

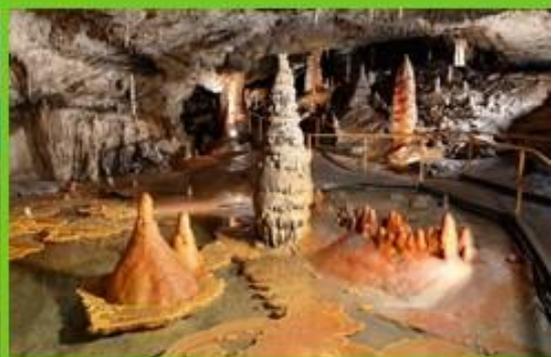
7th Workshop of Slovak Clay Group



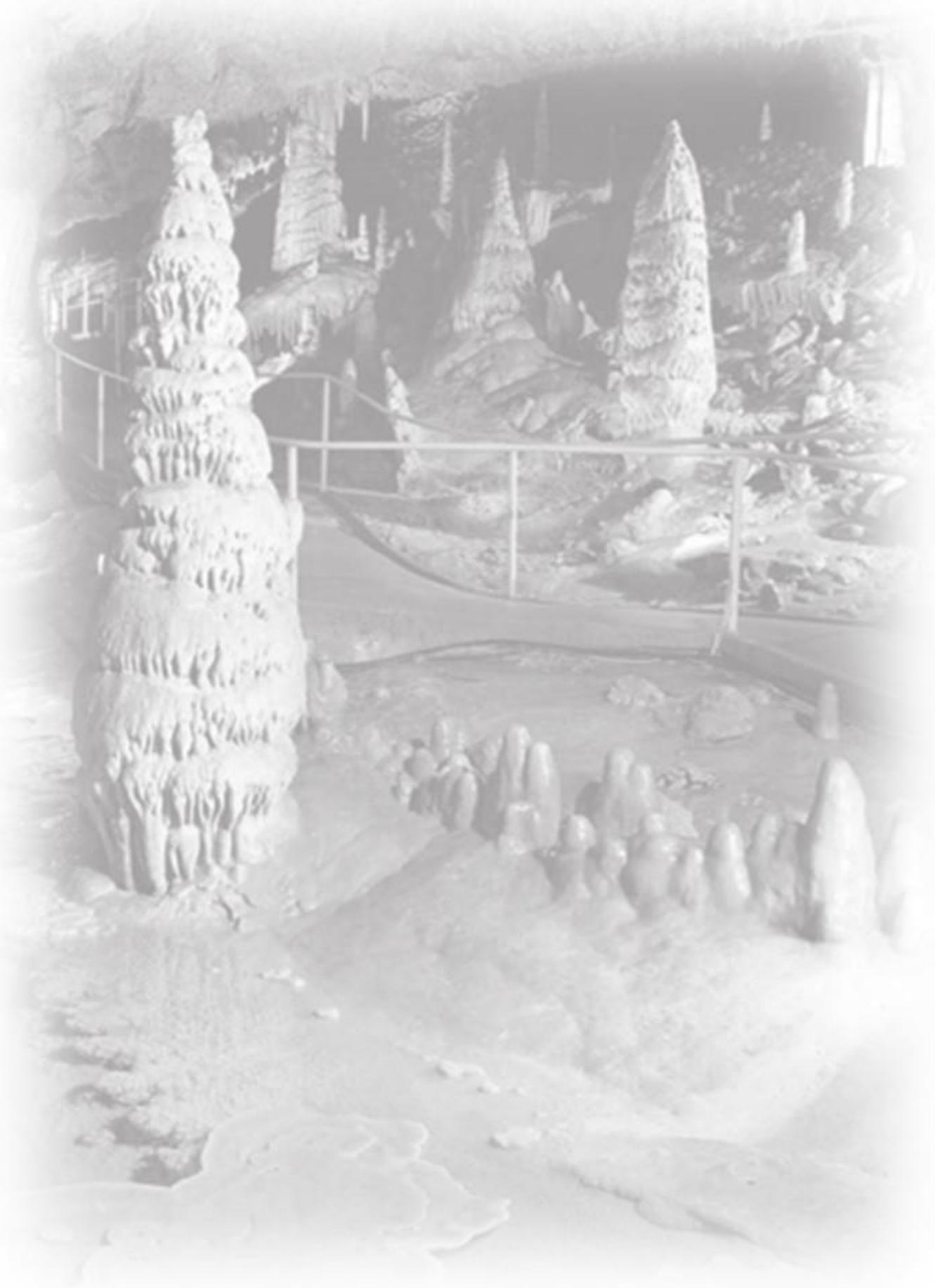
CLAY MINERALS AND SELECTED INDUSTRIAL MINERALS IN MATERIAL SCIENCE, APPLICATIONS AND ENVIRONMENTAL TECHNOLOGY

Book of abstracts

September 7 – 9, 2020, Demänovská dolina, Slovakia



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CONTENTS

MINERALOGICAL CHARACTERIZATION OF CLAYS FROM DOLNA VES DEPOSIT - A SOURCE OF CMS SPECIAL CLAY ILLITE-SMECTITE (ISCZ-1) Y. Bai, et al.....	1
THE MECHANISM OF RHODAMINE DYE MOLECULAR AGGREGATION IN STABLE COLLOIDAL DISPERSIONS OF MONTMORILLONITE T. Baranyaiová, et al.....	3
CLAY MINERALS AS CARRIERS AND LUMINESCENCE ENHANCERS OF RHODAMINE 6G DYE IN THE PRESENCE OF TWO DIFFERENT TYPES OF SURFACTANTS M. Barlog, et al.....	5
APPLICATION OF IRON NANOSCALE STRUCTURES AS EFFECTIVE METHOD FOR DEHALOGENATION OF CONTAMINATED SOILS AND REMOVING OF OLD BURDENS V. Bizovská Kureková et al.....	7
ORGANICALLY-MODIFIED HECTORITE-COATED SILICA PARTICLES FOR ENVIRONMENTAL APPLICATIONS, P. Boháč et al.	9
PHOTOPHYSICAL PROCESSES IN THE COMPOSITE MATERIAL BASED ON SAPONITE, DEXTRAN, AND PHLOXINE B J. Bujdák et al.	11
EFFICIENCY OF ORGANOCLAY BASED ON SAPONITE AND METHYLENE BLUE ON STAPHYLOCOCCUS AUREUS IN PHOTODYNAMIC INACTIVATION H. Bujdáková et al.	13
HIGH TEMPERATURE PHASES OF FUNCTIONALIZED LAYERED SILICATES WITH PHOTOLUMINESCENT PROPERTIES M. Čičkan, M. Janek	15
ANTIMICROBIAL EFFECTIVENESS OF HYBRID FILMS BASED ON SAPONITE AND IMMOBILIZED PHOTOACTIVE DYES PHLOXINE B AND METHYLENE BLUE, N. Dadi, M. Štefánek M., et al	17
ZNO NANOPARTICLES WITH DIFFERENT MORPHOLOGY AS A HIGH-EFFICIENT PHOTOCATALYST D. Furka et al.....	19
NOVEL COMPOSITE NANOMATERIALS FOR MEDICAL DEVICES S. Furka et al.....	20
DECREASED VITALITY AND VIABILITY OF ESCHERICHIA COLI BY ADHERENCE TO SAPONITE PARTICLES B. Gaálová et al.	21
STABILITY OF POLYMERIC COMPOSITE MATERIALS IN PHYSIOLOGICAL ENVIRONMENT D. Hromníková et al.	22
ADDITIVE MANUFACTURING OF CERAMIC MATERIALS M. Janek.....	23
THE CONFORMATION OF ORGANIC CATIONS IN CLAY MINERAL INTERLAYERS J. Madejová, L. Jankovič	24
STRUCTURAL CHANGES OCCURRING UPON DRY GRINDING OF DIOCTAHEDRAL AND TRIOCTAHEDRAL SMECTITES H. Pálková et al.....	25
THE INFLUENCE OF ORGANIC CATION SIZE ON STRUCTURAL CHANGES IN MONTMORILLONITE SUBJECTED TO DRY GRINDING H. Pálková et al.	27
SPECTRAL PROPERTIES OF REICHARDT'S DYE ADSORBED ON AN ORGANOMODIFIED SAPONITE IN COLLOIDAL DISPERSION	

M. Pribus et al.....	29
A COMPUTATIONAL STUDY OF DIURON-BEIDELLITE INTERACTIONS	
D. Moreno Rodríguez et al.....	31
THEORETICAL STUDY OF INTERACTIONS IN THE Mg-VERMICULITE AS A PERSPECTIVE MATERIAL FOR REINFORCING OF ORGANOCLAY POLYMER MATRIX	
E. Scholtzová.....	33
THE SURFACE OF POLYCAPROLACTONE MODIFIED WITH SAPONITE AND METHYLENE BLUE	
E. Skoura et al.....	34
HEXAVALENT CHROMIUM ADSORPTION BY TETRAHEXYLPHOSPHONIUM-MODIFIED BEIDELLITE CLAY – COMBINED THEORETICAL AND EXPERIMENTAL STUDY	
P. Škorňa et al.....	36
THE ANALYSIS OF THE SYSTEM $3\text{NaF}-\text{AlF}_3-\text{FeF}_3$	
F. Šimko et al.....	38
THERMOANALYTICAL TECHNIQUES APPLIED FOR CHARACTERIZATION OF WATER IN PERLITES	
P. Uhlík et al.....	39
LIST OF PARTICIPANTS	42

MINERALOGICAL CHARACTERIZATION OF CLAYS FROM DOLNÁ VES DEPOSIT - A SOURCE OF CMS SPECIAL CLAY ILLITE-SMECTITE (ISCZ-1)

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KEYWORDS: Dolná Ves | Illite-smectite | Mineralogy | Chemical composition

The Dolná Ves deposit is situated in Kremnické vrchy Mt. and is related to products of rhyolite volcanic activity of the Jastrabá Formation. It is used as ceramic clays with annual production less than 5,000 tones ^[1]. The usual thickness of the productive zone is ~10 m, but locally reaches up to 60 m, with reserves ~9 Mt ^[2]. The major minerals are mixed-layered illite-smectite (I-S) and quartz. Economic accumulation of I-S is unique, only several similar clay deposits are mined around the world (e.g. Füzerradvány, Tokaj Mts., Hungary ^[3]). The clays from Dolná Ves contain pure I-S in clay fraction ^[4]. This is ideal for the investigation of I-S properties from variable perspectives. Therefore, V. Šucha collected sample and sent it to Clay Minerals Society (CMS) in the 90ties. The I-S (30%S) from Dolná Ves with name ISCz-1 is in the collection of Special clays of Source Clays.

SARMAT firm produced ceramic clay in the Dolná Ves deposit about 15 years. Despite small production, the deposit surface has been changed and open pit mine has been created with size approximately 100x75x7 m. Five samples from the recent surface of the deposit have been collected to characterize and compare them with ISCz-1. The aim of our study is not only to review theoretical changes of properties of clays during 15 years of mining but also to verify the potential of offering a new I-S standard for CMS in case of depletion of the recent source.

From previous research, Dolná Ves I-S is mostly of R1 type with 1M polytype and expandability mostly between 6 and 45 %, with a trend of increase from north to south. The polytype distribution of the I-S minerals showed no relation to expandability. R3 ordering occurred in samples with expandability <15 % and samples with expandabilities >45 % are very rare. The samples with the largest amount of expandable layer are K-rectorites with regularly interstratified 1.0 and 1.7 nm layers ^[4]. The distributions of fundamental particles and mixed-layer crystals are internally consistent and dominated by bilayer fundamental particles, mixed-layer crystals often contain even numbers of layers ^[5]. The transformation of the I-S minerals was accompanied by dissolution of cis-vacant 2:1 layers and reprecipitation of trans-vacant 2:1 layers, and during the neoformation of trans-vacant illite layers, the interlayer K cations increased ^[6]. Šucha et al. ^[7] reported the weathering of I-S produces an increase in CEC and total surface area. They also reported rhodamine 6G dye (R6G) interactions with I-S, and indicate the origin of both the high- and low-charge sites ^[8]. In addition, Galamboš et al. ^[9-10] also make some researches on adsorption of cesium using mixed-layer I-S, and the results confirmed Dolná Ves mixed-layer I-S have lower sorption properties than smectites.

Five new samples were characterized by grain size distribution, X-ray diffraction (XRD) analyses, cation exchange capacity (CEC) and infrared spectroscopy.

For grain size distribution, the >2000 μm size fractions are higher in DV19/1 and DV19/2, reaching 55.8 wt% and 40.0 wt%, respectively. In contrast, DV19/3 and DV19/4 showed almost do

not contain this size fractions. The 500-2000 μm size fractions in all samples are relatively small (< 3.2 wt%). The 63-500 μm size fractions in DV19/2, DV19/3, and DV19/4 are relatively smaller than DV19/1 and DV19/5, and DV19/1 and DV19/5 are basically the same at 14.8 wt% and 15.5 wt%, respectively. For the 2-63 μm size fractions, DV19/4 has the highest content and DV19/1 has the lowest content, being 78.4 wt% and 11.7 wt%, respectively. Among all samples <2 μm size fractions, DV19/3 contained highest, reaching 49.8 wt%, and the remaining four samples did not show much different, between 14.5-25.1 wt%.

For mineral composition, the bulk samples are composed of illite-smectite (38.7-90.1 wt%) quartz (1.8-60.2 wt%), 1-6.7 wt% of feldspars (K-feldspar and plagioclase) and traces (0.1-3.4 wt%) of other minerals (amphibole, biotite and opal C/CT). In all samples, 2-63 μm size fractions contained a higher amount of I-S and a lower amount of quartz compared with 63-500 μm . The bulk samples contained the highest amount of I-S for all samples, meanwhile 63-500 μm size fractions contained the highest amount of quartz (17.6-87.3 wt%). Interestingly, 63-500 μm size fractions of DV19/3 contained the highest amount of feldspar (64.7 wt%), much higher than any other bulk samples and their size fractions.

DV19/1, DV19/2 and DV19/5 have a similar expandability (percentage of smectitic interlayers in I-S) between 20-24 \pm 3 %, while DV19/3 and DV19/4 have a higher expandability at 42 \pm 3 %. The expandability has positive correlation with CEC (in range from 25 to 41 meq/ 100g).

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THE MECHANISM OF RHODAMINE DYE MOLECULAR AGGREGATION IN STABLE COLLOIDAL DISPERSIONS OF MONTMORILLONITE

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KEYWORDS: metachromasia | non-Arrhenius behaviour | diffusion-controlled processes

Metachromatic behavior, which relates to the formation of molecular aggregates of organic dyes, is manifested by significant color changes [1]. Dye molecular aggregation is a spontaneous phenomenon that occurs in concentrated aqueous dye solutions and complex reaction systems composed of polyelectrolytes, biological macromolecules, nanoparticles of noble metals, or dispersed particles of layered silicates [2]. Despite dye molecular aggregation in smectite dispersions has been well documented in recent decades [3], some aspects of the interaction of planar dye molecules with silicate particles have not been described yet.

In our previous study, close relationships between the course and extent of rhodamine dye molecular aggregation and the changes in the stability of montmorillonite (Mnt) dispersions after the rapid adsorption of dye cations were observed [4]. We have also reported a slow formation of dye aggregates at the Mnt particle interface, which is surprising given the non-covalent character of dye molecules association. The molecular aggregation in aqueous solutions is an instantaneous process, the rate of which is determined by the diffusion of dye cations. On the other hand, the spectral equilibrium in dye / smectite dispersions is reached within a few hours, and the rate constants of dye aggregation are more than ten orders of magnitude lower than in the case of dye aqueous solutions ($\sim 10^9 \text{ s}^{-1}$, [5]). To shed more light on the mechanism of the slow processes involved in the formation of dye aggregates at colloidal particle interface, our recent research was focused on the investigation of the effect of temperature, stirring rate, and reactants concentration on dye aggregation kinetics.

Reaction kinetics measurements of rhodamine 123 (R123) aggregation in Mnt dispersion were realized using the combination of a stopped-flow rapid mixing device and UV-Vis spectrophotometer with a diode-array detector. The loading of R123 was kept constant at 0.02 mmol g^{-1} for all the investigated dispersions, which corresponded to 1.75% of the cation exchange capacity of Mnt. In the next step, the recorded absorption spectra (more than 10,000) were analyzed by the chemometric method that resulted in spectral and concentration profiles of R123 monomers and molecular aggregates. The spectral profiles of the respective dye species were interpreted in accordance with the exciton theory. Subsequently, the parameters of the kinetics of R123 aggregation were calculated using a non-linear regression analysis of the calculated concentration profiles.

The interaction of rhodamine cations with Mnt particles to the greatest extent led to the formation of oblique J-aggregates of the dye. The fraction of R123 cations forming J-aggregates was dependent neither on the reaction temperature (T), nor on the stirring rate and reactants concentration. This observation confirms that the extent of dye aggregation is related to the layer charge of the smectite. The mechanism of dye aggregation was described by two parallel processes

with exponential kinetics. The obtained values of rate constants were in the range from 10^{-3} s^{-1} to 10^{-2} s^{-1} . Kinetic parameters of R123 aggregation were not affected by the concentration of the reactants nor the stirring rate. The rate constant of the processes increased with an increasing T . However, the variation of the rate constants did not follow the Arrhenius equation. The observed super-Arrhenius behavior and a linear dependence of the rate constants on T indicate the key role of the diffusion processes in the formation of R123 aggregates.

The results confirm that the interaction of dye cations with smectite particles is a complex process involving two stages. The first phase corresponds to the rapid adsorption of R123 molecules on the surface of Mnt particles. This process occurs almost instantaneously after the mixing of the reactants and is controlled by the diffusion of dye cations to the oppositely charged surface. Diffusion-controlled dye adsorption is in many cases associated with the production of initially-formed dye aggregates. The second stage represents the slow formation of the oblique J-aggregates. The suggested, double-exponential model for the reaction mechanism indicates the presence of different active sites on the surface of Mnt particles. The slow course of the association of R123 molecules is due to the dye adsorption, which prevents their rapid migration on the surface. Most probably, the kinetics of dye aggregation is controlled by the rate of the lateral diffusion of adsorbed dye cations. Their motion along the electrical double layer surrounding the Mnt particles allows the cations to reach the active sites and enables the formation of dye aggregates after longer reaction times.

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CLAY MINERALS AS CARRIERS AND LUMINESCENCE ENHANCERS OF RHODAMINE 6G DYE IN THE PRESENCE OF TWO DIFFERENT TYPES OF SURFACTANTS

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KEYWORDS: rhodamine 6G | luminescence | layered silicates | fluorescence | molecular aggregates

The main motivation of the present work was the development of hybrid materials exhibiting interesting luminescent properties that would be suitable for modification of industrial polymer surfaces. The materials were based on organoclays prepared from montmorillonite (Mt) or saponite (Sap) modified with two cationic surfactants (tetraoctylammonium, TOA, tetraoctylphosphonium, TOP) and functionalized with a laser dye, rhodamine 6G (R6G). The influence of the type and extent of the modification, the dye concentration, and clay mineral type was investigated. The optical properties of the dye were characterized by spectroscopy methods in the visible spectral region (diffuse reflectance, emission, and excitation spectra).

The content and structure of the organic phase in the samples were controlled by carbon elemental analysis and X-ray diffraction (XRD). Various amounts of the organic surfactants relative to the cation exchange capacity (CEC) were applied for organoclays' preparation; (25, 50, 70, and 100 %). Organoclays derived from Mt (Mt-Surf₂₅ - Mt-Surf₁₀₀) contained higher amounts of the surfactants compared to those based on Sap (Sap-Surf₂₅ - Sap-Surf₁₀₀) because of the higher CEC of Mt. No significant difference between TOA and TOP contents were observed for the samples with the same loading and the same clay mineral. Based on the organic phase amount determined by elemental analysis, an almost complete exchange was obtained for Sap, while Mt was saturated to only 83 and 88 % with respect to the CEC. The expansion of interlayer space was registered and reflected the surfactant loading. Raw smectites showed d_{001} , 1.25 nm (Mt) and 1.23 nm (Sap). The basal spacing gradually increased reaching 2.19 nm and 2.58 nm, respectively, for samples fully saturated with the surfactants (Sap-Surf₁₀₀ and Mt-Surf₁₀₀). A higher atomic radius of phosphorus resulted in slightly higher d_{001} values detected for some of Mt-TOP and Sap-TOP samples in comparison with Mt-TOA and Sap-TOA counterparts. No significant changes in d_{001} values were registered for the samples modified with both surfactant and R6G.

The optical properties of prepared samples varied primarily due to the formation of various spectral forms of the dye, including molecular aggregates. The absorption spectra were calculated from the measurements of diffuse reflectance spectroscopy. The maxima of the main band were centred at $\lambda \sim 555$ -575 nm in dependence on the R6G content. The higher concentration of R6G resulted in the shift of the main band to higher λ and the appearance of low intensities bands at shorter λ (<510 nm). The spectra collected for the samples with co-intercalated surfactant and R6G showed further shifts of the main absorption band to higher λ , due to splitting of the excited states.

The contribution of fluorescent species to the shape of emission spectra was analysed. Differences in the layer charge and charge distribution in smectite layers led to the variations in the shape of R6G-Sap and R6G-Mt spectra. The higher charge density of Mt caused the formation of non-luminescent aggregates resulting in lower intensities compared to Sap. The emission band of J-aggregates at about 590 nm prevailed, however, the higher concentration of R6G evoked the red

shift of the band to longer wavelength (>600 nm) and a sharp decline in the intensity. The incorporation of the surfactants generally caused significant changes in the spectral profiles a significant enhancement of the emitted light (over an order of magnitude with respect to the samples without the surfactants). The most pronounced increase in the intensities was recorded for the organoclays with R6G at the loading $0.005 \text{ mmol}\cdot\text{g}^{-1}$. The presence of the surfactants suppressed the formation of H-aggregates and on contrary supported the formation of luminescent types of aggregates.

The chemometric and statistical analyses of the emission spectra were applied to shed more light on the components contributing to the spectral shape and the evaluation of possible aggregated species developed in prepared systems. The analysis revealed several types of components, which were attributed to monomers with a significant red-shift (570 nm) and different forms of photoactive molecular aggregates, as dimers (589 nm) and larger aggregates (614 - 655 nm). The highest proportion of the emission from monomers and J-dimers was observed for the powder samples with the lowest R6G concentration, while higher R6G and surfactant contents led to the increasing emission from higher J-aggregates.

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APPLICATION OF IRON NANOSCALE STRUCTURES AS EFFECTIVE METHOD FOR DEHALOGENATION OF CONTAMINATED SOILS AND REMOVING OF OLD BURDENS

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KEYWORDS: decontamination | nanoscale iron | aromatic hydrocarbons | infrared spectroscopy

Contamination of environment due to chemical industry focused on production of pesticides is still serious problem. Hazardous are especially soils containing high concentration of chlorinated hydrocarbons that can subsequently contaminate ground waters. Their degradation is usually realized by permeable reactive barrier (Fig. 1) containing of nanoscale zerovalent iron (ZVI), but it is very expensive process. ZVI, in anaerobic condition, act as reductant for dehalogenation of chlorinated hydrocarbons.

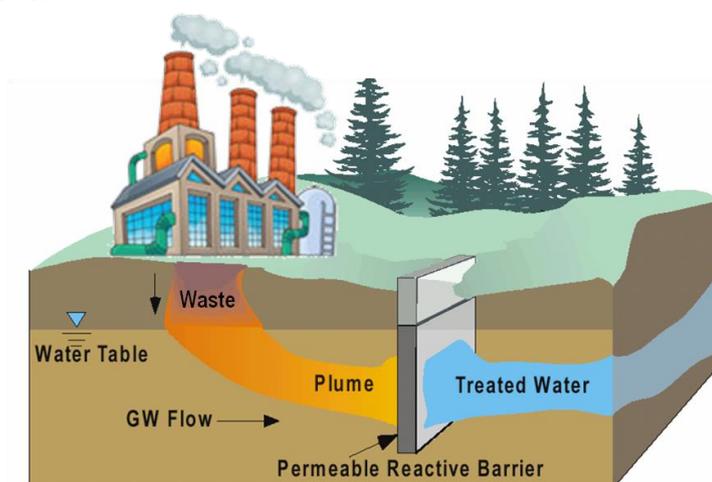


Fig. 1. Schematic picture of permeable membranes

The objective of this work was to describe mechanism of dehalogenation of aromatic hydrocarbons using ZVI achieved from waste materials, what can significantly reduce costs of building process. Decontamination was observed on physical model of permeable reactive barrier in laboratory conditions. Without commonly used methods for determination of contaminant concentration (mass spectroscopy and gas chromatography) we have been used X-rays powder diffraction, infrared spectroscopy and microscopic methods (Fig. 2) to characterize structures of irons compounds.

Emerging function nanoscale structures of irons compounds occurred during dehalogenization reaction. Efficiency of decontamination process depends on presence of irons compounds and especially on their transformation. The presence of various anions (SO_4^{2-} , CO_3^{2-} , Cl^-) is very important parameter, because they can act as substituent in iron compounds and influence decontamination process. Emerging nanoscale Fe-structures have large surface area, therefore sorption of chlorinated aromatic hydrocarbons was investigated along redox reaction. Important result of our study was detection of significant migration of emerging functional nanoscale

structures of iron behind barriers border, thus the reaction volume increased. As consequence of the larger reaction volume of Fe-structures, the width of barrier can be reduced.

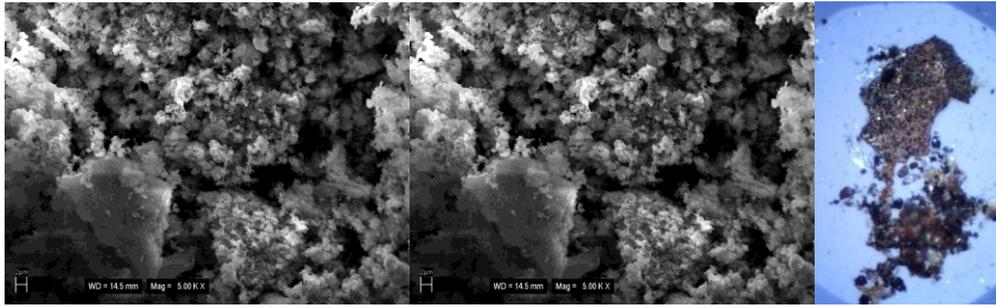


Fig. 2. Observed changes in the morphology of Fe surface due to formation of oxyhydroxides: left – Fe-initial, middle and right Fe-phases after 3 months

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This contribution/publication is the result of the project implementation Investigation and verification of catalytic dehalogenation on reactive barriers technologies - treatment of contaminated water from polluted industrial site (No.:ITMS 26240220078) supported by the Research & Development Operational Programme funded by the ERDF

ORGANICALLY-MODIFIED HECTORITE-COATED SILICA PARTICLES FOR ENVIRONMENTAL APPLICATIONS

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KEYWORDS: Adsorption | organic pollutants | organoclay

Contamination of environments with chemical substances from the anthropogenic activities including organic pollutants, solvents, and heavy metals is a serious environmental concern. The organic contaminants of potential risks include pharmaceutical and personal care products, pesticides, herbicides, dyes, and plastics, and their additives. To avoid the risks to human health, numerous processes have been developed and applied for the remediation of contaminated environments. Adsorption is a good strategy for the removal of organic contaminants from the environment, regarding its advantages as easy handling, inexpensive process, high selectivity, and less probability of the generation of toxic by-products.

Layered materials such as the smectite group of clay minerals are one of the class of adsorbents, where expandable interlayer space and layer charge are key parameters for their adsorption efficiency. Clay minerals can be modified to form hydrophobic and microporous materials to selectively uptake various anionic and non-ionic pollutants [1].

The disadvantage of the use of smectites and its hybrid materials in environmental technologies is the difficulty of manipulation. The size and the formation of the stable colloids and gels complicate the use of smectites in the adsorption columns. Sedimentation and filtration processes are not mostly efficient to separate the smectite sorbents from supernatants.

The goal of the presented work was to prepare the material with the adsorption properties similar to clay minerals, which would be easy to manipulate with. For this purpose, hectorite-coated silica (CS) particles have been synthesized by the hydrothermal synthesis following the Tajima and Okada method [2]. As a core of the materials, microporous silica gel based on the particles with an approximate diameter of 300 μm has been used. The coatings on the particles were achieved by the hydrothermal synthesis at 99.5°C after 48 h. The presence of hectorite has been confirmed by the combination of the IR spectroscopy, XRD, and SEM.

Subsequently, prepared materials have been modified using cetyltrimethylammonium bromide (CS-CTM) or by poly(diallyldimethylammonium) chloride (CS-PDDA) to achieved hydrophobic character and a charge reversal. Prepared materials have been tested by adsorption experiments of three analgesics: paracetamol (PAR), ibuprofen (IBU-Na), and diclofenac (DCF-Na), two antibiotics: norfloxacin (NOR) and ofloxacin (OFL) and one pesticide metazachlor (MTZ).

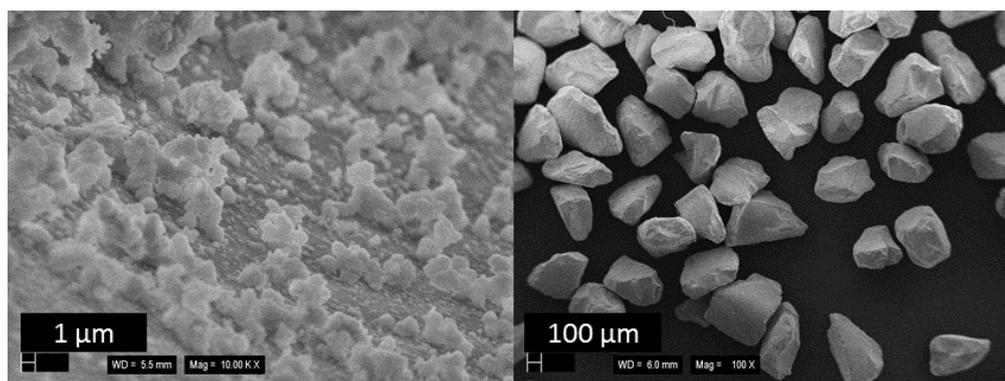


Figure 1: SEM of the hectorite-coated silica particles.

Sample CS-CTM showed a high affinity to antibiotics NOR and OFL, as well as a pesticide MTZ. The concentrations of antibiotics in the supernatants were decreased to the limits of detections. Sample CS-PDDA showed good adsorption properties of analgetics DCF-Na, IBU-Na and antibiotics NOR, and OFL (Table 1). The prepared adsorbents are thanks to their particle size easy to separate from the liquid phase and suitable for the use in the adsorption columns. The low adsorption capacities q_e were caused by the bulk character of the core of the prepared materials. This could be increased by using smaller SiO₂ cores. Prepared materials represent very suitable materials with potential in the application in environmental remediation of some organic pollutants.

Pollutant	Pollutant decrease in %		Adsorption capacity q_e (mg/g)	
	CS-CTM	CS-PDDA	CS-CTM	CS-PDDA
PAR	11	16	0.22	0.33
IBU-Na	4	87	0.09	1.74
DCF-Na	1	99	0.01	1.97
NOR	100	91	2.13	1.91
OFL	100	91	1.76	1.60
MTZ	67	46	1.32	0.92

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PHOTOPHYSICAL PROCESSES IN THE COMPOSITE MATERIAL BASED ON SAPONITE, DEXTRAN, AND PHLOXINE B

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KEYWORDS: photosensitizer | polymer | organic dyes | fluorescence | nanocomposites

Introduction

The hybrid materials of organic dyes and inorganic templates based on layered nanoparticles represent an interesting group of functional materials [1]. In the present study, complex materials were synthesized involving a derivate of organic polymer – dextran. Saponite (Sap) was chosen as a layered silicate template typical of small particles and forming colloidal dispersions exhibiting high stability. Sap was modified using two dextran derivatives both functionalized with positively charged alkylammonium groups. The second derivative was labelled also with fluorescein luminophore groups (FITC). The complex particles of modified materials based on various ratios of Sap/dextran were still bearing a partially positive charge, which was favorable for further functionalization with anionic dye, phloxine B (PhB).

The interpretations of the properties of the prepared systems had to take into account all the possible interactions, mainly electrostatic attraction between negatively charged Sap particles and positively charged dextran polymer chains. The composition of both the colloids and films has been designed to have the amount of fluorescently active components constant and only the ratio between the components was varied by changing Sap content and concentration. Based on this approach, the optical properties of the materials were evaluated based on the interactions and equilibria taking place between the components. The main methods applied were absorption and fluorescence spectroscopy to evaluate photophysical properties of the films and their colloidal precursors.

Interactions between the components in colloids

The negative charge of Sap was balanced by positively-charged alkylammonium groups in dextran. In the materials of high Sap/dextran ratios, the negative charge of Sap effectively saturated the polymer charge, which in some cases led to the loss of colloidal stability of the composite. For the stable colloids, the composite particles had to bear a residual positive charge to have an efficient electrostatic stabilization of the colloids.

The complex character of the prepared colloids was manifested by changes in the photophysical properties of some components depending on the ratio and interaction between the components, and several photophysical phenomena. For example, some spectral properties were explained by the equilibria between various forms of the chromophores (FITC, PhB). The complexity of the systems was due to the competing interaction of anionic FITC groups present in the dextran and PhB anions.

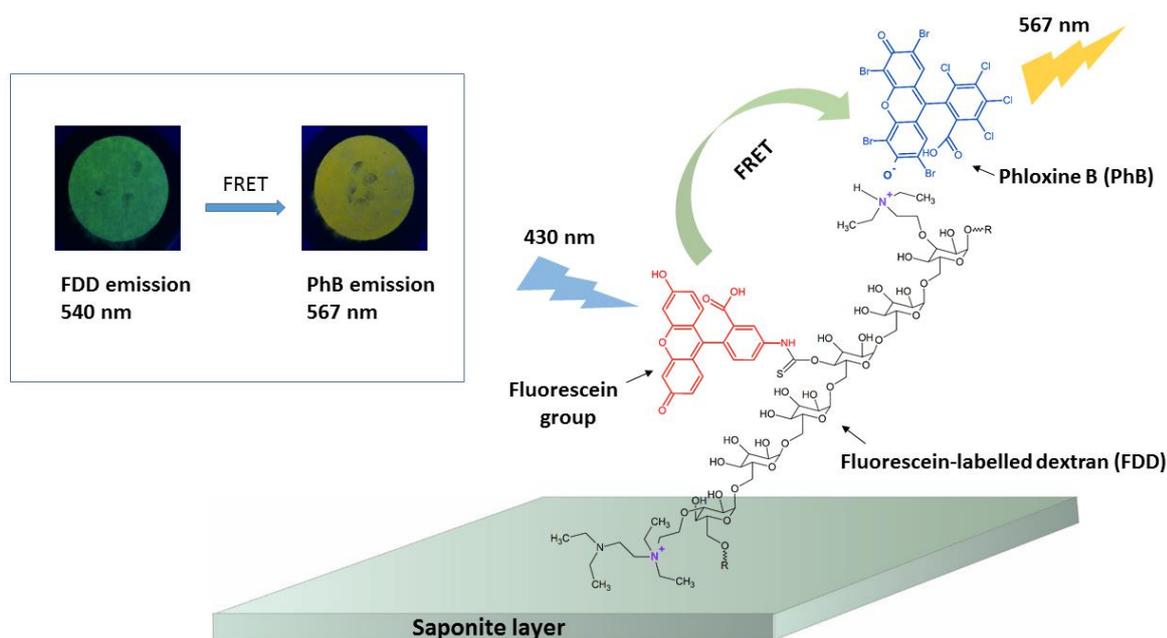
The properties of the films

The colloidal dispersions were used as precursors for the preparation of thin films. The solid films were prepared by the method of vacuum filtration. As mentioned above the ratio of the components significantly affected the equilibria between the charged species which was also significantly reflected in the photoactivity and fluorescence properties of the samples. The aim was to prepare films that exhibit efficient absorption of visible light and excitation energy transfer from FITC groups to PhB molecules.

Despite the complex character of these materials, it was relatively easy to design and prepare suitable systems that exhibited interesting properties. The films exhibited an efficient absorption in a relatively wide range of the visible spectrum. The intermolecular distances between FITC groups and PhB anions in the complexes were short enough to achieve efficient energy transfer ending with the emission from PhB molecules.

Conclusions

Photoactive materials were developed exhibiting visible light harvesting and efficient transfer of light energy to phloxine B photosensitizer. Such materials could be used as photosensitizing agents with efficient light-harvesting systems which can be activated by the excitation at a relatively broad range of visible spectrum and would be applicable for the use with polychromatic light. Further study is planned and should be focused more on photosensitization concerning the biological activity of such systems.



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EFFICIENCY OF ORGANOCLAY BASED ON SAPONITE AND METHYLENE BLUE ON STAPHYLOCOCCUS AUREUS IN PHOTODYNAMIC INACTIVATION

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KEYWORDS: photodynamic inactivation | clay mineral | quaternary ammonium salt organoclay | *Staphylococcus aureus*

Photodynamic inactivation (PDI) is one of the promising alternative strategies for the eradication or inhibition of pathogenic microorganism. The photoactive agents can act alone or can be immobilized on a carrier that provides transport and mediates interaction between microbial cells and photoactive molecules. In this work, the effectiveness of organoclay based on saponite (Sap) and immobilized photosensitizer methylene blue (MB) was tested against methicillin-resistant isolate *Staphylococcus aureus* L18 and compared to the control susceptible strain *Staphylococcus aureus* CCM 3953. Using ultraviolet–visible spectroscopy, MB in solution was present mainly in the form of monomers, but in combination with Sap, it formed molecular aggregates. To reduce the dye aggregation, Sap particles were modified with a quaternary ammonium salt dodecyltrimethyl ammonium chloride (C12). The design of the preparation of organoclay is shown in Fig. 1.

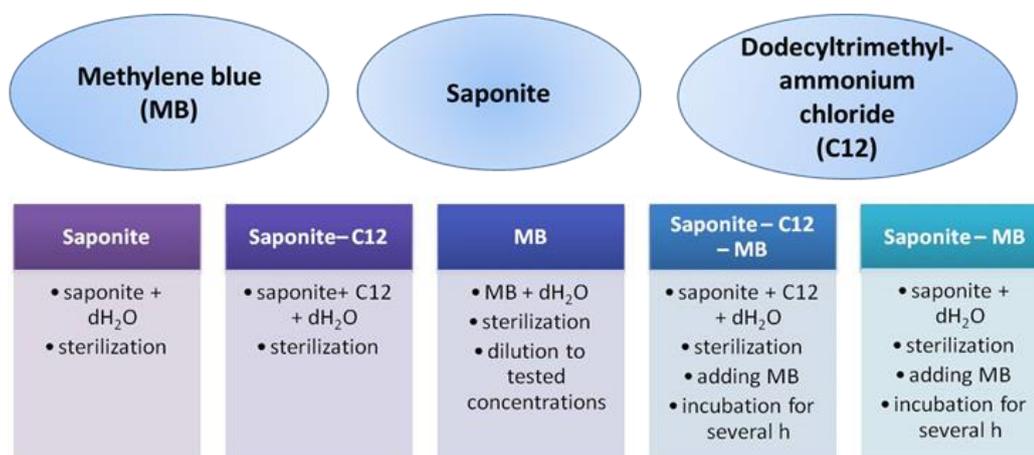
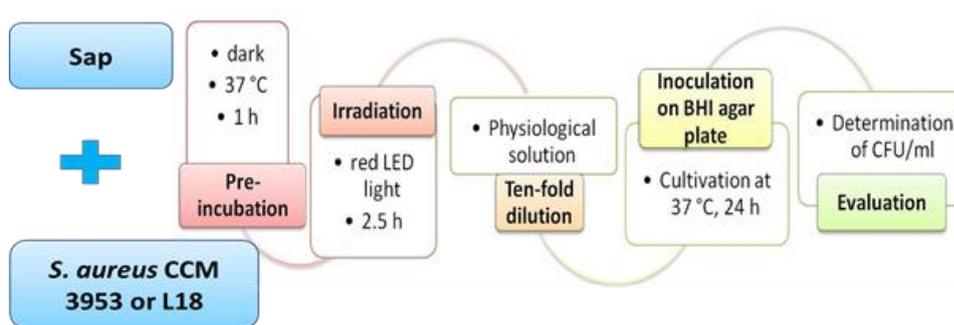
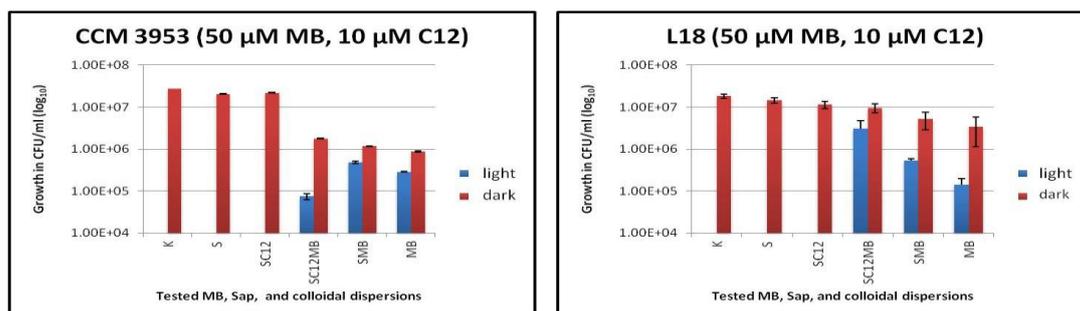


Fig. 1 Preparation of organoclay based on Sap and MB.

Concentrations of the components, incubation, and irradiation period were optimized to achieve a significant antimicrobial effect. The effectiveness of MB alone, MB immobilized on Sap particles and organoclay modified with C12 was studied using PDI. The samples were illuminated with the red LED light (1.67 mW.cm⁻², wavelength 576 – 672 nm and fluence 15 J.cm⁻²). The assay is summarized in Fig. 2.

Fig. 2 Protocol of testing LED organoclay on *S. aureus* strains in PDI.

The most efficient PDI of clinical isolate *S. aureus* L18 was achieved in the presence of 50 μM MB and Sap colloidal suspension (0.65 g/l) with immobilized 50 μM MB. The reduction in the number of living cells was by 2 \log_{10} compared to the control. In the experiments with the colloidal suspension containing MB and MB alone, the growth of microorganisms in the control samples without illumination was not inhibited. On the other hand, the highest inhibition of growth was observed in the presence of the organoclay with immobilized 50 μM MB on the reference strain *S. aureus* CCM 3953; the reduction was by 2.53 \log_{10} compared to the control sample without agents. In the experiments without illumination, the reduction in the growth of the microorganisms was not higher than 1.01 \log_{10} compared to the sample without the colloid. The susceptibility testing of MRSA strain L18 on C12 showed considerably decreased susceptibility to this agent. Probably, this was a reason, why organoclay was less effective compared to the reference strain (Fig.3).

Fig. 3 Effectiveness of MB, Sap, and organoclay on *S. aureus* strains in PDI.

The cytotoxicity of the colloidal suspensions and MB was tested on the HeLa cell line. While Sap and Sap-modified with C12 did not show any inhibitory effect, the determination of toxicity of organoclay was not possible to estimate because of a strong binding the substrate on Sap. Scanning electron microscopy confirmed a high capacity of the organoclay to bind bacteria but did not show a direct damage of bacterial cells.

Taken together, results proved inhibitory effect of PDI on the MRSA strain and Sap showed to be a suitable carrier of photosensitizers. Additional experiments are necessary to optimize composition of an organoclay to obtain a maximal reduction in the survival of resistant bacteria.

Acknowledgement

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HIGH TEMPERATURE PHASES OF FUNCTIONALIZED LAYERED SILICATES WITH PHOTOLUMINESCENT PROPERTIES.

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KEYWORDS: up-conversion | photon conversion | layered silicates | rare earth elements

Scientists from all over the world have been studying light and optical phenomena for many years. Lanthanoid doped nanoparticles appeared in the late 1990s. In recent years, photon conversion has become a more topical issues such as up-conversion. This represent an optical phenomenon in which the absorption of two or more photons leads to the emission of light with a shorter wavelength (higher energy) than the excitation wavelength. This phenomenon can be observed in both organic and inorganic materials containing elements that are able to transfer energy to each other and thus cause photon conversion through various mechanisms (1,2). Suitable inorganic matrices include, for example, silicates, layered minerals which contain cations with different charge sizes in their interlayer space. It is these cations that can be replaced by doping elements that are capable of converting photons. In the case of inorganic materials, d- and f-elements (eg Gd³⁺, Eu³⁺, Yb³⁺ and various combinations of their contents) are used for the conversion of photons (3). It is also possible to convert low-energy photons to high-energy photons using heat (4).

Up-converting nanoparticles are widely used, for example, in medicine, bioapplications, as well as in energy devices. A current problem in the preparation of photon up-converters is their synthesis with respect to the efficiency of emitted radiation (5). The development of a reproducible synthesis to control the content of rare elements and the size of nanoparticles is necessary for the use of these materials in practice (6). In this work we will deal with the preparation of suitable materials (doped silicates) and their optical properties at different temperature conditions. The aim of the work is to create material showing the most efficient up-conversion.

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ANTIMICROBIAL EFFECTIVENESS OF HYBRID FILMS BASED ON SAPONITE AND IMMOBILIZED PHOTOACTIVE DYES PHLOXINE B AND METHYLENE BLUE

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KEYWORDS: Saponite | hybrid films | Phloxine B | Methylene blue | Antimicrobial activity

In the healthcare-associated infections the excessive usage of antibiotics is no longer feasible option concerning the development of antimicrobial resistance[1]. Preparation of novel films by modifying the medical equipment using nanomaterial with immobilized photosensitizers is a favourable method as it possesses a minimal impact on the development of resistance. This research was focused on developing novel hybrid films based on saponite(Sap) with immobilized photoactive dyes Phloxine B (PhB) and Methylene blue (MB). Sap (1 g/L) was deposited on a cover glass and surface was further modified with octadecyltrimethylammonium (ODTMA) bromide, and finally, 0.05 mM PhB was added on the surface (Fig 1A). The concentration of 0.05 mM was determined by preliminary antimicrobial assays with different concentrations of PhB (0.001, 0.005, 0.01, 0.05, 0.1 mM). Physicochemical characterizations were conducted to identify ODTMA and PhB stability (X-ray diffraction) photoactivity of PhB (fluorescence spectroscopy) and hydrophilic and hydrophobic nature of the films (water contact angle). Antimicrobial effectiveness was assessed by photodynamic inactivation (PDI) against standard strain *Staphylococcus aureus* CCM 3953 along with methicillin-resistant *Staphylococcus aureus* (MRSA). This assay was performed in dark and light. One group of samples was irradiated (green LED light; 2.5 h) and other groups remained in the dark. PDI showed a reduction in growth of bacteria from 3- \log_{10} to over 1- \log_{10} compared to the control samples with Sap only.

To explore the capabilities of the hybrid films, films with MB was prepared and tested for antimicrobial activity against the yeasts of *Candida auris* a major emerging multi-resistant nosocomial pathogen [2]. In mentioned hybrid system, Sap (1g/L) was modified by dodecyltrimethylammonium (DDTMA) chloride (0.8 mM/1g Sap) and further 0.1 mM MB was added. These samples were filtered through teflon membrane (0.1 μm PTFE), covered with polyurethane (Fig 1B) and dried at room temperature in the dark. The antimicrobial activity of these hybrid films was tested against three different yeast's strains; *Candida auris* H261, *Candida auris* S, and *Candida auris* R. A 24-h biofilm was cultured on the hybrid films and then irradiated it for 300s (corresponding to 100.9J) with the red laser ($\lambda=660\text{nm}$, 190 mW/cm^2). The control group (Sap) and a set of the hybrid films were kept in the dark. Hybrid films from the irradiated group have shown a reduction in the number of living cells between 1 \log_{10} and 2 \log_{10} reduction. These results are preliminary and experimental conditions have to be optimized to obtain higher reduction in yeast

survival. Further experiments performed on bacterial and polymicrobial biofilms are needed to assess the viability of this novel hybrid material thoroughly.

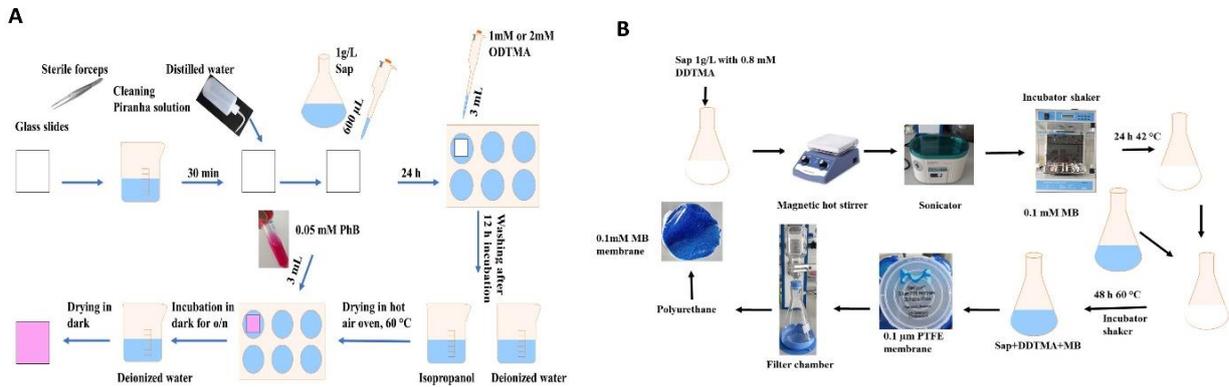


Fig. 1 Preparation of hybrid film with PhB (A) and MB (B)

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ZNO NANOPARTICLES WITH DIFFERENT MORPHOLOGY AS A HIGH-EFFICIENT PHOTOCATALYST

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KEYWORDS: ZnO | photocatalysis | dye decomposition | boron doping

Water pollution by organic pollutants is a significant problem in current society, and therefore this topic is increasingly growing challenge in a modern science. However, the Earth's enormous regeneration capacity have largely masked the problem growing for decades. Organic wastewater pollutants that are also difficult to eliminate or remove by conventional water treatment methods include antibiotics, drugs, chemotherapy and their metabolites, as well as hormonal contraception supplements. The elimination of huge diversity of substances from the environment requires cheap, efficient and easy approaches offered also by the photocatalytic degradation. For this reasons, were studied the photocatalytic reactivity of pure and boron-doped ZnO nanoparticles with different morphology for degradation of selected model substances. Influence of morphology and the level of boron content on the change of the optical band-gap (E_g) were determined. The effect of different crystal planes reactivity on the efficiency of photodegradation within comparable E_g of different nanoparticles was proved. As model organic substances, organic dyes Phloxine B, Oxazine 170 and Rhodamine 123 easily detectble by UV-VIS spectrophotometry were used. These dyes differ in their chemical structure, hence are simulating range of possible organic pollutants. The photolysis was investigated in a 3D printed multi-cell photoreactor with a narrow wavelength range (365 nm \pm 5 nm). The results of the work can be used in the designing of equipment intended for cleaning the wastevater by photocatalytic degradation.

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NOVEL COMPOSITE NANOMATERIALS FOR MEDICAL DEVICES

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KEYWORDS: phloxine B | composite material | antimicrobial effect

The key challenge of modern medicine is the use of technological methods of rapid-prototyping. This process is important to reflect the individual needs of patients, but also in the production of components during times of crisis with low availability of commercial components such as humanity found out during the COVID-19 pandemic. Three-dimensional printing is a powerful tool for rapid-prototyping and for printing a small series of mechanical components from a wide scale of differently designed composite materials. The preparation of new materials is possible directly in the laboratory by mixing appropriate compounds together, while the 3D printer then forms prepared material into the final shape. We have developed a composite organic-inorganic hybrid materials based on thermoplastic polyethyleneterephthalate-glycol (PET-G) or polylactic acid (PLA). To prevent the formation of non-specific bacterial biofilms, we have choosed organic dye Phloxine B (PhB) with proven antimicrobial activity against methicillin-resistant *S. aureus*. PhB was intercalated into the synthetic layered silicate. So prepared hybrid silicate was mixed up with PET-G or PLA matrix using double-screw extruder and extruded into the filament. Antimicrobial activities of prepared materials were evaluated. Prepared filaments were immediately used for 3D-printing of interconnecting valves and airways in the emergenci artificial lung ventilator Q-vent. This work describes the production of the novel antimicrobial materials together with the most suitable possibilities of their application using 3D-printing.

Acknowledgement:

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DECREASED VITALITY AND VIABILITY OF *ESCHERICHIA COLI* BY ADHERENCE TO SAPONITE PARTICLES

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KEYWORDS: saponite | bacteriostatic activity | surface structures

Present work was aimed on detailed analysis of the interaction between Gram-negative bacteria of *Escherichia coli* and synthetic saponite (Sap) with the main focus on the changes in viability (survival) and /or vitality (metabolic activity) that are relevant parameters for the evaluation of fitness of different microorganisms. The tested bacterial strains originated from various environmental and clinical sources representing *E. coli* with different properties regarding resistance and biofilm production. This included characteristics related to the cell surface structures (adhesins) that are thought to facilitate the adhesion of bacteria to Sap particles. Sap particles in the concentration of 5 mg/mL proved an antimicrobial effect on all tested *E. coli* isolates. The other tested concentrations (2.5 and 1.25 mg/mL) were efficient in a strain dependent manner. The interaction between bacteria and Sap particles was affected rather viability than vitality, indicating a bacteriostatic mode of action by Sap. To get deeper insights into the mode of action of Sap, microscopy evaluations including fluorescence in situ hybridization (FISH) were used. Results of FISH assay showed the ratio of live/dead *E. coli* cells after the adhesion to Sap particles in different time periods (4 h, 12 h and 24 h) and revealed that the cells adhered to Sap particles remained active but lost their ability to multiply. Moreover, after the 18 h-incubation, inactive bacterial cells were detected in the inner layers of Sap. Scanning electron microscopy confirmed damage of the cell surface of bacteria firmly bound to Sap particles. From the group of 4 tested genes for the fimA, pap, afa, and aaf adhesins, only the FimA and Pap genes were proven by PCR in some strains and the correlation between changes in viability/vitality and those genes was not observed. It seems that rather physico-chemical interactions than bacterial surface structures play a significant role in the interaction between Sap particles and the bacterial surface.

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STABILITY OF POLYMERIC COMPOSITE MATERIALS IN PHYSIOLOGICAL ENVIRONMENT

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KEYWORDS: phloxine B | composite material | physiological environment

During the COVID-19 crisis, novel materials with antimicrobial activity based on polyethyleneterephthalate-glycol or polylactic acid as a thermoplastic matrix were developed. Antimicrobial activity of the materials was performed by saponite with intercalated antimicrobial dye. Described materials were developed in regard to the 3D-printing of medical devices, including tracheostomical and intravenous cannulas. The stability of material was tested for pH, ionic strength and temperature change. Stability in physiological environment was also studied. To simulate physiological environment, we have used three different solutions. First solution was 10x Phosphate-Buffer Saline (PBS). PBS belongs to the group of isotonic buffers. In molecular biology, it is usually used for washing the cell cultures like human stem cells, in situ hybridization, for immunohistochemical staining of tissues and for microsurgical tissue fixation [1-3]. The second solution was 0.9% normal saline, which has approximately the same osmolarity as blood plasma. Normal saline simulates the intravenous solutions commonly used in the clinical setting, for treatment of metabolic alkalosis and for use as a carrier in the parenteral administration of drugs during endoscopic procedures. The last solution tested was Insect saline, usually used for biological assays, for necropsy and isolation of insect organs, or for cell cuts. The results of the research showed that the proposed materials are stable in all simulation physiological environments and the possible release of the antimicrobial component per kilogram of human weight is about thousands of times lower than is allowed by European health standards. The results of research indicate that material should be used for the production of wide scale of different medical devices intended for a long-term intrabody use.

Acknowledgement:

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ADDITIVE MANUFACTURING OF CERAMIC MATERIALS

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KEYWORDS: Additive manufacturing | 3D print | shaping | ceramic

Additive manufacturing (AM or 3D print) represent technology of 3D objects forming by their addition layer-by-layer as contradiction to subtractive technologies where material is cut of the original bulky piece of material. The history of additive manufacturing can be dated from 1892, when Joseph Blantner in Austria patented method of country relief producing by connecting wax layers. Modern 3D printing technologies are connected to application of object forming from the digital object data using computers. The development of additive manufacturing was supported by invention of computer tomography in 1971 by Sir Godfrey Hounsfield. In the same year Pierre Ciraud in France filed the pattend for forming of the layer from powder material, melted together by laser or some other high energy source. Up-to-date there are several distinct technologies applicable for 3D printing of ceramic objects known as litography, powder bed, fused deposition techniques. All AM technologies must challenge and solve the features demanding by the nature of the ceramic materials. This includes mainly the two-stage processing: i) the production of green body objects, and ii) object firing and sintering without its significant shape deformation. The application of novel ceramic materials in production chain is hence affected by availability of both suitable 3D forming technology and starting processing material e.g. dispersion, powder or composite filament. The attractivity of fused deposition of ceramics (FDC) can be seen in simplicity of fused deposition modelling (FDM) technology as one of the most easily available and spread additive manufacturing technologies. The FDM as melt extrusion technology proved its value in solving practical technical tasks in the production chain thanks to material development and functional parts applications. One of the most attractive utilisations intensified in last years include hard tissue replacements, since bone is one of the tissues which is the most frequently transplanted and can be successfully replaced by other biocompatible and/or bioactive materials.

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THE CONFORMATION OF ORGANIC CATIONS IN CLAY MINERAL INTERLAYERS.

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KEYWORDS: organic surfactant | alkylammonium | infrared spectroscopy

Organoclays are inorganic/organic hybrid materials utilized in different applications such as removal of organic pollutants, as reinforcing fillers for plastics, or host structures for direct intercalation of polymers. In this study XRD and IR analysis were performed to probe the arrangement of organic surfactants in montmorillonite interlayers. The samples were prepared from a sodium-saturated <2 μm fraction of bentonite Jelšovský Potok (JP, Slovakia) and trimethylalkylammonium (C_N-TMA⁺) and alkylammonium (C_N-NH₃⁺) cations with increasing length of alkyl chain from C₆ to C₁₈. The XRD patterns showed consecutive transition of the alkyl chains arrangement from monolayer to bilayer and pseudotrimolecular configuration with increasing alkyl chain length. Higher d_{001} values for C_N-TMA-JP comparing to C_N-NH₃-JP were found for surfactants containing the same number of methylene groups. The conformation of alkyl chains was examined by vibrations of CH₂ groups observed in the middle (MIR) and near (NIR) regions. While it is well known that the positions of fundamental CH₂ stretching bands are very sensitive to the ordering of carbon chains, the changes of the vibrational modes of methylene groups appearing in the NIR region were not studied in details yet. The MIR spectrum of C₆-TMA-JP showed the asymmetric ($\nu_{as}CH_2$) and symmetric (ν_sCH_2) stretching bands at 2930 cm⁻¹ and 2862 cm⁻¹, respectively. For C₁₈-TMA-JP the bands were shifted to 2922 and 2852 cm⁻¹, indicating decreasing number of disordered (*gauche*) conformers in favour of more ordered (*all-trans*) conformers. Similar trend was observed also C_N-NH₃-JP samples, the CH₂ stretching bands were shifted to lower wavenumbers by 8 cm⁻¹. The NIR spectra of organo-montmorillonites showed complex band in the 6100-5600 cm⁻¹ region related to 2ν_{CH} vibrations of CH₃ and CH₂ groups. The position of the most intense component related to 2ν_{as}CH₂ was shifted from 5811 cm⁻¹ for C₆-TMA-JP to 5784 cm⁻¹ for C₁₈-TMA-JP confirming creation of more ordered structure of surfactants with the increasing alkyl chain length. Similarly, the 2ν_{as}CH₂ band of C_N-NH₃-JP was shifted to lower positions by 38 cm⁻¹. The magnitude of the 2ν_{as}CH₂ shift was clearly higher than observed in the MIR region for CH₂ stretching modes which benefit the utilization of the NIR spectroscopy for probing the conformation of alkyl chains.

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STRUCTURAL CHANGES OCCURRING UPON DRY GRINDING OF DIOCTAHEDRAL AND TRIOCTAHEDRAL SMECTITES

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KEYWORDS: high energy grinding | smectites | mass profiles | infrared spectroscopy | MAS NMR spectroscopy

Fine fractions of two montmorillonites (Jelšový Potok, Kunipia), hectorite (SHCa-1, Laponite RD) and saponite (Sumecton) were selected to evaluate the influence of smectite type on the extent of structural changes occurring upon mechanical treatment.

All smectites samples were subjected to dry grinding in high energy planetary mill for: 2, 4, 6 min and structural changes were evaluated using various methods. Analysis of IR spectra in the middle region showed pronounced alteration of the absorption bands of montmorillonites already after 2 min of dry grinding. The intensities of the bands attributed to structural OH groups (near 3630, 915, 878 and 845 cm^{-1} in Fig. 1a,b) were significantly perturbed after 6 min of grinding and mostly the bands of amorphous siliceous phase remained present in the spectra indicating strong alteration of dioctahedral smectites structure. On other side, the same type of bands (near 3680 and 667 cm^{-1} in Fig. 1c-d) remained clearly detected in the spectra of all trioctahedral samples, i.e. natural and synthetic hectorite, synthetic saponite.

The results are complementary to those achieved from MAS NMR spectra method. ²⁹Si MAS NMR spectra showed transformation of the signals attributed to silicon tetrahedra in layered structure of montmorillonites to signals of Si in amorphous phase confirming thus the extensive modification of the montmorillonite layers after 6 min of grinding. Hectorite and saponite ground for the same periods remained more intact, clearly showing the signals Q³(0Al), Q³(1Al) and Q². The formation of amorphous phase was indicated by the widening of the signals and decrease in their intensities. ²⁷Al MAS NMR spectra revealed significant decrease of Al_{oct} intensity. On contrary, the intensity of Al_{tet} increased. Such results suggest possible transformation of dominant Al_{oct} to Al_{tet} for both montmorillonites. In addition, signals were shifted towards lower values of chemical shift δ for tetrahedral Al and contrary to higher δ values for octahedral Al. Shifts were most probably caused by transformation of layered structures into amorphous phase.

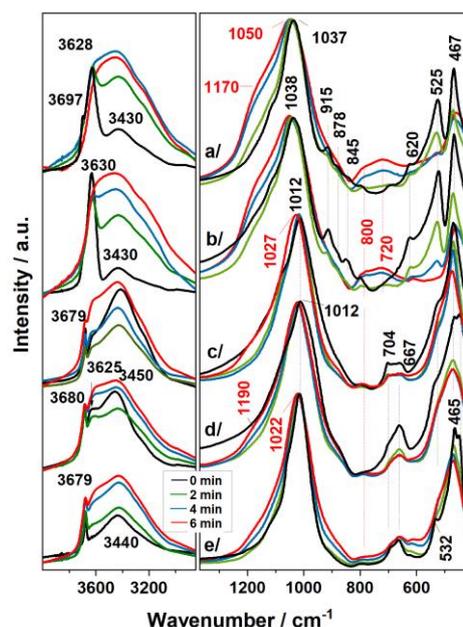


Fig. 1. MIR spectra of a – Jelšový Potok, b – Kunipia, c – SHCa hectorite, d – Laponite RD, e – Sumecton

DTG profiles together with H₂O mass profiles provided information on dehydration/dehydroxylation process occurring upon smectites grinding (Fig. 2). Decrease of water content present as hydration shell of exchangeable cations (peak near 120°C) was reflected in the diminishing intensity of lower temperature peaks in mass profiles. On contrary to dehydration process, dehydroxylation of layered structure depended on the smectite type. Initial samples showed significant differences in their DTG profiles. The first dissimilarity is detection of two DTG minima for montmorillonites while natural hectorite SHCa-1 showed only one peak (Fig. 2C) with minima at higher temperatures compared to Jelšovský potok and Kunipia (Fig. 2A,B). One sharp peak was also observed in DTG profiles of both synthetic smectites, however minima occurred at lower temperatures than for natural hectorite. Dehydroxylation peaks disappeared from the profiles of montmorillonites ground for 6 min, while they remained clearly visible in the profiles of trioctahedral smectites subjected to grinding for the same interval.

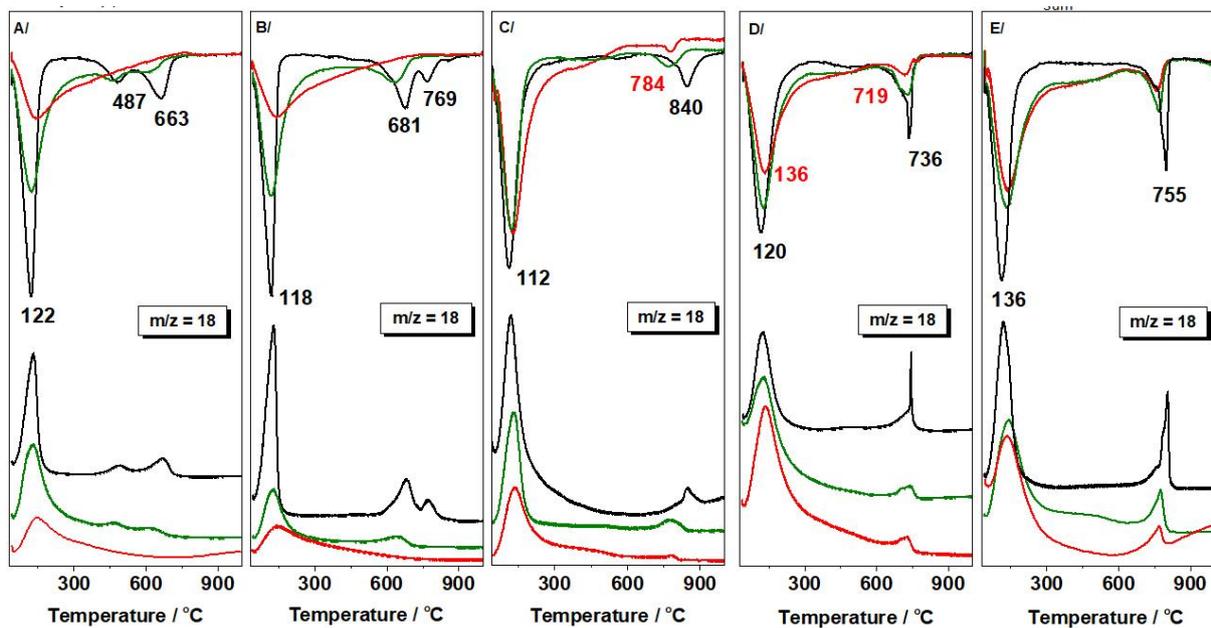


Fig. 2: TG profiles (upper part) and H₂O mass profiles of smectites before (black line) and after grinding for 2 (green) and 6 min (red line): A/ Jelšovský potok, B/ Kunipia, C/ natural hectorite SHCa, D/ synthetic hectorite Laponite, E/ synthetic saponite Sumecton

Presented methods unambiguously confirmed higher stability of trioctahedral smectites compared to dioctahedral ones after their mechanical treatment using high-energy mill.

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THE INFLUENCE OF ORGANIC CATION SIZE ON STRUCTURAL CHANGES IN MONTMORILLONITE SUBJECTED TO DRY GRINDING

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KEYWORDS: organic surfactant | alkylammonium | alkylphosphonium | infrared spectroscopy | smectites

Organo-exchanged montmorillonite (Jelšový potok) were prepared using four organic cations: tetraoctyl- and tetrabutyl-ammonium (Bu₄N, Oc₄N) and -phosphonium (Bu₄P, Oc₄P). Samples were subjected to dry grinding in high energy planetary mill for: 2, 4, 6 min.

Reflections detected in XRD pattern of the initial montmorillonite completely disappeared for sample ground for 6 min, showing almost complete amorphization of structure. XRD analysis of Bu₄N and Bu₄P samples exhibited similar trends, indicating that dry grinding had the same effect. On contrary, much less pronounced alteration was detected for the samples exchanged with larger organic cations Oc₄A and Oc₄P. Even upon the most extensive grinding, the reflections typical for layered montmorillonite structure are clearly visible in patterns (Fig. left).

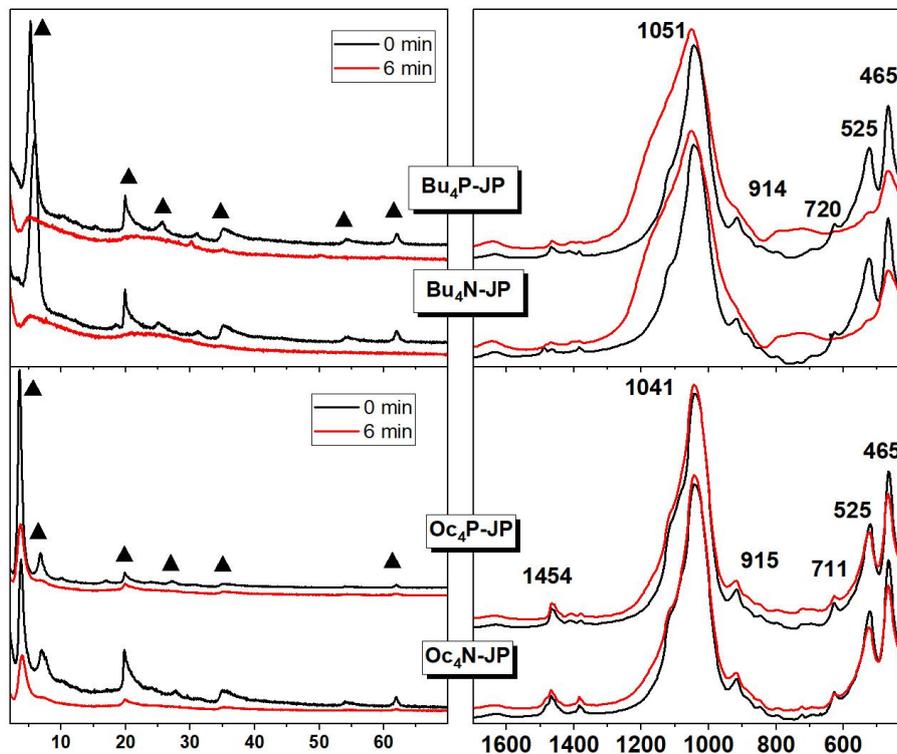


Fig. XRD patterns (left) and IR spectra (right) of montmorillonite modified with organic cations prior (black line) and after grinding for 6 min (red line).

While the IR spectra of tetrabutyl-ammonium and phosphonium exchanged samples undergone pronounced alteration of the bands intensities, similar to un-modified montmorillonite, the spectra

of tetraoctyl-onium forms showed only slight changes in positions and intensities of the bands reflecting the higher resistance to mechanical treatment for these samples (Fig. right).

Organo-montmorillonites exchanged with larger organic surfactant subjected to mechanical treatment showed therefore higher stability of the layered structure of montmorillonite compared to initial sample.

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SPECTRAL PROPERTIES OF REICHARDT'S DYE ADSORBED ON AN ORGANOMODIFIED SAPONITE IN COLLOIDAL DISPERSION

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KEYWORDS: Reichardt's dye | spectroscopy | saponite

Hybrid nanomaterials based on layered silicates modified with organic molecules are nowadays extensively studied due to their interesting properties, such as quenching of fluorescence or its inducing, light-harvesting, photosensitization, antibacterial properties, etc. This work was aimed at the interaction of Reichardt's dye (RD) with saponite (Sap). RD is a substance that changes its colour and optical properties in dependence on the polarity of the environment. In this work, we used synthetic Sap – Sumecton with well-defined composition, structure, and properties. It is because the chemical composition and physicochemical properties of natural saponites are extremely variable, and the samples can contain mineral admixtures and impurities [1]. RD is notable for its solvatochromic properties, it changes its colour with the solvent in which it is dissolved in. It has one of the largest known solvatochromic effects [2] with colours that cover the entire visible spectrum [3].

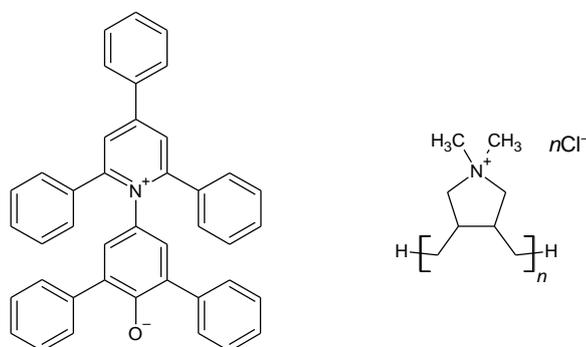


Figure 1. Structural formula of Reichardt's dye (left) and PDDAC (right)

RD molecules do not adsorb on the clay mineral particles, so at the first step, the Sap surface was modified with polyelectrolyte – poly(diallyldimethylammonium chloride) (PDDAC) with an average molar mass of 200 000 – 350 000 g·mol⁻¹. The final concentration of Sap in studied systems was 0.1 g·dm⁻³ and the loading $n(\text{PDDAC})/m(\text{Sap})$ was 0.5 mmol·g⁻¹ with respect to the monomer units of PDDAC. At the second step, RD was adsorbed on the prepared organoclay, and the RD loading $n(\text{RD})/m(\text{Sap})$ varied from 2.5·10⁻³ to 0.08 mmol·g⁻¹. UV-Vis and fluorescence spectra of prepared colloidal dispersions were measured to characterize the optical properties of the adsorbed dye molecules.

The UV-Vis spectra of RD adsorbed on the organoclay were very similar to that of the dye solution. The absorbance maximum of the dye in water/ethanol solution was at 305 nm and when adsorbed on organoclay particles it shifted to higher wavelengths (316 nm). The RD solutions did not exhibit significant fluorescence, but when the dye was adsorbed on the organoclay, there was

one broad fluorescent band with the maximum at 487 nm (The excitation wavelength was 337 nm.). The fluorescence intensity was a logarithmic function with respect to the amount of the adsorbed dye, although the absorbance values were a linear function in accordance with the Lambert-Beer's law.

Langmuir adsorption isotherm was also measured for this system to find out, how much dye can be adsorbed on the organoclay particles and to get more light on the mechanism of adsorption.

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A COMPUTATIONAL STUDY OF DIURON-BEIDELLITE INTERACTIONS

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KEYWORDS: Diuron | DFT method | Beidellite

Diuron (D) is a systemic broad-spectrum herbicide that belongs to phenylurea herbicides group (PUHs) [1]. This compound presents a high toxic potential for animals [2] and environment [3]. Clay minerals are highly hydrophilic, showing a very limited adsorption capacity for hydrophobic organic pollutants [4]. In spite of this, it is possible to modify the clay surface with high cation exchange capacity, such as beidellite (Bd), by organic surfactants in order to obtain a higher adsorption.

The purpose of this study is a characterization of the interactions that occur in the interlayer space of Bd among the $[\text{Na}(\text{H}_2\text{O})_4]^+$, tetramethylphosphonium cation (TMP) and D.

Density Functional Theory method (DFT) in solid state was used for study the interactions and stability of the diuron-smectite complexes. The PBE functional [5] with the DFT-D3 scheme for dispersion corrections [6] was used for calculations, which have been performed by the Vienna Ab Initio Simulation Package (VASP) program.

Two models were suggested: 1. D intercalated in the Bd (D-Bd); 2. D and TMP cation intercalated in the Bd (DTMP-Bd).

The results showed that diuron has a flat arrangement in the interlayer space of Bd (Figure 1). The interactions formed between D and the clay surface in the interlayer space are weak hydrogen bonds in both models. Preliminary calculations showed that the stability appears higher in D-Bd complex (-118.68 kJ/mol) than in DTMP-Bd (-17.78).

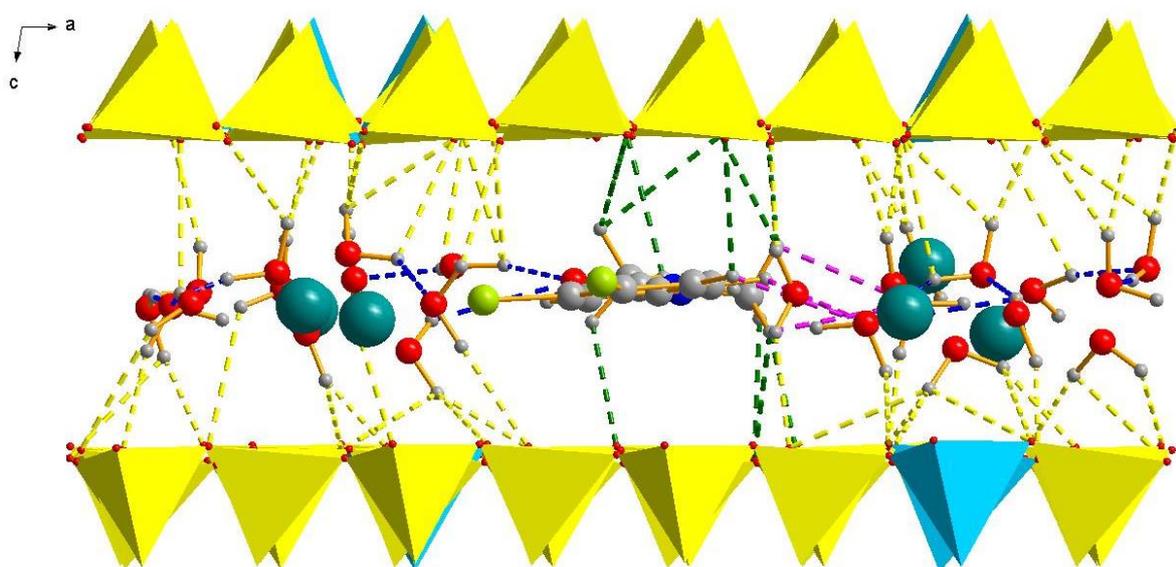


Figure 1. Hydrogen bonds in the D-Bd model: green (C-H...O_b), magenta (C-H...O_w), yellow (O_w-H...O_b), blue (O_w-H...O_w).

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THEORETICAL STUDY OF INTERACTIONS IN THE Mg-VERMICULITE AS A PERSPECTIVE MATERIAL FOR REINFORCING OF ORGANOCLAY-POLYMER MATRIX

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KEYWORDS: Mg-vermiculite | DFT-D3 | interactions | hybrid materials

Hybrid materials with both inorganic and organic components attract more and more attention because of its improved properties. To reinforce the polymers with nanosized inorganic particles is an effective way to improve the properties [1]. Just like montmorillonite, vermiculite (V) is a 2:1 phyllosilicate, in which the negatively charged aluminosilicate layer is composed of one octahedral sheet sandwiched between two tetrahedral sheets. The thermal and mechanical properties of composites increase as the V is added into polymer [2].

In the present study the interactions in the double layered Mg-V, V with intercalated hydrated Mg cations, are studied by means of the DFT method in solid state implemented in VASP program. The DFT-D3 scheme [3] for dispersion corrections together with PBE functional was used to describe properly the weak interactions in the Mg-V structure. The model was prepared according to experimental structure [4] (Fig.1a). Preliminary calculations revealed moderate to strong $O_{\text{water}} - H_{\text{water}} \cdots O_{\text{basal}}$ hydrogen bonds (Fig. 1b) and clearly distinguish the vibrational modes in the FTIR spectra by means of calculated projected vibrational density of states (Fig. 1c).

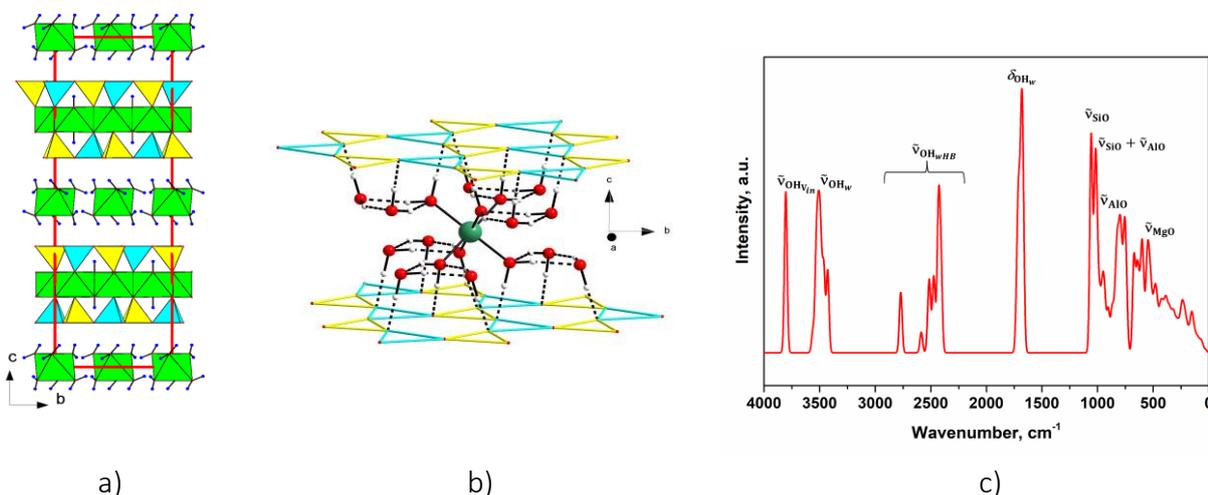


Fig. 1: a) Structural model of Mg-V; b) $O_{\text{water}} - H_{\text{water}} \cdots O_{\text{basal}}$ hydrogen bonds; c) Calculated and FTIR spectra of Mg-V, in – internal OH group, w – water, wHB – water OH group involved into hydrogen bonds.

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THE SURFACE OF POLYCAPROLACTONE MODIFIED WITH SAPONITE AND METHYLENE BLUE

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KEYWORDS: smectite | photosensitizer | organic dye | polymer nanocomposite

Hybrid materials based on clay minerals and organic dyes were first reported since ancient times. Maya blue a pigment material consisting of natural dye indigo and palygorskite crystals was used as a pigment for paintings since pre-Columbian Mesoamerican civilizations. This pigment showed excellent resistance against the atmospheric variation during the time up to now. In this study, the materials were based on the cationic dye, MB. The intercalation of MB molecules into a clay mineral requires full delamination of the layers to increase the access to the surface and absorption capacity of the inorganic host. This is achievable using expandable smectites [1]. MB cations tend to aggregate in the hybrid systems with smectites. This phenomenon is also known as metachromasy. The aggregates are classified into two main categories, H- and J-aggregates. This phenomenon affects the properties of dyes/clay mineral hybrid system.

In this work, synthetic saponite (Sap) was modified via intercalation reaction with hexadecyltrimethylammonium bromide (HDTMA) leading to highly hydrophobic material. Subsequently, the organoclay was functionalized with variable amounts of methylene blue (MB). The prepared suspensions of organoclays functionalized with MB were filtered through Teflon membranes to prepared thin films. The synthesis of nanocomposites with polycaprolactone (PCL) involved the surface modification of the polymer with the functionalized organoclays via melt diffusion at the interface of the film and the polymer. Pristine and modified materials, as well as the final nanocomposites, were characterized by a combination of analytical techniques including UV-Vis absorption and fluorescence spectroscopy.

A colloidal dispersion of Sap was prepared using Millipore deionized water and stirred for 24 h and mixed with an HDTMA solution to prepare organoclay with the HDTMA/Sap ratio of 0.8 mmol/g. MB was dissolved in deionized water and the concentration determined by UV/Vis spectroscopy. It was appropriately diluted and mixed with the organoclay to get MB/Sap ratios (in mmol/g): 0.0005 (MB1), 0.001 (MB2), 0.00125 (MB3), 0.0025 (MB4), 0.005 (MB5), 0.01 (MB6), 0.0125 (MB7), 0.025 (MB8), 0.05 (MB9) and 0.1 (MB10). The colloids were filtered via the Teflon membranes and dried on air to get MB/HDTMA/Sap films. Teflon membranes with the films were covered with PCL and melted in an oven at 80°C for 30 min to achieve the penetration of organoclays into the polymer matrix. The final nanocomposites were developed with ten different concentrations of MB (Mb1-MB10).

The Teflon membranes with the Sap/HDTMA/MB films and their composites with PCL are shown in fig.1. As the concentration of MB increased the blue color got more intense.

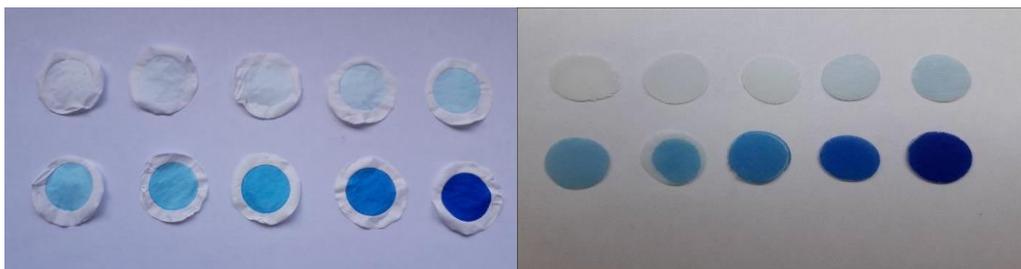


Fig. 1. Photographs of the films deposited on membranes (left) and their composites with PLC (right).

Absorption spectra were measured for a basic characterization. The samples with low MB concentration were characterized by the peak assigned to monomers (670 nm). The band at 545 nm attributed to H-aggregates was identified in the samples of higher MB concentrations. The peak at 634 nm, appearing in the spectrum of MB5, probably corresponds to H-dimers[2]. The fluorescence spectra (Fig.2) of PCL nanocomposites show the trend reflecting MB concentration. At lower concentrations, the fluorescence intensity increased with the dye concentration achieving the maximum for MB4. At higher concentrations, the presence of H-aggregates led to the quenching of fluorescence and the shift of maximal emission to partially higher wavelengths. Fluorescence quenched completely for the samples of the highest MB concentrations (MB9 and MB10) [3].

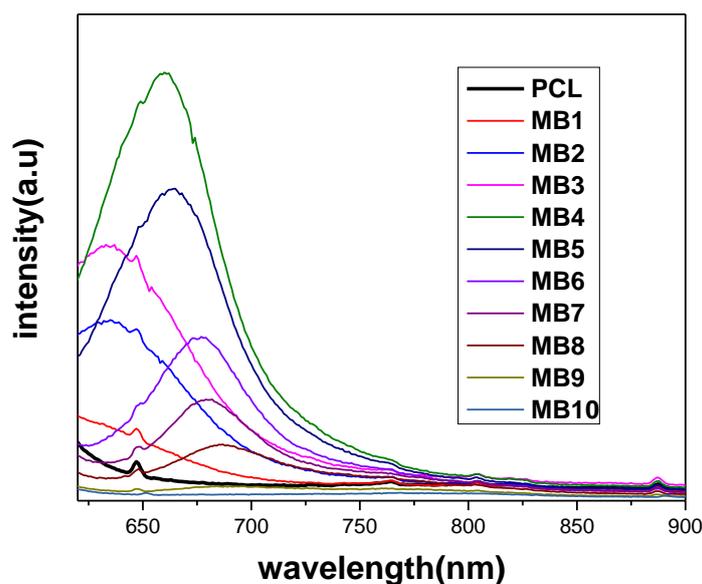


Fig. 2. Fluorescence spectra of MB1-MB10 polymer composites.

The optical properties and photoactivity of the dye reflect the composition of the composites. The specimens exhibiting high photoactivity were successfully prepared.

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HEXAVALENT CHROMIUM ADSORPTION BY TETRAHEXYLPHOSPHONIUM-MODIFIED BEIDELLITE CLAY – COMBINED THEORETICAL AND EXPERIMENTAL STUDY

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Clay minerals are hydrated aluminosilicates with the silicate (SiO_4^{4-}) tetrahedral and aluminate (AlO_4^{4-}) octahedral sheets. Clays are useful in many areas of technology and science. They find application in purification of gases, in separation of liquid mixtures, in catalysis, and in environmental protection [1,2]. They are defined by high chemical and mechanical stability, high specific surface area, and a variety of surface and structural properties [3, 4]. Pore structure and the chemical nature of the clay surface mainly determine the adsorption abilities of clays. In the liquid phase sorption, the chemical properties of surface groups influence the equilibrium to a large extent [5].

This paper presents the study of the adsorption of toxic chromium (Cr^{VI}) anionic species into the interlayer space of tetrahexylphosphonium (THP) modified and unmodified beidellite clay. Beidellite (Bd) belongs to the smectite clay family. Beidellite modified with different types of organocations is comprehensively investigated due to their excellent properties and various interactions [6]. The main goal of this work is to provide detailed information about the structure of studied models. For the determination of the stability of individual systems, the strength and number of hydrogen bond interactions in combination with the calculated intercalation energies were analyzed. The vibrational modes obtained from the calculated spectra using the *ab initio* molecular dynamics (AIMD) approach and measured FTIR spectra were studied.

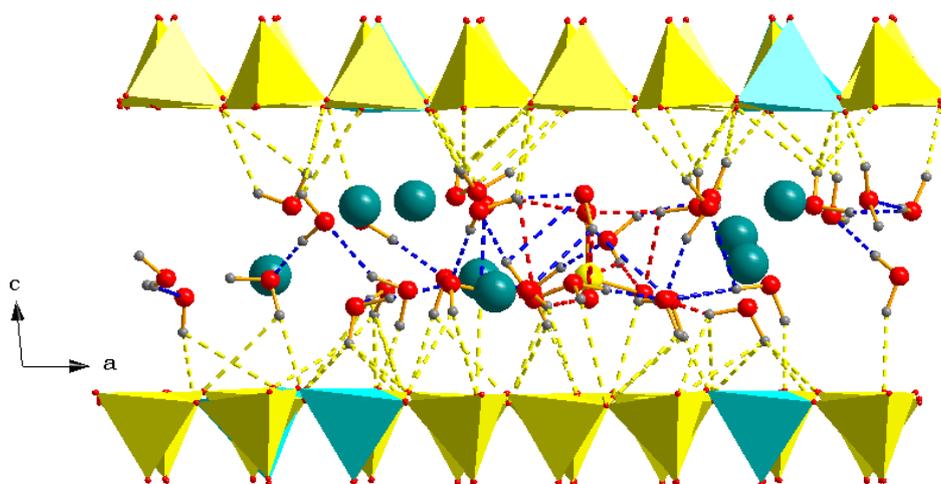


Figure 1: Cr-Bd model after optimization with various types of hydrogen bonds

The initial structures and unit cell parameters of all calculated models were fully optimized (Fig. 1). After the optimization, the c vector for both studied products was reduced, a and b lattice vectors were relatively similar with the initial parameters. For the Cr-Bd and Cr-THP-Bd models, the calculated (experimental) d_{001} values were 14.0 (12.8) and 15.6 (15.3) Å. In the case of Cr-THP-Bd, the THP cation was added to the interlayer space of beidellite clay and one hydrated sodium cation was removed to maintain charge equilibrium of the system. After the analysis of hydrogen bonds of these models has been shown that the organic cations are keyed into the beidellite structure through weak C–H \cdots O_(b) hydrogen bonds. Cr-Bd and Cr-THP-Bd models are also characterized by the moderate-to weak O_w–H \cdots O_(w), O_w–H \cdots O_(Cr) and O_w–H \cdots O_(b) interactions created by the water molecules in the interlayer space of beidellite clay. The vibrational modes of Cr-Bd and Cr-THP-Bd systems were clearly identified from calculated spectra and compared with experimental FTIR spectra (Fig. 2). A detailed analysis of the calculated PS in the spectral region below 1200 cm⁻¹ helped to interpret the experimental spectrum by finding the individual contributions of the (CrO₄)²⁻ unit.

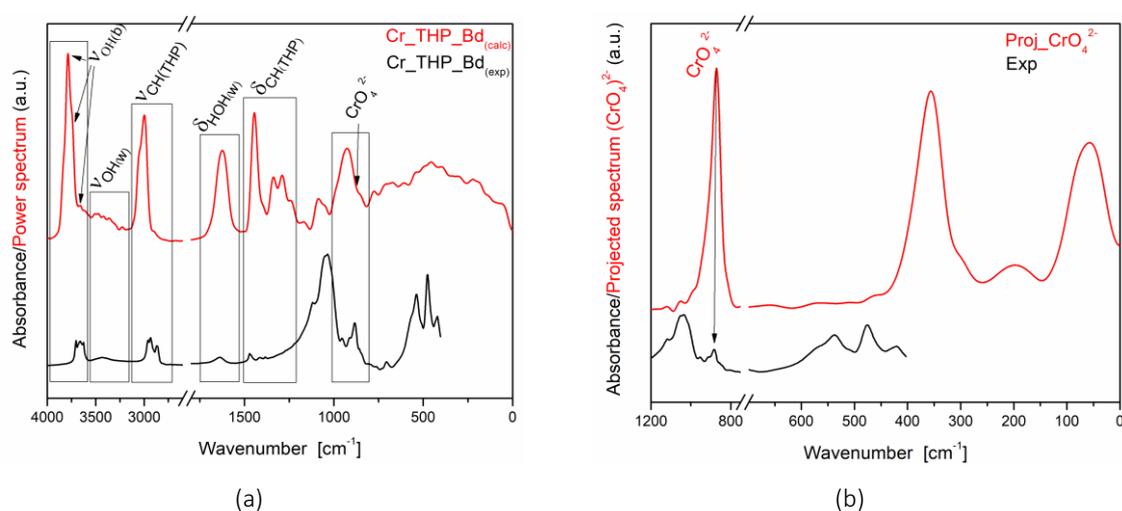


Figure 2: The experimental FTIR and calculated power spectra of Cr-THP-Bd (a). Contributions of calculated projected power spectra of CrO₄²⁻ vibrational modes and the experimental FTIR of Cr-THP-Bd (b).

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THE ANALYSIS OF THE SYSTEM $3\text{NaF}-\text{AlF}_3-\text{FeF}_3$.

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Nowadays, aluminium is produced mainly by the Hall-Héroult electrolytic process. The impurities, especially iron, plays a specific role in a critical problems of aluminium electrolysis process [1-2]. Iron (iron compounds as iron (II or III) oxides and iron (II or III) fluorides) gives rise to change of structure of electrolyte, because reacts with its components. Iron decrease of current efficiency of the process and purity of produced aluminium, too. Hence, the classification of mechanism of reactions of iron compounds with compounds of electrolyte is needed.

The complete analysis of the system $\text{Na}_3\text{AlF}_6-\text{FeF}_3$ was realized. The reaction between cryolite (Na_3AlF_6), as main component of electrolyte and FeF_3 were studied by various analytic and physicochemical techniques, like thermal analysis, X-ray diffraction method and MAS NMR technique. The existence of solid solutions of „cryolite“ and „chiolite“ ($\text{Na}_3(\text{Al}_x\text{Fe}_y)\text{F}_6$ and $\text{Na}_5(\text{Al}_x\text{Fe}_y)_3\text{F}_{14}$, $x + y = 1$, respectively) structures were found with increasing concentration of FeF_3 . Only one stable product was observed in the system at the higher concentrations of FeF_3 (up to 60 mole %), namely NaFeF_4 . Analysis of volatile flows indicated the presence of NaAlF_4 .

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THERMOANALYTICAL TECHNIQUES APPLIED FOR CHARACTERIZATION OF WATER IN PERLITES

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KEYWORDS: industrial minerals | thermal analysis | perlites | water content

Perlite is an important industrial rock with major industrial utilization in the form of expanded perlite, which is produced by quick heating at high temperatures receiving a pale to white granular and foamy material with extremely low density and high specific surface area. Physical-chemical properties of expanded perlite induce high sound and thermal isolation capacity, heat resistance, chemical inertness and high filtration ability leading to the applications of perlite in various branches of industry. Very important characteristic of perlites is their water content. It may influence final properties of perlites after expansion process.

Perlite samples from different places of deposit Lehôtka pod Brehmi with variable amount of water and textures were studied (Table). For comparison reason, obsidian sample from locality Viničky was added to studied samples.

Table: Mass loss determined from loss on ignition and thermal analysis

Sample	Mass loss					
	LOI	TG (%)				
	(%)	Temperature interval °C				
		35-1000	35-150	150-250	250-500	>500
PL-4a	4.57	4.29	0.18	0.45	2.83	0.83
PL-6a	4.28	4.16	0.06	0.34	2.90	0.86
PL-19	3.49	3.28	0.06	0.27	2.37	0.58
PL-24a	3.21	3.07	0.08	0.22	2.24	0.53
PL-29a	3.50	3.11	0.06	0.23	2.28	0.54
PL-29b	3.83	3.43	0.25	0.29	2.28	0.61
PL-72b1	4.42	4.11	0.37	0.32	2.55	0.87
PL-91a3	3.28	3.20	0.06	0.18	2.24	0.72
PL-95	4.46	4.33	0.11	0.44	3.01	0.77
OBS-V	0.58	0.54	0.04	0.09	0.11	0.30

Mass spectroscopy accompanied by simultaneous temperature-dependent IR spectra measurement was applied in order to track the evolution of the main volatile species from the samples. The mass profiles registered for H₂O species exhibit a shape similar to that of the DTG profiles (albeit inverted), indicating that the features detected in the DTG profiles are predominantly connected with the evolution of water. The profiles of m/z = 18 amu show a dominant peak with a maximum at a temperature between 355-407°C,

depending on the sample. The samples PL-29b and PL-72b1 also display a small peak at lower temperatures with a maximum at about 150°C, indicating a higher amount of weakly-bound water than other selected samples. As reported for rhyolitic glasses, the release of water molecules is a fast process relative to dehydration of hydroxyls and the hydroxyls have higher resistance to be eliminated from the samples [e.g. 1], and their removal occurred at higher temperatures.

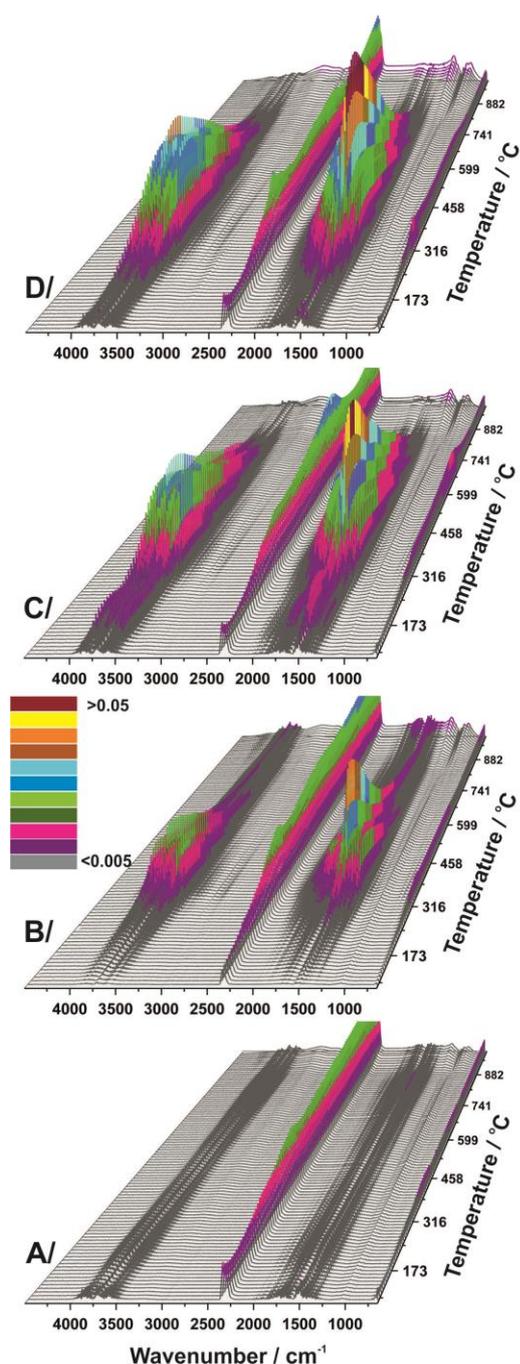


Figure S5. Temperature-dependent 3D-IR spectra of samples OBS-V (A), PL-29a (B), PL-72b1 (C), and PL-95 (D).

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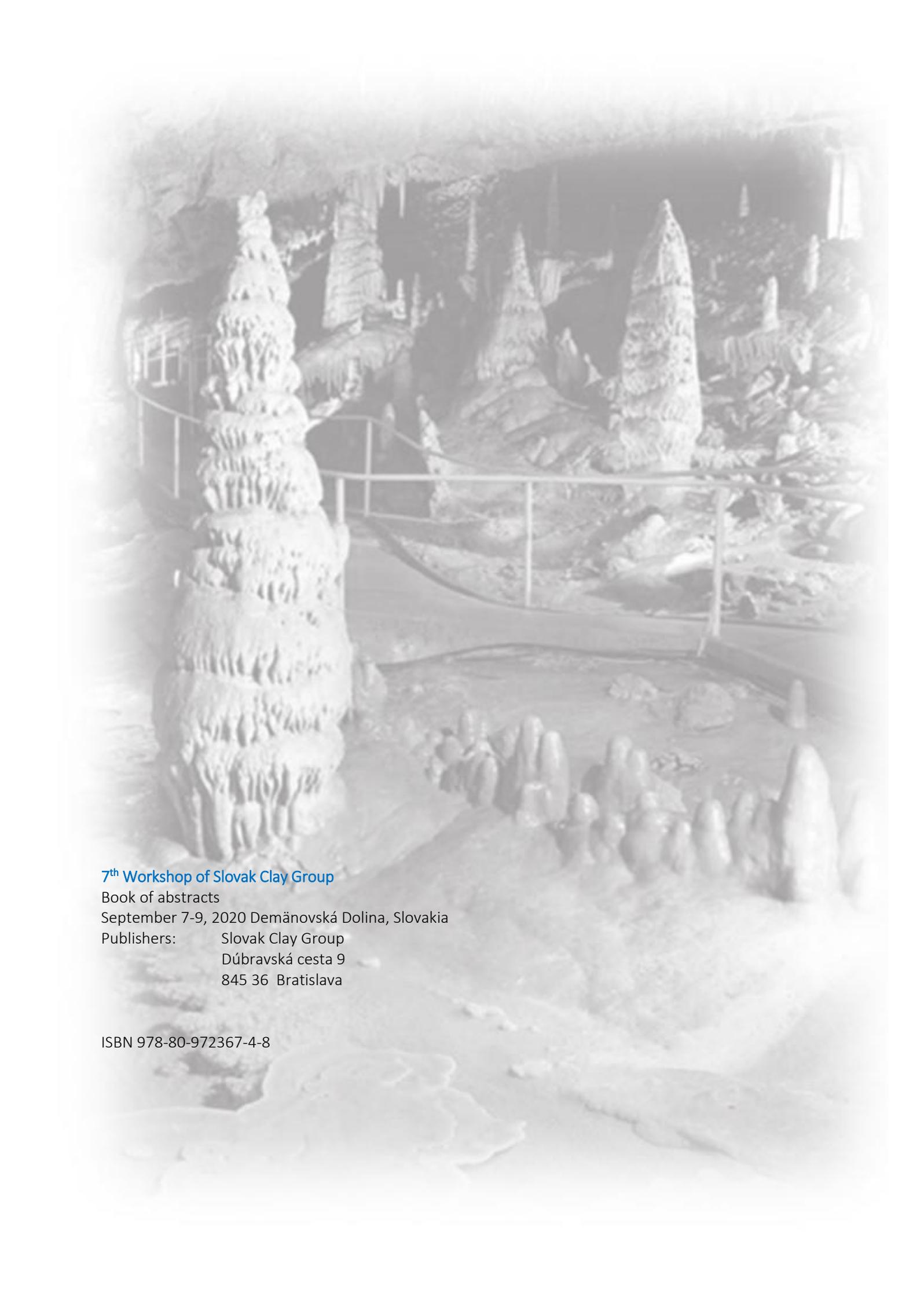
The vibrational-rotational 3D-IR spectra of the gases evolved during thermal analysis of samples showed complementary information detected by mass spectroscopy (Fig). The OH stretching mode of water vapour over the range of 4000-3500 cm⁻¹, and the corresponding bending mode spread out below 2000 cm⁻¹, are the most intense bands in the IR spectra. In addition, the stretching mode of CO₂ was observed at 2364 cm⁻¹. OBS-V, as the sample with the lowest content of water and/or hydroxyls evidenced by means of TG/DTG/MS analysis, exhibits absorption bands of negligible intensities. The maximal intensities (I_{\max}) of water absorption bands detected for samples selected for measurement, PL-29a, PL-72b1, PL-95 follow the order observed for mass loss detected from TG analysis (Table), i.e. $I_{\max}(\text{PL-95}) > I_{\max}(\text{PL-72b1}) > I_{\max}(\text{PL-29a})$. PL-29a, one of the perlite samples with the lowest mass loss (3.11%) according to the TG analysis (Table), shows sharper profile along the z-axis indicating that the volatile species evolve within a narrower temperature region than for PL-95 and PL-72b1. The results point to the sensitivity of the 3D-IR method regarding gas evolution: despite relatively small differences in the water content or mass loss between perlite samples from the same deposit, the IR spectra of the gaseous product reliably reflected even small variations in the water content.

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