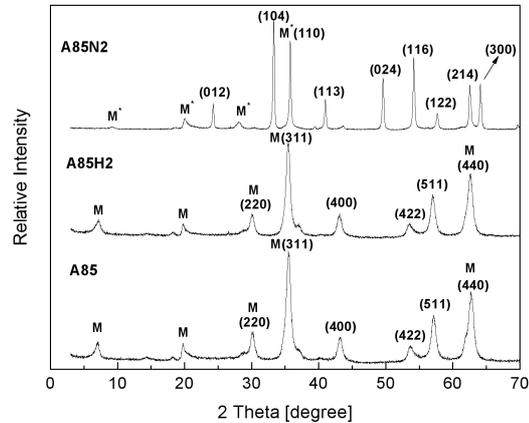


Figure 1 XRD pattern of A85 composite unheated and heated in N₂ and H₂ atmosphere

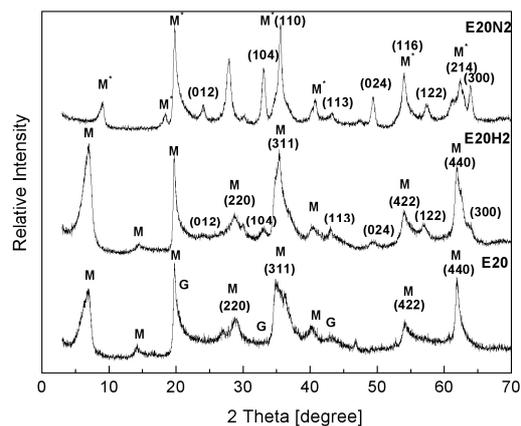


Figure 2 XRD pattern of E20 composite unheated and heated in N₂ and H₂ atmosphere

A detail of the morphology of the unheated composite material A85 and heated in reductive atmosphere to 300 °C, observed by SEM, is shown in Figures 3, 4. The effect of higher temperature 650 °C on the morphology of composite A85 is shown on Figure 5; in comparison to the previous samples, this sample is more homogeneous due to the started densification.

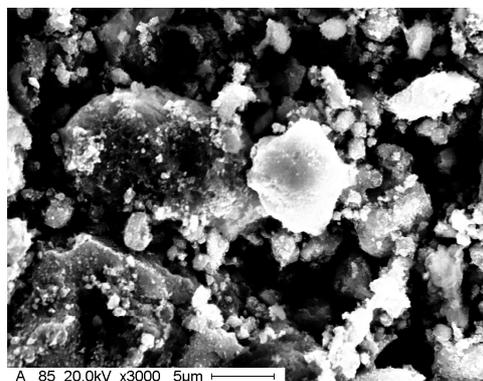


Figure 3 SEM micrograph of the unheated composite A85

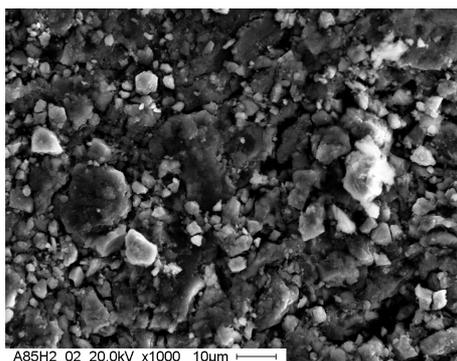


Figure 4 SEM micrograph of the composite A85 heated to 300 °C in H₂ atmosphere

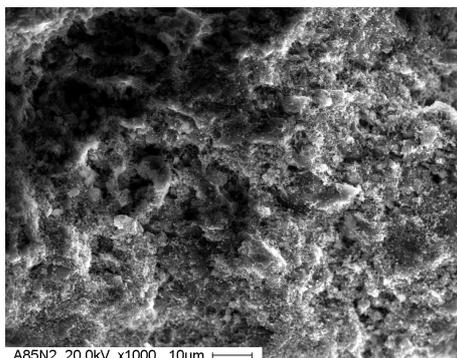


Figure 5 SEM micrograph of the composite A85 heated to 650 °C in N₂ atmosphere

Comparing the pore size distributions of the composite A85 on Figure 6, it can be deduced, that the unheated sample has the highest total pore volume (mesopores and macropores). As it was shown earlier [21], the precipitated oxides create secondary mesopores structure, thus the volume of composite mesopores is dependent on the content of iron oxides. The heating of the composite A85 to the temperature of 300 °C in H₂ atmosphere caused the shifting of distribution curve towards smaller pores. The curve became narrower, almost symmetrical, with maximum of pore size around 10 nm, showing a decrease of mesopores and macropores (see total pore volume, Table 1).

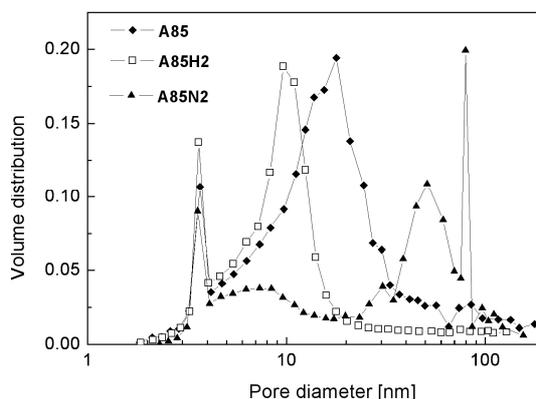


Figure 6 Pore size distribution of composite A85

The different form of hysteresis loops, Figure 7, for unheated sample A85 and heated to temperature 300 °C indicates, that the thermal treatment caused changes observable also in pores shapes. It can be concluded, that by the heating of the composite A85 to the temperature 300 °C in a reductive atmosphere is possible to obtain clay/oxides composite that is more uniform in pore size, where due to

the changes of pore shape a decrease in surface area was observed. The using of H₂ atmosphere caused the partial maghemite to magnetite reduction, as it was documented by Mössbauer spectroscopy (not shown here).

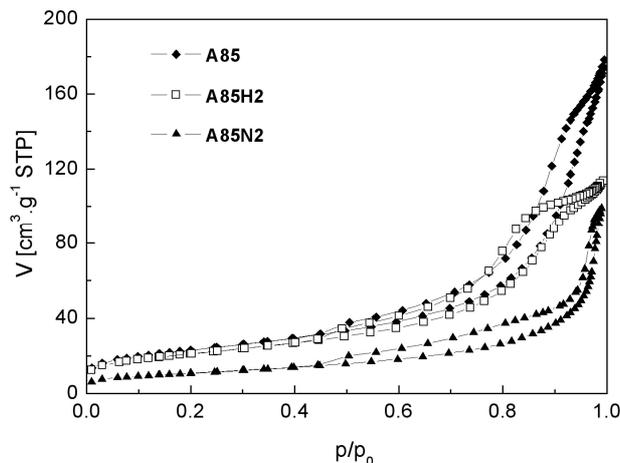


Figure 7 Adsorption and desorption isotherms of composite A85

After heating to the temperature 650 °C in the atmosphere N₂, some destruction in pores is visible, the curve contains two maxima: one broader peak around 7 nm, maximum of the other is around 50 nm, suggesting the increase of macropores. The material heated to the temperature 650 °C contains less pores, became slowly denser. Following the XRD analysis, the formation of hematite occurred in the heated composite. The transformation of maghemite to hematite in the sample was accompanied by a reduction in specific surface area due to sintering of iron oxides particles [22].

The pore size distribution of the composite E20 is shown on Figure 8. As the weight ratio of bentonite to iron oxide in composite E20 is 5:1, the total pore volume is lower. The shape of hysteresis loops of unheated composite and heated to the temperature 650 °C is very similar; the later is shifted to lower values of adsorbed volume, Figure 9. The influence of temperature is analogous as at the composite A85: increasing the temperature of heating, the total pore volume decreases. It is consistent with the changes detected by XRD measurements, where at temperature 300 °C in H₂ atmosphere the goethite particles, comprising approximately one third of the maghemite content were transformed to hematite, and at temperature of 650 °C the additional hematite, due to transformation of maghemite, occurred. The values of specific surface area, Table 1, decreased for composite heated to both temperatures.

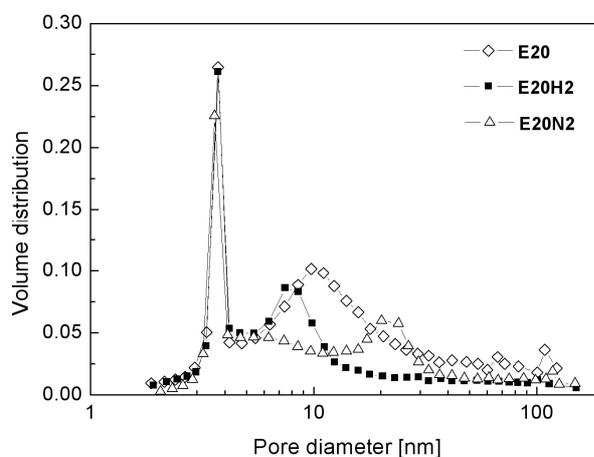


Figure 8 Pore size distribution of composite E20

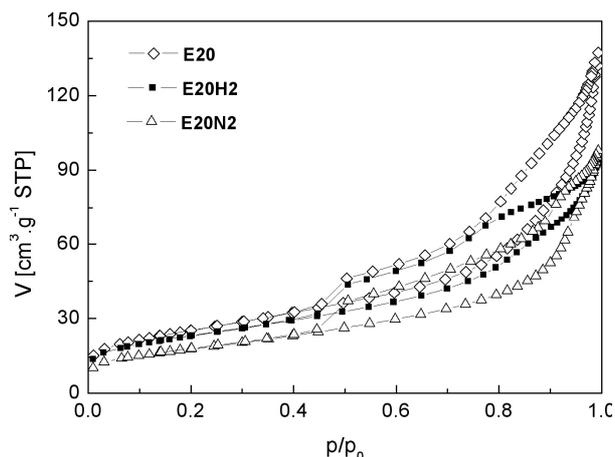


Figure 9 Adsorption and desorption isotherms of composite E20

The low temperature nitrogen adsorption isotherms were used for the calculation of the surface fractal dimensions applying the Frankel-Halsey-Hill (FHH) equation. The fractal dimension D characterizes the nature of adsorbents and heterogeneities of pores. It followed from the Table 1, that only a very slight difference in the values of fractal dimensions were obtained, but the trend of their decrease is proportional to the observed decrease of surface heterogeneity of composite samples.

Table 1 Surface and pore characteristics of composites A85 and E20 after thermal treatment

Composite	S_{BET} [$m^2.g^{-1}$]	V_a [$cm^3.g^{-1}$ STP]	V_{micro} [$cm^3.g^{-1}$ STP]	S_i [$m^2.g^{-1}$]	D
A85	82.92	0.251	0.0032	74.15	2.5332
A85H2	75.71	0.170	0.0035	66.17	2.5328
A85N2	38.49	0.125	0.0012	24.42	2.5296
E20	90.69	0.187	0.0023	84.23	2.6258
E20H2	82.60	0.136	0.0031	73.99	2.6214
E20N2	63.74	0.139	0.0014	59.20	2.6128

TG and DTA curves of heated composites A85 and E20 are shown in Figures 10, 11. The dominant mass loss at the beginning of the TG curve, Figure 10, corresponds to the dehydration of sample A85, showing an endothermic peak with maximum at 120 °C. The composite continues to loss mass not so sharply up to the partial transformation of maghemite to hematite at temperature below 600 °C, as documented by a small exothermic peak. The mass loss in temperature range from 600 – 700 °C is related to the dehydroxylation of clay composite, evidenced by another endothermic peak with maximum around 650 °C. The next small exothermic peak should be related to the continuation of maghemite to hematite transformation.

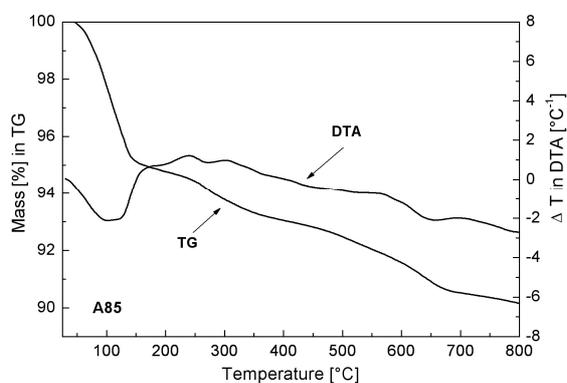


Figure 10 DTA and TG curves for heated composites A85

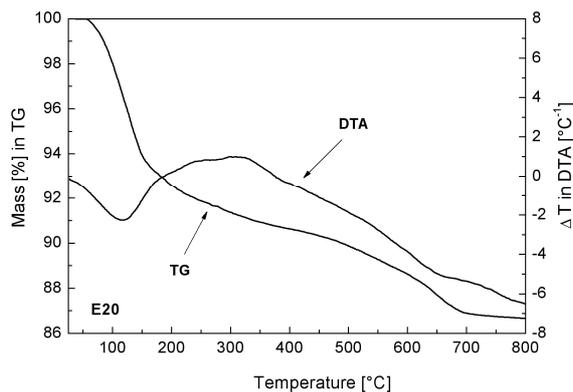


Figure 11 DTA and TG curves for heated composites E20

In case of composite E20 also two mass losses can be observed with maxima of corresponding endothermic peaks around 120 and 650 °C, ascribed to the dehydration and dehydroxylation of composite. An exothermic broadening in temperature range from 200-350 °C was observed, but due to a very small amount of goethite in composite (approximately 5%) it was very difficult to identify an exothermic peak related to the transformation of goethite to hematite observed by XRD at temperature 300 °C.

CONCLUSION

The thermal treatment of montmorillonite/iron oxides up to temperature 650 °C showed that the heating is influenced by the iron oxide content consisted in composites A85 and E20. By heating of the composite A85 in a reductive atmosphere to 300 °C, a partial maghemite to magnetite reduction in composite occurred. It was possible to obtain montmorillonite/maghemite + magnetite composite with narrower distribution of pores. The further increase of temperature in the same atmosphere should probably lead to higher content of magnetite in composite. The heating of A85 up to 600 °C in inert atmosphere yielded to the not complete transformation of maghemite phase to hematite, accompanied with decrease of specific surface area due to sintering of iron oxides particles.

The treatment with composite E20 has shown two transformations of iron phases. At temperature 300 °C, the goethite phase was transformed to hematite; at heating of composite in N₂ atmosphere up to 650 °C the presence of additional hematite phase coming from transformation of maghemite was recorded, a montmorillonite/hematite system with low specific surface area was obtained.

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REFERENCES

- [1] 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.
- [2] 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.
- [3] 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.
- [4] Krajňák, A., Galamboš, M., Rosskopfová, O., Viglašová, E., Rajec, P. (2012). Slovak bentonites as engineering barriers in radioactive waste management. *Proceeding from the European Nuclear*

- Conference, ENC 2012, Transactions and of Use, 9-12. december 2012, Manchester, United Kingdom, European Nuclear Society.
- [5] 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.
- [6] 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.
- [7] Galamboš, M., Suchánek, P. Rosskopfová, O. (2012). Sorption of anthropogenic radionuclides on natural and synthetic inorganic sorbents. *Journal of Radioanalytical and Nuclear Chemistry*, vol. 293, pp. 613-633.
- [8] Safarik, I., Pospiskova, K., Horska, K., Safarikova, M. (2012). Potential of magnetically responsive (nano)biocomposites. *Soft Matter*, vol. 8, pp. 5407-5413.
- [9] Safarik, I., Horska, K., Pospiskova, K., Safarikova, M. (2012). One-step preparation of magnetically responsive materials from non-magnetic powders. *Powder Technology*, vol. 229, pp. 285-289.
- [10] Rozumová, L., Seidlerová, J., Šafařík, I., Šafaříková, M., Gabor, R. (2012). Sorption of Pb on magnetically modified biological materials. *Proceeding from NANOCON 2012*, 23.-25. october 2012, Brno, Czech Republic.
- [11] Wang, W.-Q., Feng, Q.-M, Dong, F., Li, H., Zhao, X. (2010). Preparation and properties of Fe₃O₄/clinoptilolite magnetic composite. *Wuji Cailiao Xuebao/Journal of Inorganic Materials*, vol.25, pp. 401-405.
- [12] Randelović, M., Purenović, M., Zarubica, A., Purenović, J., Matović, B., Momčilović, M. (2012). Synthesis of composite by application of mixed Fe, Mg (hydr)oxides coatings onto bentonite - A use for the removal of Pb(II) from water. *Journal of Hazardous Materials*, vol. 199 -200, pp. 367-374.
- [13] 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.
- [14] Kluchova, K., Zboril, R., Tucek, J., Pecova, M., Zajoncova, L., Šafarik, I., Mashlan, M., Markova, I., Jancik, D., Sebel, M., Bartonkova, H., Bellesi, V., Novak, P., Petridis, D. (2009). Superparamagnetic maghemite nanoparticles from solid-state synthesis - Their functionalization towards peroral MRI contrast agent and magnetic carrier for trypsin immobilization. *Biomaterials*, vol. 30, pp. 2855-63.
- [15] Orolínová, Z., Mockovčiaková, A. (2009). Structural study of bentonite/iron oxide composites. *Materials Chemistry and Physics*, vol. 114, pp. 956-961.
- [16] Mockovčiaková, A., Orolínová, Z., Škvarla, J. (2010). Enhancement of the bentonite sorption properties, *Journal of Hazardous Materials*, vol. 180, pp. 274-281.
- [17] Gaviria, J.P., Bohe, A., Pasquevich, A., Pasquevich, D. M. (2007). Hematite to magnetite reduction monitored by Mössbauer spectroscopy and X-ray diffraction. *Physica B*, vol. 389, pp. 198-201.
- [18] Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquérol, J., Siemieniewska, T. (1985). Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Applied Chemistry*, vol. 57, pp. 603-619.
- [19] Storck, S., Bretinger, H., Maier, W.F. (1998). Characterization of micro- and mesoporous solids by physisorption methods and pore-size analysis. *Applied Catalysis A: General*, vol. 174, pp. 137-146.
- [20] Ye, X., Lin, D. Jiao, Z. and Zhang, L. (1998). The thermal stability of nanocrystalline maghemite Fe₂O₃. *Journal of Physics D: Applied Physics*, vol. 31, pp. 2739-3744.
- [21] Orolínová, Z., Mockovčiaková, A. (2008). Magnetically modified bentonite and study of its improved sorption properties. *Chemicke Listy*, vol. 102, no. 15 spec.iss., p. 834-838.
- [22] Sidhu, P.S. (1988). Transformation of trace element-substituted maghemite to hematite. *Clays and Clay Minerals*, vol. 36, pp. 31-38.