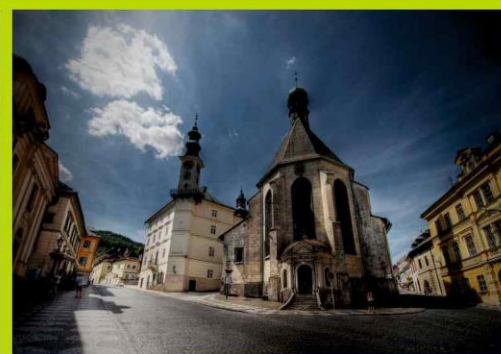
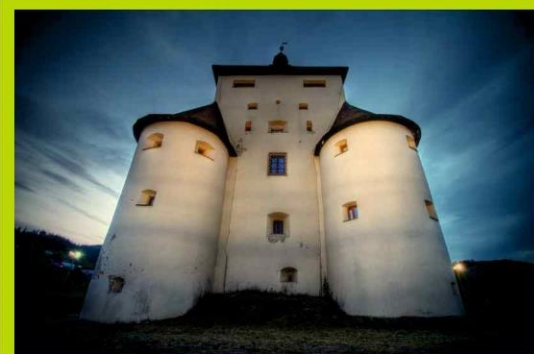


# 5<sup>th</sup> Workshop of Slovak Clay Group



## CLAY MINERALS AND SELECTED NON-RAW MATERIALS IN MATERIAL SCIENCE, INDUSTRIAL APPLICATIONS AND ENVIRONMENTAL TECHNOLOGY

### Book of abstracts



May 21 – 23, 2018, Banská Štiavnica, Slovakia

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SCIENCE, INDUSTRIAL APPLICATIONS AND ENVIRONMENTAL  
TECHNOLOGY



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# ORAL PRESENTATIONS







# Effects of dye surface concentration on molecular aggregation of rhodamine dye in montmorillonite colloids

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*Keywords: chemometric analysis | dye aggregation kinetics | stopped-flow*

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The formation of dye molecular aggregates at colloidal particle interface is a complex phenomenon including various processes [1]. Dye aggregation results in significant changes of the spectral properties of dye [2].

The aim of this work was a detailed investigation of the effect of dye surface concentration on the mechanism and extent of rhodamine 123 (R123) molecular aggregation in the dispersion of montmorillonite Kunipia F (MntK, Na<sup>+</sup>-form). Reaction kinetics measurements of the dye molecular aggregation were performed using a UV-Vis spectrophotometer in combination with a thermostatic stopped-flow rapid mixing device. An average surface concentration of the dye was altered by changing the value of the R123 loading for tested reaction mixtures, which corresponds to the ratio of the R123 amount to the MntK mass. Spectral and concentration profiles of R123 monomers and aggregates were identified using the chemometric method - Multivariate Curve Resolution-Alternating Least Squares. The construction of the reaction mechanism model and the estimation of the parameters of the R123 aggregation kinetics were based on a non-linear regression analysis of the concentration profiles of the respective dye species.

Very rapid adsorption of R123 cations was followed by the formation of oblique J-aggregates, which were formed by association of adsorbed dye molecules on the surface of smectite particles. The surface concentration of the dye affected the course of the formation of R123 aggregates and the kinetic aspects of dye molecular aggregation. The amount of dye aggregates initially formed increased with the surface concentration of R123. A reverse trend was observed after longer reaction times. In the case of dispersions with high R123 loadings, the spectral equilibrium was reached shortly after reactants mixing, and the extent of dye aggregation did not change significantly over reaction time. For these reaction systems, a partial flocculation of the dispersions was observed, caused by the neutralization of the surface charge of MntK particles at high R123 loadings. The formation of R123 oblique J-aggregates in the dispersions of low dye loading proceeded slowly, and at the end of the reaction, a high extent of aggregation was observed. The mechanism of R123 molecular aggregation was described by two main parallel processes, both of which proceeded by first-order reaction kinetics but differed in their reaction rate. As the R123 loading increased, the rate constants of the processes increased and the values of total half-life of aggregation decreased. The results presented in this work are important for understanding the details of dye/clay mineral interaction.

## Acknowledgement:

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## Hybrid systems of tetraoctylammonium and –phosphonium exchanged smectites and laser dye

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Keywords: laser dye system | organoclays

Various types of cationic surfactants have been used for the preparation of organically-modified clay minerals. Such materials have further been used for the preparation of hybrids with laser dyes. Systems based on smectites modified with alkylammonium cations have shown to be effective in preventing dye aggregation, a phenomenon that reduces dye luminescence (e.g. SASAI et al., 2009). The aim of this work was to study the effect of organic cations on the final properties of organoclays and to investigate the interactions within hybrid systems with laser dye rhodamine 6G (R6G) by means of XRD and IR spectroscopy.

Synthetic saponite Sumecton (Sap) was modified with tetraoctylphosphonium (TOP) and tetraoctylammonium (TOA) cations in amounts equal to 25, 50, 75, 100% of the cation exchange capacity (CEC). Furthermore, another series of samples with R6G was prepared with the R6G/Sap ratio 0.02 and 0.1 mmol/g and variable amounts of the organic surfactants. Carbon content showed a substantial increase with the amount of surfactants. The intercalation of organic cations caused an expansion of the interlayer spaces from 1.2 nm (detected for a pure Sap) up to 2.1 and 2.2 nm for 100%TOA- or 100%TOP-Sap, respectively. Higher  $d_{001}$  within the TOP-Sap series could be attributed to the larger P atom radius compared to the N atom. The addition of R6G to Sap caused a visible change in  $d_{001}$  for both tested dye concentrations, while for the systems based on organoclays, the interlayer space remained more or less unchanged. Based on carbon content values, organoclays adsorbed less R6G than pure Sap.

IR spectra in the middle (MIR) and near infrared (NIR) regions were measured to follow the influence of the organic cations on the shape of the spectra. Upon loading of both cations to Sap layers, the bands attributed to the C-H vibrations of methyl and methylene groups appeared in the spectra: stretching  $\nu$ C-H between 3000 – 2800  $\text{cm}^{-1}$  and bending  $\delta$ C-H within 1600-1300  $\text{cm}^{-1}$ . The shapes of the C-H bands were modified compared to the pure organic salts spectra. The most intensive bands detected in the salts became less resolved, but the spectral differences between the two organic surfactants were also transferred into spectra of organoclays. The areas of organic cation absorption bands were evaluated for the spectra normalised to  $\nu$ Si-O band of Sap. Both TOP-Sap and TOA-Sap showed an enlargement in the band areas of  $\nu$ C-H and  $\delta$ C-H with increasing carbon content. The intercalation of R6G in the samples was clearly confirmed by the appearance of sharp peaks attributed to  $\delta$ C-H and to vibrations of aromatic rings between wavenumbers 1700 – 1300  $\text{cm}^{-1}$ . These bands did not overlapped with wavenumber of  $\delta$ C-H bands of the surfactant cations, thus they were also observable in the spectra of TOP-Sap and TOA-Sap samples modified with R6G. Their intensity increased with the concentration of R6G.

NIR spectra of TOP-Sap and TOA-Sap provided complementary information to that obtained from the MIR spectra. In addition to the first overtones ( $2\nu$ ) and combination vibrations ( $\nu+\delta$ ) of structural OH of Sap (7186 and 4321  $\text{cm}^{-1}$ ) and of water molecules (6834 and 5258  $\text{cm}^{-1}$ ), the NIR spectra also showed a complex band in the 6000-5400  $\text{cm}^{-1}$  region related to the  $2\nu$ CH vibrations, and ( $\nu+\delta$ )CH vibrations detected below 4500  $\text{cm}^{-1}$ . The appearance of an unidentified band at 6748  $\text{cm}^{-1}$  that was not visible in the pure R6G spectrum, could be attributed to the interactions of dye cations with Sap and its organic derivatives.

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## Experiences with antimicrobial testing and data evaluation in microbial biofilms formed *in vitro*

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Keywords: photodynamic inactivation | methylene blue | biofilm

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This presentation summarizes some experiences and troubleshooting related to data validation extracted from the experiments focused on antimicrobial testing using various antimicrobial agents, materials and microorganisms (yeast *Candida albicans*, bacteria of *Streptococcus mutans*, *Staphylococcus aureus*, and *Escherichia coli*). In screening of anti-biofilm activity when many samples are tested, 3 approaches are fundamental: the determination of a number of survived cells (colony forming units - CFU), measurement of metabolic activity, and microscopy. These techniques can be combined by different ways, using various substrates or dyes. An evaluation through metabolic activity, the most easy approach, uses spectral measurements at A<sub>560</sub> (MTT assay) or A<sub>490</sub> (XTT assay). The substrates used in both the techniques are associated with the activity of dehydrogenases and are reduced to final products detected by spectroscopy. The methods are suitable for testing biofilms formed on stable materials (for example, single or dual biofilms formed by *C. albicans* and *S. mutans* on hydroxyapatite blocks). However, the compounds participating in the redox reactions can significantly diminish an activity of both the substrates. An example of such compounds is photoactive dye methylene blue that is used as active component in abiotic materials. Similarly, colloidal dispersions containing clay minerals interact with the substrates used in the determination of metabolic activity. In testing of such materials, the determination of CFU is the most common choice. Taking into account those limitations, challenging approach is the molecular quantification of live/dead cells in microbial biofilms by real-time PCR. The intercalating dyes ethidium monoazide and propidium monoazide can be selected in respect to microorganisms (for example, *S. mutans* vs. *E. coli*).

The mentioned methods do not make it possible to describe many details in biofilms. Microscopic techniques in combination with appropriate dyes (confocal laser scanning microscopy) or nucleotide probes (fluorescence in situ hybridization), but also SEM (scanning electron microscopy) can help to prove a real fitness and architecture of microbial consortia.

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## Hydrothermal synthesis of pure and Boron doped nanoparticles of ZnO and their optical and dielectric properties in far infrared region

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Keywords: ZnO | semiconductor | THz-TDS

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Increased demand for semiconductors and Inorganic/Organic hybrid materials, intended for the production of precision sensors, solar cells, drugs, and many other applications, require the preparation of new materials with low cost and appropriate parameters. As reasonable alternative were investigated Zinc oxide (ZnO) nanoparticles prepared by co-precipitation hydrothermal synthesis. ZnO is a semiconductor with a wide band gap (~3.34eV) and suitable optical transparency in the UV-VIS spectrum. This way of preparation offer simple-controllable conditions to achieve good homogeneity in specific shape and size during growth of ZnO nanoparticles. The dielectric response of ZnO can be affected by synthesis conditions or doping [1]. Doping means the introduction of impurities into a semiconductor crystal. The dopant is integrated into the lattice structure of the semiconductor crystal, what leads to the defined modification of conductivity. For the first time, the boron (B) was used for doping ZnO during co-precipitation hydrothermal synthesis. Also different loading of ZnO in inorganic/inorganic nanocomposite materials can affect resulting optical and dielectric properties. THz time domain spectroscopy was utilised to investigate the dielectric response of prepared ZnO nanoparticles. The aim of our work was to verify the co-precipitation hydrothermal synthesis of (B) doped ZnO nanoparticles and to characterize the frequency depend dielectric properties of ZnO nanoparticles with different morphology and dopant concentration in composite mixtures. Well-defined and doped ZnO nanoparticles combined with clay nanolayers can find utilization in gas sensors, photocatalytic or electronic applications.

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# Antimicrobial nanomaterials based on photoactive dyes and saponite and their practical application using 3D print

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Keywords: Phloxine-B | Nanomaterials | 3D-print

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The challenge of achieving appropriate disinfection without the formation of harmful disinfection byproducts by conventional chemical disinfectants, as well as increased demand for water treatment and recycling systems, calls for new materials or technologies for efficient and nature-friendly disinfection. Several materials have demonstrated strong antimicrobial properties through diverse mechanisms. One of the most efficient mechanism is the photocatalytic production of reactive oxygen species (ROS), which leads to the disintegration of the bacteria cells.

As a reasonable alternative, phloxine B (PhB) was investigated. PhB is a most commonly used dye in cosmetic products that exhibit the absorption of ultraviolet and visible radiation ( $\text{Peak}_{\text{Max}} @ 540\text{nm}$ ). Photosensitized PhB induces  $\text{Ca}^{2+}$  release, cell cycle arrest and DNA damage by generating ROS [1]. Due to solubility in water, PhB can be easily incorporated into the intralayer spaces of clay minerals by a cation-exchange mechanism. Preliminary experiments confirmed increased PhB adsorption to organically-modified saponite (Sap). The effect of Sap particles modification with octadecyltrimethylammonium was investigated. Organically modified clay minerals with intercalated PhB molecules are suitable precursors for clay/polymer nanocomposites of antimicrobial surface properties.

3D printing is a process in which material is joined or solidified under computer control to create a three-dimensional solid objects of precise shapes. In the current study, we demonstrate the incorporation of antimicrobial PhB in a clay mineral and the subsequent 3D printing of the composite material. The 3D printouts will be tested as abiotic materials for inhibition of biofilm formation. Inorganic/Organic hybrid materials based on PhB attached to the 3D-printouts may in the future open new possibilities for the construction of functional medical devices.

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## Reaction of methylene blue with ascorbic acid

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*Keywords: methylene blue | reaction kinetics | redox reactions*

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This work was focused on the determination of reaction kinetics and the rate constant of redox reaction of methylene blue with ascorbic acid. Ascorbic acid causes reduction of methylene blue to its reduced, leuco-form. The decrease in methylene blue absorbance was observed using absorption spectroscopy in the ultraviolet (UV) and visible (VIS) light region. At the same time, a new spectral peak appeared in the UV region, which was assigned to the leuco form of the dye. Using chemometry, it was found that the reduced form of the dye absorbed in the same region as ascorbic acid. The objective of this work was to investigate the effect of varying concentrations of ascorbic acid on the reduction of methylene blue. The measurements were made with varying concentrations of the reactants, as well as by the changes of the concentrations of hydrochloric acid while focussing on the kinetics of the reaction. We also examined the influence of clay minerals on reaction mechanism. It was found that methylene blue adsorbed on the surface of clay mineral particles was less reactive and did not lead to the decomposition of the dye. The probable cause was the formation of molecular aggregates which stabilized methylene blue.

### Acknowledgement:

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## Study of montmorillonite modified with different surfactants from the series of primary amines by IR spectroscopy

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Keywords: montmorillonite | conformation | near-IR spectroscopy

Infrared (IR) spectroscopy is one of the most commonly used method for characterization of organoclays. Over the past decades, these inorganic/organic hybrid materials found application in a wide variety of industrial and scientific applications such as adsorbents of organic pollutants, pharmaceutical and cosmetic additives, reinforcing fillers for plastics, water treatment or host structures for direct intercalation of polymers. The behaviour and properties of organoclays strongly depend on the structure and arrangement of the intercalated surfactants, most often alkylammonium cations, in clay mineral interlayers. Detailed information on the arrangement of organic cations provides also near-infrared (NIR) spectroscopy.

The objective of this paper was to study the arrangement/conformation of the primary alkyl ammonium surfactants in the montmorillonite interlayers. The organo-montmorillonites were prepared from a Na-saturated <2  $\mu\text{m}$  fraction of bentonite Jelšovský Potok (JP, Slovakia) and alkylammonium ( $\text{C}_n\text{-NH}_3^+$ ) salts with increasing length of alkyl chain from C5 to C19. The X-ray diffraction analysis was used to probe the arrangement of alkylammonium cations in the interlayers. The KBr pressed disk technique was applied for measurements in the middle-IR (MIR) region and diffused reflection (DRIFT) techniques was used for NIR.

The X-ray diffraction analysis showed basal spacing ( $d_{001}$ ) in the range 1.35–1.95 nm (C5-JP – C19-JP) in dependence on the alkyl chain length. The basal spacing was almost the same ( $\sim 1.33 - 1.37$  nm) for montmorillonite saturated with C5 – C8 cations suggesting a monolayer arrangement. With further increase of the alkyl chain length the  $d_{001}$  values gradually increased from 1.41 nm (C9-JP) through 1.75 nm (C14-JP), 1.83 nm (C16-JP) to 1.95 nm (C19-JP), indicating consecutive transitions from monolayers to bilayers and pseudotrimolecular layer arrangement. The most pronounce increased of the  $d_{001}$  value was observed between C11 and C12 ( $\sim 1.51-1.66$  nm). The positions of the absorption bands related to the stretching vibrations ( $\nu\text{CH}_2$ ) and the first overtone ( $2\nu\text{CH}_2$ ) of the methylene groups were found to be very sensitive to the alkyl chain arrangements. The MIR spectra of organo-montmorillonites showed a gradual replacement of the asymmetric  $\nu_{\text{as}}(\text{CH}_2)$  and symmetric  $\nu_{\text{s}}(\text{CH}_2)$  stretching bands from 2934 to 2922  $\text{cm}^{-1}$  and from 2862 to 2851  $\text{cm}^{-1}$ , respectively. A gradual shift towards lower wavenumber with increasing alkyl chain length confirmed a transition from disordered (*gauche*) to more ordered (all-*trans*) conformers of the surfactants.

The NIR spectra of organo-montmorillonites showed a abroad complex band related  $2\nu(\text{CH})$  in the 6100–5600  $\text{cm}^{-1}$  region and the combination ( $\nu+\delta$ ) bands of  $\text{CH}_2$  groups in the 4500–4000  $\text{cm}^{-1}$  region. The positions of the  $2\nu_{\text{as}}(\text{CH}_2)$  ( $\sim 5830-5786$   $\text{cm}^{-1}$ ),  $(\nu+\delta)_{\text{as}}\text{CH}_2$  ( $\sim 4362-4330$   $\text{cm}^{-1}$ ),  $(\nu+\delta)_{\text{s}}\text{CH}_2$  ( $\sim 4276-4255$   $\text{cm}^{-1}$ ) signals were used as an indicator of the *gauche/trans* conformer ratio. For all bands a shift towards lower wavenumber with increasing the alkyl chain length suggested a transition from disordered liquid-like to more ordered solid-like structures of the surfactants. The most significant shift of the bands was observed between samples C10 and C11 (10  $\text{cm}^{-1}$ ), indicating critical point of length dependent conformational change. The magnitude of the overall shift of  $2\nu_{\text{as}}\text{CH}_2$  (46  $\text{cm}^{-1}$ ) was significantly higher than those observed for  $\nu_{\text{as}}\text{CH}_2$  (12  $\text{cm}^{-1}$ ) or  $\nu_{\text{s}}\text{CH}_2$  (11  $\text{cm}^{-1}$ ), showing the NIR spectroscopy to be very suitable for studying the conformation of surfactants in organo-clays.

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# Biological weathering and clay formation with industrial and environmental utilization

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*Keywords: weathering | minerals | bioleaching*

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Recent research demonstrates that biological weathering accelerates elemental release from rocks and minerals in aquatic environment [1]. In laboratory experiments, temperature and nutrient variability showed major changes in the mineral decompositions by bacteria and suggest the different intensity of biological weathering process in nature. Other factor of the biological decomposition includes the mineralogy of the rocks and the nature of bacterial species. Consequently, silicate rocks in environments adhered by bacteria are consecutively decomposed, so that formed corrosive holes on the surface of minerals with amorphous precipitates. This biological weathering of silicates can favor the neof ormation of clay minerals from these amorphous precipitates [2].

In biological leaching, the heterotrophic bacteria produce a range of organic acids and enhance dissolution of the different impurities such as Fe for ceramic and glass industry. For progressing bacterial Fe reduction and dissolution under anoxic conditions, a supply of organic source is necessary. Several experiments confirmed that heterotrophic bacteria enhance the purification of quartz sands by dissolution of Fe minerals and by releasing clays from quartz surface. Sugars and molasses was used as the bulk carbon source to enhance biomass growth and production of organic acids as leaching agents. The bioleaching steps not only dissolve and release iron impurities coating the surface of quartz grains but also increasing the amount of iron removal by subsequent magnetic separation. This bioleached treatment may be applicable to the extraction of fine iron minerals from non-metallic materials such as quartz sands, kaolin, and feldspars and other non-metallics. The feasibility of the bioleaching treatment has to be tested specifically to each type of silicate raw materials [3].

In the soil and sediment environment, many microorganisms play important role in biogeochemical cycling. Bacteria are ubiquitous in the geological environments and play an important role in toxic elements mobilization and immobilization. The ability of hydrocarbon-degrading bacteria to degrade a wide variety of hydrocarbon is well known and utilized in bioremediation. Toxic elements mobility is unclear for predicting the magnitude of any observed effects under natural conditions, but it can be utilized for decontamination under regulated conditions and nutrients additions. Indigenous heterotrophs increased the dissolution of Cu and Zn from the soil and of Zn and As from the sediment sample in laboratory conditions. Based on the results of laboratory experiments we can determine bioremediation effect and the quantity of nutrients under field conditions [4].

The biological reactions occurring in the geological environment play a significant role in the natural remediation and subsequent bioavailability of metals and metalloids to plants and the food chain. Many observations clearly confirm the important role of bacteria on the biological weathering of minerals and rocks, the importance to investigate of the biochemical processes with the possibilities of the economical utilization for industrial and environmental applications [5].

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# The mechanism of high-pressure methane adsorption on clay minerals

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Keywords: methane adsorption | clay texture | surface properties

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The majority of methane (CH<sub>4</sub>) present on Earth is stored underground in clay-rich sediments, including shales [1]. Due to high-pressure, a significant part of CH<sub>4</sub> resources is adsorbed on the surface and in micropores, partly due to clays occurrence [1, 2]. Unfortunately, CH<sub>4</sub> – clays interaction under high-pressure has been studied only in a few papers in which spatial relationship in crystal structure – CH<sub>4</sub> adsorption was investigated, while influence of the other factors were discriminated. The aim of this work was to understand whether the crystal structure of clay minerals has the main impact of high-pressure methane adsorption behavior or it is mainly controlled by other factors.

In the present study, experiments were performed on Cs-, Li-, Mg-, Ca- and Tetramethylammonium (TMA)-exchanged montmorillonite (MONT). Samples were dried *in situ* subsequently at 60, 110, and 210 °C. Adsorption of CH<sub>4</sub> was conducted after every drying step.

The measured TMA-MONT's isotherms were three times higher than those of Cs-MONT. Cs- and Li-MONT's isotherms reached similar maximum and did not change much with pre-drying temperature, whereas CH<sub>4</sub> adsorption on Mg- and Ca-MONT decreased significantly after drying at 110 °C, in respect to that at 60 °C. Mg- and Ca-MONT showed a hysteresis loop that did not close even under vacuum.

Variability in the adsorption results suggest change in adsorption sites availability and/or affinity for CH<sub>4</sub> that was connected to the type of exchangeable cations present and the amount of removed water from the sample. Tentatively, we explain the observed difference by changes in availability of the interlayers for methane; limited access after interlayer width decrease due to drying; hysteresis caused by migration and retention of CH<sub>4</sub> to the interlayer at very high pressure (which was not accessible in low-pressure region). On the other hand, the lack of hysteresis and height of Cs-MONT's or Li-MONT's isotherms montmorillonite in comparison to TMA-MONT's isotherms may be the evidence of no changes in interlayer space accessibility.

## Acknowledgement:

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**NOTES:**

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# POSTER PRESENTATIONS





## Utilization of clays modified with Fe/Mn-oxide for As<sup>v</sup> removal from aqueous solutions

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*Keywords: sorption | bentonite | zeolite*

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This work was done to assess the arsenate (As<sup>v</sup>) removal from the model solution by clay sorbents based on modification by Fe/Mn-oxide particles. The surface modification of the natural materials aims at the enhancement of sorption properties towards selected toxic ions. The characterization of changes of physico-chemical properties of natural materials after their modification is significant for their further applications. Two samples were compared in sorption properties, bentonite/ Fe-oxide composite (ratio 2:1) and zeolite modified by MnO<sub>2</sub> particles. The concentration of some toxic metals especially arsenic are higher than permissible discharge levels in effluents. Dangerous arsenic concentrations in natural waters is now a worldwide problem. Arsenic contamination may be prevalent at mining and industrial sites, requiring risk assessment that includes information on the potential mobilization of As in soils. It, therefore, becomes necessary to remove arsenic from wastewaters by an appropriate treatment before releasing them into the environment.

The value of specific surface area of both samples were studied by the low temperature nitrogen adsorption measurement. For the structural changes of the samples were used X-ray diffraction method, Mössbauer spectroscopy and field-emission scanning transmission electron microscopy. The results from the batch adsorption experiments of As<sup>v</sup> removal were processed by the Langmuir adsorption isotherm.

The effect of pH and initial metal ion concentration was investigated in this study. The optimum pH for arsenic adsorption by both samples was found to be about 3.0. The adsorption increased very significantly with decreasing pH for both samples. The bentonite/Fe-oxide sample achieved the maximum adsorption capacity 6,1 mg.g<sup>-1</sup> As<sup>v</sup> while for zeolite/MnO<sub>2</sub> sample it was only 0,37 mg.g<sup>-1</sup>. The adsorption of As<sup>v</sup> on both samples bentonite/Fe-oxide and zeolite/MnO<sub>2</sub> increased with the increasing initial metal ion concentration up to 50 mg.l<sup>-1</sup> and then an equilibrium was established.

The results obtained from this study confirmed that bentonite/Fe-oxide sample (B-85) is a suitable sorbent of arsenic from the aqueous solution at low concentrations compare to the zeolite modified sample. The effect of B85 sample on As(V) sorption is more pronounced. This sorbent can be utilized for cleaning of soil and sediment leachates (after bioleaching of the soil or sediment sample) where the concentration of arsenic varies from the 4,5 mg.g<sup>-1</sup> to 10 mg.g<sup>-1</sup>. This study will be continued with sorption experiments designed in column (dynamic conditions), where the filtration layer will be based on composite materials or material based on iron oxide coated sand for removal of As<sup>v</sup> from the bioleachates.

However, further study of the sorption properties of these materials in batch experiments, as well as materials combined in different layers in columns in dynamic regime will allow to obtain the information about the selectivity of particular materials towards toxic ions.

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## Dye surface concentration and its influence on the energy transfer efficiency in hybrid nanomaterials with smectite

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*Keywords: FRET | hybrid nanomaterials | surface concentration | rhodamine 6G | oxazine 4 | Poisson probability density function*

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Hybrid nanomaterials in the form of colloidal dispersions were prepared from a synthetic layered silicate of saponite type (Sap) and cationic laser dyes rhodamine 6G (R6G) and oxazine 4 (Ox4). Förster resonance energy transfer (FRET) was investigated using steady-state and time-resolved fluorescence (TRF) spectroscopies. The energy transfer occurred from R6G cations playing the role of energy donor to the Ox4 cations representing the energy acceptor. FRET efficiency increased with the density of dyes adsorbed on the surface of silicate particles. Considering the sensitivity of FRET efficiency on the distance between interacting particles the Poisson probability density function was applied to model the characteristics of the dye molecules distribution on the Sap particles. High concentrations of dye cations led to rather narrow distribution of distances whereas lowering the concentrations was characterized by a distance distribution broadening. The expected values of FRET efficiencies for the hybrid systems with given surface concentration of dyes were calculated as a function of the distance derived using the model. The theoretical and experimental results of FRET efficiencies were in very good agreement. Since the photoactivity of dyes is strongly affected by the interactions associated with the states of relatively high concentrations and consequently their short intermolecular distances the theoretical model presents a good tool for predicting photophysical properties of such hybrid systems. The statistical approach for characterization of the distance distribution between organic dye cations adsorbed on the clay mineral surface brought a considerably higher accuracy than a simplified model using average intermolecular distances.

### Acknowledgement:

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## Hydration properties of organically modified montmorillonite

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Keywords: organo-montmorillonite | alkyl chain conformation | water adsorption

Modification of montmorillonites with cationic surfactants is widely used method to prepare inorganic/organic hybrid materials with properties suitable for different applications. Understanding microstructure and hydration potential of organo-montmorillonites is of high importance in clarifying their adsorption characteristics towards different organic compounds. The objective of the present work was to examine the effect of loading amount of mono- (1C8), di- (2C8), tri- (3C8) and tetra- (4C8) octylammonium cations on their arrangement within the montmorillonite interlayers and to follow the hydration properties of prepared organo-montmorillonites. The montmorillonite from Jelšový Potok, Slovakia (JP) and organic salts in loading concentration range of 0.2 - 2.0 mmol.g<sup>-1</sup> (corresponding to 20 - 200 % of the CEC of JP) were used for organoclays preparation. Carbon analysis, XRD, and IR spectroscopy were used for the samples characterization. The degree of surfactant adsorption calculated from measured carbon content was 93% of CEC for 1C8, while 172 %, 180% and 196 % saturation of CEC was determined for 2C8, 3C8 and 4C8, respectively, at 2.0 mmol.g<sup>-1</sup> of the organo-cation used for the preparation. It is assumed that in addition to 2C8, 3C8 and 4C8 cations the organic salts were co-adsorbed to MMT interlayers and/or outer surfaces. The  $d_{001}$  value of 1C8-JP showed creation of monolayers while for 2C8-, 3C8- and 4C8-JP formation of monolayers, bilayers and paraffin arrangement was confirmed in dependence on the number of alkyl chains and loading amount. The bands related to CH<sub>2</sub> stretching (3000-2800 cm<sup>-1</sup>) and the first overtones (near 5800 cm<sup>-1</sup>) modes were used to probe the ordering of the intercalated cations. With growing amount of 2C8, 3C8 and 4C8 surfactant the bands were shifted from the position characteristic for disordered *gauche* conformers to lower wavenumbers indicating increasing number of ordered *all-trans* conformers. The hydration properties of the samples were investigated by NIR spectroscopy and gravimetry. Difference in the area of the H<sub>2</sub>O combination band near 5250 cm<sup>-1</sup> at 100% and 0% relative humidity reflected the quantity of adsorbed water. The spectra showed decreasing content of water with growing amount of surfactants and octyl chains number. The NIR results correlated very well with the values obtained from gravimetric analysis. Almost linear decrease of water content from 9.4 to 5.0 mass % for 1C8, from 8.1 to 1.8 mass % for 2C8, from 7.2 to 1.1 mass % for 3C8 and from 7.0 to 1.0 mass % for 4C8 was observed with increasing loading cation content from 0.2 to 1.0 mmol.g<sup>-1</sup>. Further increase of the cation adsorption content reduced the amount of water only negligible. During the hydration was observed also the shift of the first overtone of CH<sub>2</sub> groups to the lower wavenumber. The change of band position pointing to the increasing number of ordered *all-trans* conformers and decreasing of disordered *gauche* conformers was observed mainly for 2C8-JP and indicated that the water molecules supported the change of cations configuration from the high degree of disorder to the more ordered.

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## Water quantification in perlites by NIR spectroscopy

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Keywords: perlite | water quantification | water adsorption

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The potential of a near-infrared (NIR) spectroscopy to water quantification in perlites (PI) has been introduced. PI is volcanic glass and belongs to the group of silicate industrial rocks that's economically interesting deposits occur also in Slovakia therefore detailed studies of their properties have received a great deal of attention not only due to their industrial potential but also from the scientific point of view. Water plays an important role in the application of this material. PI contains a various types of water, especially important are water molecules trapped in the inner pores and microcracks causing the expansion when rapidly heated.

The objective of this study was to examine the potential of NIR spectroscopy to water quantification in PI samples from different localities (Lehôtka pod Brehmi – SK, Jastrabá skala – SK, Viničky – SK) with variable amount of water and textures. The water in PI samples was investigated mainly by modern methods of NIR spectroscopy, supplemented with traditional gravimetric and thermal analysis. The amount of water in PI samples was investigated by NIR DRIFT accessory. The combination band of water molecules  $(\nu+\delta)_{\text{H}_2\text{O}}$  near  $5240\text{ cm}^{-1}$  was used to water quantification because the region is free from the other silicates bands and can be used to provide information on the water content in samples. The area of this band reflects the amount of molecular water in PI samples. The  $(\nu+\delta)_{\text{H}_2\text{O}}$  band areas plotted as a function of water content obtained from the thermogravimetric analysis (TG) and loss on ignition (LOI) showed correlation  $R^2 = 0.78$  and  $0.74$ , respectively. Internal standards have been used to improve water quantification. The hexadecyltrimethylammonium bromide (HDTMA) and talc (GP-1) were used as internal standards because of their very low affinity to water and absence other vibration bands in area of the water band. In HDTMA standard the area of the first overtone of CH groups (near  $5800\text{ cm}^{-1}$ ) was used to normalize spectra while in GP-1 the combination vibration band of structural OH groups from talc (near  $4180\text{ cm}^{-1}$ ) was used. This way the correlations with TG and LOI analyses for HDTMA were  $0.89$  and  $0.86$ , respectively, and for GP-1  $0.88$  and  $0.86$ , respectively. The extent of hydration was followed by NIR UpDRIFT accessory enabling the measurements of the samples directly in closed glass vials. The  $(\nu+\delta)_{\text{H}_2\text{O}}$  band was used to characterize the hydration properties of the samples hydrated at 100 % relative humidity for 2 weeks. Difference in the area of  $(\nu+\delta)_{\text{H}_2\text{O}}$  band of hydrated and dried sample reflects the quantity of adsorbed water. NIR spectra as well as gravimetric analysis proved very poor hydration ability. The maximal amount of adsorbed water was only 3.3 mass %. Dehydration properties of PI samples were monitored by special NIR DRIFT temperate cell susceptible to in-situ measurement of the spectra in a temperature range  $25\text{-}800^\circ\text{C}$ . With increasing temperature the area of  $(\nu+\delta)_{\text{H}_2\text{O}}$  band fell down in different ways. The slow decline of band intensity reflected the  $\text{H}_2\text{O}$  held strongly within structure while the significantly decrease already at low temperatures points to the presence of weakly bound water molecules.

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## Hybrid systems of saponite and natural, luminescent alkaloid berberine

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Keywords: cationic dyes | layered silicates | antibacterial properties

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Hybrid materials represent composites with the components in the molecular or nanometer size range. Hybrids of layered nanoparticles containing organic compounds, including natural bioactive substances, attract much attention due to their unique properties and potential applications. Berberine (Berb) is an alkaloid that is produced in the cells of certain plants, such as *Mahonia aquifolium*. Berb is a cationic, photoactive and luminescent dye that absorbs light in the UV and partially also in visible range. Berb is easily adsorbed and electrostatically bound to negatively charged particles of layered silicate, saponite (Sap) [1]. The colloidal and solid hybrid substances of Berb and Sap were prepared and characterized by absorption and fluorescence spectroscopy. The hybrid systems showed slightly different properties than the dye solution. The molecular aggregation, that reduces Berb photoactivity, occurred only in the systems of highest Berb concentrations. Under an optimum ratio of the components, Berb photoactivity remain unchanged, as confirmed by fluorescence spectroscopy. The spectral shifts observed for both absorption and emission spectra to lower energies confirmed slight changes in the shape of the adsorbed Berb molecules. The results of X-ray diffraction and linearly-polarized absorption spectroscopy confirmed the orientation of the molecules lying flat on the surface of the Sap.

The biological experiments were aimed to characterize photosensitizing properties of Berb. Cell survival (CS) of the Gram-positive bacterium *Staphylococcus aureus* was evaluated. Samples of the hybrid colloids were irradiated either with a blue laser (445 nm, 500 mW, 100 s) or cold white LED light source (electrical power 100 W, 5 h). Berb bound to Sap particles was slightly more efficient than the free dye. For example, antimicrobial properties of the Berb/Sap colloid (1 mmol/g) caused a reduction of CS to 22% for the laser illuminated sample, with 77% surviving cells in a similar system without Sap. No inhibition was observed for the experiments without illumination.

The presented results show perspectives for hybrid materials containing natural bioactive substances in hybrid materials.

### Acknowledgement:

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## Adsorption of pesticides on alkylphosphonium organoclays

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*Keywords: alkylphosphonium | organoclay | pesticide*

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The large use of chemicals in agriculture, especially herbicides, has been serious environmental concern because of the potential run-off and leaching of these compounds through the soil, contaminating surface and ground waters. Herbicide run-off and leaching down the soil profile have become a serious environmental problem and a primary source for polluting surface- and groundwater. Widely used herbicides such as atrazine, isoproturon, diuron and alachlor are the main compounds found in groundwater. The most common technique for removal of pesticides like atrazine from water involves use of an activated carbon adsorption system. Unfortunately, activated carbon lacks selectivity for atrazine and adsorbs innocuous organic compounds. As a consequence, it is desirable to investigate complimentary supplements to activated carbon such as organically intercalated clays.

The clay exchanged with suitable organic cations forms a basis for ecologically acceptable formulations of herbicides with reduced leaching, ground water contamination and enhanced weed control efficacy. Incomplete neutralization of the clay surface charge by an organic cation may be advantageous in achieving maximal adsorption of hydrophobic herbicides. One conclusion from these studies is that optimization of clay-based herbicide formulations requires a selection of structurally compatible organic cations preadsorbed on the clay at optimal coverage.

The objective of the research reported herein was to create alkylphosphonium based organoclays with four structurally different phosphonium organocations: tetrabutylphosphonium (4P4), tetraoctylphosphonium (4P8), tributylhexadecylphosphonium (3P4-C16) and trioctylhexadecylphosphonium (3P8-C16) and to investigate the ability of these organoclays to sequester atrazine from water. The studies characterized the apparent adsorption of atrazine on and desorption from organoclays created with the surfactant and a purified montmorillonite, and quantified the impact of the ratio of surfactant to clay in the organoclay.

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## Crystallite termination, iron and vacancies distribution in the 2:1 and interlayer sheets of the Mg-Fe chlorites

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Keywords: chlorites | X-ray diffraction

Seven monomineralic chlorite samples representing the Mg-Fe chlorites series were carefully selected for structural studies using powder X-ray diffractometry (PXRD). All samples were prepared as oriented and disoriented specimens and measured in the Bragg-Brentano and Debay-Scherrer geometry, respectively.

The diffraction profiles of all samples (background, zero shift, unit cell, and profile parameters, including asymmetry) were fitted using La Bail method implemented in the program package Jana2006 [1]. All analyzed samples were classified as nearly pure trioctahedral chlorites, polytype IIb (some of them possess little impurities, total below 3%). In all samples the semi-random stacking in  $c^*$  direction was observed, which manifests in the slowly decreasing intensity bands in the region between 22 to 26  $2\theta$  (CoK $\alpha$ ), where the  $hkl$  band with  $k \neq 3$  are present. The structure models, in all seven chlorites, were assumed in triclinic C-1 space group based on Bailey and Bown (1962) [2] suggesting that all chlorites with semi-random stacking would have triclinic symmetry as the result of averaging of two triclinic and one monoclinic possible layer symmetries.

The main goal of the study was to obtain the structure refinement regarding the distribution of iron and octahedral vacancies in the 2:1 and interlayer sheets. New calculation approach was implemented in Sybilla program package developed by Chevron<sup>TM</sup> [3]. Following the significant influence of the outer surface layers of clay crystallites on the distribution of basal reflection intensities [4], the two additional crystal models of termination, with 2:1 layers or octahedral hydroxide layers were added. In all cases, the information about total content of iron and vacancies (found with microprobe analysis and Mossbauer spectroscopy) in the cell was used as a constrain during the refinement. The results show that, depending on established model, the distribution of iron between 2:1 and interlayer sheets can differ. For all models in Mg-chamosites, however, total content of iron in 2:1 layer reached 55-60%. In turn, the calculations for samples with low iron content suggest that more than 70% of total iron is located in the 2:1 layer.

The PXRD measurements were also performed on an iron-rich chlorite after thermal treatment. Upon isothermal heating at temperatures up to 450°C for 24 hours, providing mixed dehydroxylation and dehydrogenation [5], 14Å chlorite is still present and no new phases occur. Together with increasing temperature of isothermal heating, the peaks became broader and additional chlorite fraction with smaller  $d_{001}$  seems to appear.

This results were also presented in International Clay Conference in Grenada 2017.

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## Interaction of pyridine with acid-treated montmorillonite

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*Keywords: Near-IR spectroscopy | montmorillonite | pyridine adsorption*

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The effect of montmorillonite structure degradation on the creation of acid sites was investigated by near infrared (NIR) spectroscopy using pyridine as probe molecule. Na-form of SAz-1 montmorillonite was dissolved in HCl for 2-8 hours. Dried samples were placed in desiccator with pyridine vapors and then the NIR spectra were measured. To examine the strength of the pyridine bonding the samples were heated at 110, 170, 230°C prior to NIR analysis. Gradual decrease of the intensities of the bands related to structural OH groups reflected a release of the octahedral atoms from Na-SAz upon HCl treatment. New band near 7315 cm<sup>-1</sup> due to SiOH overtone confirmed the creation of protonated silica in the reaction product. The montmorillonite structure was partly disturbed after 2 h and significantly after 4 h treatment. The spectrum of SAz-8h corresponded to protonated silica. The adsorption of pyridine on acid-treated samples modified the first OH overtone (2ν<sub>OH</sub>) region. While the position of the 2ν<sub>OH</sub> band remained nearly unchanged the 2ν<sub>SiOH</sub> band almost completely disappeared. Silanol groups as a weak Brønsted acid sites formed H-bonds with pyridine-nitrogen. As a result the SiOH overtone was shifted to lower wavenumbers and overlapped with broad complex band near 7100 cm<sup>-1</sup>. After pyridine adsorption the CH overtone band (2ν<sub>CH</sub>) corresponding to physisorbed and/or H-bonded pyridine appeared near 6000 cm<sup>-1</sup> in the spectrum of Na-SAz. The shape and position of the band was only slightly changed if pyridine was adsorbed on acid-treated samples. Upon heating the H-bonded pyridine molecules were released as confirmed the reappearance of the SiOH band and decreased intensity of the 2ν<sub>CH</sub> overtone. Almost complete loss of pyridine band was observed for Na-SAz and amorphous silica heated above 170 °C, while well-resolved 2ν<sub>CH</sub> band was still present in the spectra of 2 and 4 hours treated samples. Its position, however, was considerably shifted to the higher wavenumbers. Partly decomposed montmorillonite provided protons for creation of pyridinium cations. Thus the bands at 6096 and 6065 cm<sup>-1</sup> in the spectrum of SAz-2h heated at 230°C were assigned to C-H vibrations of pyridinium cations. The obtained results showed that NIR spectroscopy can distinguish different pyridine species adsorbed on montmorillonite surface.

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## Study of Atrazine-Beidellite interactions –theoretical approach

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Keywords: *Organoclay | DFT | Atrazine*

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Atrazine is one of the most employed pesticides belonging to the s-triazine family and has a negative impact on the environment and health [1]. Clay minerals, e.g. montmorillonite or beidellite are suitable candidates to immobilize organic contaminant, like atrazine, e.g. from waste water.

These clays are highly hydrophilic and consequently show very limited adsorption capacities for hydrophobic organic contaminants. However, a higher adsorption of organic molecules/cations can be obtained by modifying of the clay surface by organic surfactants [2].

The Density Functional Theory (DFT) D3 method with employed dispersion corrections [3] was used for study of interactions in the atrazine-beidellite (A-Bd) structure. Two models were proposed: 1. Atrazine intercalated in the Bd interlayer space (A-Bd), and 2. A-Bd together with the tetramethylphosphonium (TMP) cation as an organic surfactant in the interlayer space of Bd (ATMP-Bd).

Beidellite is aluminosilicate with predominant substitutions in tetrahedral sheets versus in octahedral ones in montmorillonite. This different charge distribution in beidellite improves a stability of prepared organoclays [4].

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## Synthesis of zeolites FAU, GIS and PHI from perlite by-product material and their utilization for removal of heavy metals from polluted soil

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*Keywords: zeolites | synthesis | perlite*

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The fine powdered perlite a by-product originated during processing of raw perlite from the Lehôtka pod Brehmi deposit (Slovakia) was used in the present study as a starting material. Fine perlite is not suitable for expansion which substantially limits a possible application for this material. The conversion of fine perlite by-product material into zeolites seems to be one of the most promising ways how to recover this kind of by-product and to obtain value-added material (i.e. zeolite) with attractive sorption properties. Experimental alteration of perlite by-product material was performed in 1 – 5 M NaOH solutions at 50 – 80 °C for 1 – 6 days. Mineralogy, chemistry and surface properties were determined for the synthesized reaction products. The pollutant removal efficiency of the synthesized zeolitic materials was assessed in the sorption experiments using pore water obtained from highly metal-contaminated (mainly Zn and Pb) alluvial soil from Příbram District (Czech Republic). The main goal was to find relationship among the synthesis conditions, properties of synthesized zeolitic materials and pollutant removal efficiency in order to minimize the accumulation of perlite by-product by its transformation to zeolites and assess a possible application for the synthesized zeolitic materials.

The results showed that the perlite by-product material consisted of 96 wt% of volcanic glass and minor amounts (4 wt%) of mica, feldspars, quartz and opal. The main reaction products identified by XRD were zeolite X (FAU), zeolite P (GIS) and phillipsite (PHI). The quantity and type of zeolite was heavily affected by experimental conditions. Phillipsite was preferentially formed in 1M NaOH. Zeolite P and X were preferentially formed in 3 and 5M NaOH solution, respectively. Generally, with increasing temperature and longer reaction time the amount of newly-formed zeolites increased. The perlite by-product material reacted with 5M NaOH solution for 6 days at 80 °C contained only 16 wt% of unaltered volcanic glass and 77 wt% of synthesized zeolites. The synthesized zeolitic materials showed contrasting physico-chemical properties (e.g. BET and CEC) mainly due to the variable zeolite content and distinct structural features between zeolite species. Similarly, the synthesized zeolitic materials showed different efficiencies in removal of heavy metals from pore water. Zeolite X-rich material removed >94 % of Zn from the pore water whereas zeolite P-rich and phillipsite-rich materials removed 87 % and 35 % of Zn, respectively. We assume that the higher Zn removal efficiency for zeolite X might be related to the larger dimensions of structural channels within zeolite X framework compared to those of phillipsite and zeolite P.

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## Immobilization of metal nanoparticles on organo-modified layered silicates

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Keywords: cationic polymer | silver nanoparticles | antibacterial activity

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Preparation of suitable supports for immobilization and stabilization of metallic nanoparticles such as Ag<sup>0</sup> is nowadays very active research area, because of the potential of such materials in the field of catalysis or medical applications. Properties of layered silicates dispose them into a wide group of such supports. Various experimental methods were applied to achieve good dispersion of nanoparticles of defined size, shape, and composition within clay matrix because all those features influences functionality of composite material. Several organic cationic species were applied for tuning of growth in size and restricting of possible aggregation of metal nanoparticles. The objective of this work was to investigate properties of composite materials based on organomodified clay minerals with immobilised Ag nanoparticles towards their application as disinfection materials.

Two clay minerals were selected for this work: synthetic trioctahedral hectorite Laponite RD (Lap) and natural montmorillonite Kunipia (Kun). Polymeric polydiallyldimethylammonium cation (PDDA) was used as dispersant of silver nanoparticles. Two samples for each clay mineral were acquired by reduction of Ag<sup>+</sup> to Ag<sup>0</sup> at different stages of synthesis. Prepared materials were characterised using infrared spectroscopy (IR), carbon elemental analysis, scanning electron microscopy (SEM). Carbon content determined for both Kun samples was 3%, while slightly higher content of 3.7% was loaded to Lap samples. Upon introduction of PDDA cations stretching vibration of νC-H methyl groups between 2970-2860 cm<sup>-1</sup> and bending vibration of δC-H in the range 1490-1380 cm<sup>-1</sup> have appeared in the infrared spectra, confirming presence of organic phase in the samples. Based on SEM micrographs registered with backscattered-electron detector (SEM-BSE) distribution and particle sizes of silver nanoparticles was heterogeneous with part of silver buried within matrix.

Antibacterial activity of studied materials was assayed using microorganisms *Staphylococcus aureus*. Preliminary results showed absolute inhibition of biofilm formation for samples prepared via same approach (Kun2 and Lap2) upon their dilution 2.5 times. Second approach led to materials with lower but still high efficiency in inhibition of biofilm development. With further dilution of samples (10x) Kun2 inhibited microorganism growth for 2.5 log (very good), while for Lap2 and Lap1 antibacterial activity was lower 1 log, Kun1 did not showed any activity against microorganism growth. The influence of samples preparation of observed features is under further investigation.

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## Tetrabutylphosphonium beidellite organoclay – DFT and experimental study

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Keywords: beidellite | DFT | stability | tetrabutylphosphonium

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Modification of clay minerals by organic cations is a subject of a great interest because of possibility to develop new materials with specific properties for new technological applications e.g. polymer-clay nanocomposites, active sorbents, drug release retardation from biocomposite hydrogels, storage of radioactive waste, reinforcement of anti-microbial paper packaging improving its tensile strength, etc. In a recent time, closer attention is also paid to phosphonium-based organic cations that could be used to prepare organoclays with improved properties and higher stability than organoclays prepared with conventional alkylammonium cations [1, 2].

This work reports experimental and modeling study of organoclays prepared from tetra-alkylphosphonium cations and beidellite (Bd). Beidellite is aluminosilicate smectite with predominant cation substitutions in tetrahedral sheet, in contrast to frequently used smectite montmorillonite (Mt), in which octahedral substitutions prevail. This leads to a different charge distribution in layer that can improve a stability of prepared organoclays from beidellite. Tetrabutylphosphonium-beidellite (TBP-Bd) organoclay was synthesized by intercalation of the organic cation into the purified sodium beidellite form and was characterized by X-ray Diffraction (XRD), Differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR) methods. Observed main thermal decomposition peak at 444 °C uncovered the enhanced thermal characteristic of this unique TBP-Bd in comparison to TBP-Mt organoclay. Infrared spectra exhibited typical beidellite vibrations at 417, 474, 534, 1041, and 3658 cm<sup>-1</sup> assigned to the vibrations of beidellite structure whereas the bands at 2962 and 2872 cm<sup>-1</sup> were assigned to the C-H stretching vibrations of the organic cation.

Further, density functional theory (DFT) method was employed to study a stability and detailed structure of beidellite intercalated with tetrabutylphosphonium cation. The eight models with different mutual positions of TBP cation and Al/Si substitution in the tetrahedral sheet were proposed for this study. The calculated intercalation energies showed a much better stability of all TBP-Bd models in comparison to the TBP-Mt model. The lowest calculated intercalation energy of the TBP-Bd (-96.5 kJ/mol) was ~25 % higher (in absolute value) than for the TBP-Mt (-72.2 kJ/mol, [2]). The predicted higher stability of the TBP-Bd organoclays is in accord with experiment.

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# Structural analysis of montmorillonite intercalated with acetylcholine and choline – theoretical study

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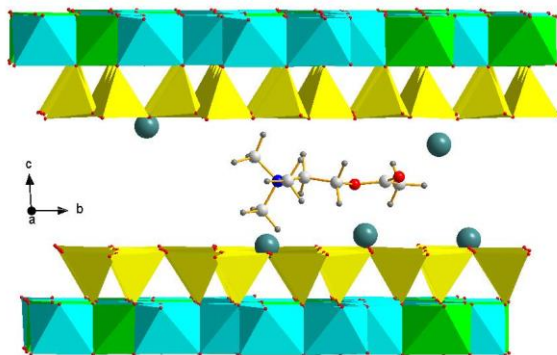
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Keywords: smectite/montmorillonite/DFT

In the last two decades, organoclays intercalated with various organic cations were intensively studied combining theoretical and experimental methods. The representant of smectite family (montmorillonite) is widely used to prepare organoclays because of its excellent properties and various chemical interactions, such as high cation exchange capacity, swelling behavior, adsorption properties, large surface area, hydrogen bonds, ion–dipole interaction, coordination bonds [1]. Montmorillonite is commonly used as a nanofiller in the preparation of polymer nanocomposites. The surface energy of montmorillonite decreases and the basal spacing expands by exchanging of sodium or calcium cations by organic cations [2].

This work is focused on the theoretical study of organoclays based on montmorillonite (Mt) intercalated with acetylcholine (AC) and choline (C) in hydrated (hAC-Mt and hC-Mt) and dehydrated (dAC-Mt and dC-Mt) form, respectively (as example see **Figure 1**). The models of the organoclays were studied by means of the density functional theory (DFT) method. DFT calculations were performed with involving dispersion corrections using a D3 scheme, which was taken as recommended for the PBE functional [3]. The results from calculations were compared with available experimental data.



**Figure 1:** Model of structure of montmorillonite intercalated with acetylcholine.

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## Microbial dissolution of iron surface coatings in industrial minerals

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Keywords: bioleaching | kaolin | bentonite

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Mined industrial minerals are generally not pure, often associated with iron hydroxide and oxy-hydroxide minerals usually in the form of Fe<sup>3+</sup> phases adsorbed onto the particle surface. Iron, the predominant impurity in quartz sands and other industrial minerals as kaolin and bentonite which are widely and extensively used in a different ways. In all cases, the presence of iron affects the colour and the physical properties of the mineral, and lowers the industrial value and limits their application.

The chemical analyses of solid phases showed that the reductive dissolution of iron from the kaolin and bentonite increased due to the heterotrophic bioleaching. The concentration of Fe in the kaolin sample K-I decreased by 2.57% in the sample K-I 15D after 15 days and by 9.29% in the sample K-I 30D after 30 days of bioleaching process and maximal concentration of dissolved iron in leachates was 1482.63 µM. The removal of iron from the second kaolin sample K-R with lower iron content was by 1.51% after 15 days and by 7.54% after 30 days of bioleaching process. The maximal concentration of dissolved iron in K-R sample was 103.9 µM. In the bioleaching process of the bentonite samples, the iron removal was lower from sample B-K with higher iron content. The concentration of iron in sample B-K after 30 days of bioleaching was decreased only by 5.33% and the maximal concentration of iron in leachates was 1451.69 µM. It probably concern with the presence of fungi in sample B-K 30D which can inhibit activity of *Bacillus* spp. in the reductive iron dissolution because loss of Fe in sample B-K15D after 15 days was 4.20%. The bioleaching of sample B-JP with lower iron content showed better iron removal than in case of sample B-K after 30 days of bioleaching process. The concentration of iron was decreased by 7.58% in the sample B-JP 15D and by 12.02% in the sample B-JP 30D, the maximal concentration of dissolved iron was 376.7 µM after 30 days. The concentration of Fe in the quartz sands sample C3 decreased by 15% in the sample C3-15D after 15 days and by 24.7% in the sample C3-30D after 30 days of bioleaching process and maximal concentration of dissolved iron in leachates was 46.95 µM.

Microbiological leaching of industrial minerals is a conversion of undesirable insoluble iron minerals into a soluble form by metabolic activities or products of microorganisms. These microorganisms need carbon as an energy source, using as substrate residues with a high organic carbon content (glucose, molasses, etc.), which involves biological metabolism such as fermentation; the products of organic acids act on the dissolution of insoluble iron oxides which is accelerated by chelation accompanied with iron enzymatic reduction. This process is economically favorable, besides producing effluents which are easy to purify.

This work has involved a fundamental study of the reactions occurring when bioleaching via organic acids are used to dissolve iron from the different non-metallic raw materials, in an attempt to optimize a commercial process.

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## Mineralogical characterisation of Batizovské pleso sediments and surrounding soils (High Tatras, Slovakia)

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*Keywords: High Tatras | mineralogy | tarn sediments*

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The High Tatras (HT) moraine relief shows a glacier stabilization in two phases, at 26-21 ka and at 18 ka [1], followed by a gradual retreat and formation of the morainic, trough and cirque lakes dated from 10 000 to 16000 cal BP on the northern slopes of the Tatra Mountains and before 10000 cal BP on its southern slopes [2]. Sedimentary record of HT mountain lakes contains two distinct lithostratigraphic sections. The uppermost part is formed of the Holocene brown detrital gyttja with high organic matter content which overlays the Late Glacial mineral light-grey silt and fine-sand which suggest deposition under dry and cold periglacial conditions [2].

The contribution intends to present the first results of the mineralogical analysis of the tarn sediments on the Slovak side of the High Tatras and belonging to complex paleolimnological study of High Tatras tarns with aim to determine a timing of the glacier disappearance and amplitude of climatic and ecological changes on the glacial/interglacial boundary (<http://www.geo.sav.sk/en/depovyt-apvv-15-0292/>).

Batizovské pleso (1884 m a.s.l) is a mountain lake (tarn) formed by a glacier. Its sedimentary record have been obtained by using a swimming platform. Drilling site was selected after a lake sonar survey, which provided high resolution 2D acoustic image on sedimentary infill. This allowed a selection of the site with the highest thickness of the sediment. Drilling was realized by steel hydraulic corer allowing to get 2 m long core. Total thickness of lake sediments was more than 3 m. Non-destructive micro-CT analysis was used to determine the internal structure of the sediment in the cores before cutting. The cores were divided to 1 cm thick samples. Part of these samples were analysed by particle size and XRD analysis (bulk and clay fraction).

Upper part of Batizovské pleso sediments is composed by gyttja (postglacial sediment with organic matter). Dominant particle size of this sediment is fraction less than 0.063 mm. 40-80 wt% of amorphous phase was determined in gyttja by XRD. The rest is composed by same minerals as were identified in light grey laminated glacial silt. Analysed silt samples are composed of quartz, albite, K-feldspar, muscovite and clay minerals: illite, smectite, chlorite and kaolinite. Most of this mineral assemblage corresponds to the surrounding rocks (mainly biotite tonalites and granodiorites; [3]). Amount of clay minerals varies from 5 to 25 wt% and is independent on depth. Quantitative changes of mineral composition are explained by different dynamics of sedimentation. XRD analysis of clay fraction confirmed presence of illite, chlorite, kaolinite and smectite. While representation of the first three clay minerals in the studied clay fraction of light grey laminated silt is practically unchanged, amount of smectite is variable, from traces to major phase. Mineral assemblage of clay minerals in surrounding soils are very similar to composition of tarn sediments. A structural ordering, however, is significantly less developed in soils.

### Acknowledgement:

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