

8TH WORKSHOP OF SLOVAK CLAY GROUP



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

Book of abstracts



September 6 – 8, 2021, Habovka, Slovakia



8th Workshop of Slovak Clay Group

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



Book of abstracts

September 6 – 8, 2021, Habovka, Slovakia

ISBN 978-80-972367-5-5

CONTENTS

TERAHERTZ RESPONSE OF Er ³⁺ /Yb ³⁺ CO-DOPED La ₂ Zr ₂ O ₇ CERAMICS	9
M. Janek, R. Klement, M. Naftaly, E. Trusova, P. Veteška, L. Bača	9
MINERALOGICAL AND CHEMICAL COMPOSITION OF MATURE FINE TAILINGS (MFT) FROM ALBERTA, CANADA	11
Y. Bai, M. Osacký, P. Uhlík, H. Pálková, L. Puškelová.....	11
APPLICATION OF ORGANO-MODIFIED LAYERED HYDROSILICATES FOR THE SYNTHESIS OF MATERIALS WITH LUMINESCENT PROPERTIES.....	13
M. Barlog, H. Pálková, J. Bujdák	13
ON THE MECHANISM OF ADSORPTION AND MOLECULAR AGGREGATION OF ORGANIC DYE ON LAYERED SILICATE PARTICLES.....	15
J. Bujdák, and T. Šimonová Baranyaiová	15
LAYERED SILICATES MODIFIED WITH RARE EARTH ELEMENT CATIONS	17
M. Čičkan, M. Janek.....	17
ANTIBIOFILM ACTIVITY OF PHLOXINE B ENTRAPPED ON SAPONITE PARTICLES ON POLYURETHANE SURFACE	19
N.Ch.T. Dadi, J. Bujdák, V. Medvecká, H. Bujdáková.....	19
TAKING A LOOK AT THE INTERACTIONS BETWEEN DIURON AND SMECTITE.....	21
D. Moreno-Rodríguez, L. Jankovič, E. Scholtzová	21
UNUSUAL FLUORESCENCE OF REICHARDT'S DYE IN SAPONITE COLLOIDAL DISPERSIONS.....	23
M. Pribus, T. Šimonová Baranyaiová, L. Jankovič, J. Bujdák.....	23
PHOTOACTIVE SURFACES OF POLYCAPROLACTONE NANOCOMPOSITES WITH SAPONITE AND METHYLENE BLUE.....	25
E. Skoura, P. Boháč, M. Barlog, H. Pálková, J. Bujdák	25
THE IMPACT OF THE ALKYL-AMMONIUM AND -PHOSPHONIUM CATIONS ON THE HYDRATION OF ORGANO-MONTMORILLONITE.....	27
M. Slaný, L. Jankovič, J. Madejová.....	27
REMOVAL OF TOXIC SELENIUM CONCENTRATIONS FROM WATER SOURCES BY MONTMORILLONITE MODIFIED WITH POLYMER MATRIX AND TETRABUTYLPHOSPHONIUM SURFACTANT.....	29
P. Škorňa, S. Bashir, E. Scholtzová, D. Tunega	29
ADSORBENTS OF ORGANIC POLLUTANTS BASED ON ORGANICALLY-MODIFIED HECTORITE-COATED SILICA PARTICLES.....	33
P. Boháč, K. Smutná, S. Vallová, H. Pálková, J. Bujdák	33
ASSAYS USED IN THE EVALUATION OF ANTIMICROBIAL PROPERTIES OF HYBRID MATERIALS	35
H. Bujdáková, B. Radochová, N. Chandra teja Dadi, J. Vargová, M. Štefánek, S. Kendra	35
SILICATES AND DRUG DELIVERY	37
D. Furka, S. Furka, S. Slopovská, V. Heger, J. Sokol, R. Sokol, M. Janek	37
SILICATES IN MODERN MEDICINE.....	39
S. Furka, D. Furka, V. Heger, M. Janek.....	39
INTERCALATION OF THE POLY(2-METHYL-2-OXAZOLINE) INTO MONTMORILLONITE.....	40
J. Madejová, M. Barlog, L. Jankovič, M. Slaný.....	40
STRUCTURAL CHANGES IN MECHANOCHEMICALLY TREATED SMECTITES INVESTIGATED BY INFRARED SPECTROSCOPY.....	42
H. Pálková, M. Barlog, J. Madejová, E. Šimon, M. Zimowska	42
THEORETICAL STUDY OF INTERACTIONS IN THE POLYCATION-MONTMORILLONITE – ADVANCED HYBRID MATERIAL.....	44
E. Scholtzová, S. Bashir	44
BASIC CHARACTERISATION OF SELECTED BENTONITES FROM KREMNICKE VRCHY – PRELIMINARY RESULTS	46

P. Uhlík, Y. Bai, O. Lintnerová, M. Osacký, M. Rybárik	46
SURFACE SEGREGATION OF THE Mg SPECIES AS A RESULT OF CHEMICAL AND HYDROTHERMAL TREATMENT OF THE LAPONITE-BASED NANOCOMPOSITES	48
M. Zimowska, M. Śliwa, R. P. Socha, H. Pálková	48
LIST OF PARTICIPANTS	51

ORAL PRESENTATIONS

TERAHERTZ RESPONSE OF Er³⁺/Yb³⁺ CO-DOPED La₂Zr₂O₇ CERAMICS

M. Janek^{1,2*}, R. Klement³, M. Naftaly⁴, E. Trusova⁵, P. Veteška¹, Ľ. Bača¹

¹ Department of Inorganic Materials, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia

² Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovakia

³ FunGlass - Centre for Functional and Surface Functionalized Glass, Alexander Dubček University of Trenčín, Študentská 2, 911 50 Trenčín, Slovakia

⁴ National Physical Laboratory, Hampton Rd, Teddington, Middlesex, TW11 0LW, UK

⁵ Belarusian State Technological University, Minsk, Belarus

* marian.janek@fns.uniba.sk

KEYWORDS: Lanthanum zirconate ceramics | Dielectric properties | THz-TDS spectroscopy | Far-infrared vibrations

The doping with specific trivalent rare earth (RE) ions promotes materials research thanks to their interesting physical properties including both optical and dielectric response. For example, the optical upconversion processes requires absorption of two or more lower-energy photons leading to the emission of a higher energy photon after energy transfer between RE ions. The upconversion and/or downconversion materials are based on the f-f transitions of rare earth dopants, which show rich luminescence spectra and large number of distinct transition lines. The materials based on lanthanum zirconate (La₂Zr₂O₇) with pyrochlore cubic structure are considered as efficient thermal barrier materials due to their low lattice thermal conductivities. In addition its nanopowders exhibit bright red and moderate green up-conversion luminescence emission under NIR excitation as reported by Gupta et al. [1,2].

The RE cations could be promising model elements for studying their terahertz (THz) response in the different solid-state systems, as the changes in absorption coefficient and refractive index of CaZrO₄ samples doped with Er³⁺/Yb³⁺ cations in the THz range were found [3]. From these reasons the main objective of this study was aimed on effect Er³⁺/Yb³⁺ doping ratio at THz frequencies using Terahertz time-domain spectroscopy (THz-TDS), for systems well described in the literature such as La₂Zr₂O₇ [4]. In addition, the study UV-VIS-NIR absorption was performed complementary to follow the changes in the diffusion reflection spectra of the prepared samples by changing the Er³⁺/Yb³⁺ ratio in the range 0.5 to 5.

Simplified sol-gel co-precipitation procedure followed by calcination method was used for preparation of La₂Zr₂O₇ with pyrochlore structure and doping. The starting solutions used were Ln(NO₃)₃ · xH₂O (Ln = La, Er, Yb) and ZrO(NO₃)₂ · xH₂O. Precipitated gel was filtered, dried at 80 °C, calcined at 800 °C for 4 hours to complete formation of amorphous oxides. For spectral characterization (UV-VIS-NIR diffusion reflection and Terahertz-time domain spectroscopy) discs of about 0.3 mm thickness and 10 mm in diameter were prepared by cold uniaxial pressing at 12.7 MPa. Prepared discs were sintered at 1400 °C for 2 hours using programmable oven with

heating and cooling ramp 10 °C / min. Sintered material was characterised by THz-TDS, X-ray diffraction, Raman and UV-VIS-NIR diffusion reflection spectroscopy.

The refractive indices showed clear wavy behaviour, associated with the refractive index change due to the presence of the absorption band in the investigated window of 0.2–1.5 THz (6.7–50 cm⁻¹). The refractive indices after the porosity correction achieved values in the range of about 4.25–4.75, indicating good dielectric properties of these materials at given frequencies, applicable also as energy storage materials. The frequency dependence of power absorption coefficient α_s of the samples, shows the presence of broad band due to the material phonon broadening in solids at room temperature Figure 1a. The absorption bands integral intensities found correlate reasonably with content of RE cations used for doping Figure 1b. In addition, it was found significant correlation between absorption integral intensities observed in VIS for electron transition $^4I_{15/2} \rightarrow ^2H_{11/2}$ at 520.5 nm (data not shown) and the band found in THz region ($R^2 = 0.911$), despite the signals originate from different phenomena. This behaviour hence proves the origin of THz band dependence on content of RE doping elements in the structure and envisions their detection and investigation also in the other solid-state systems.

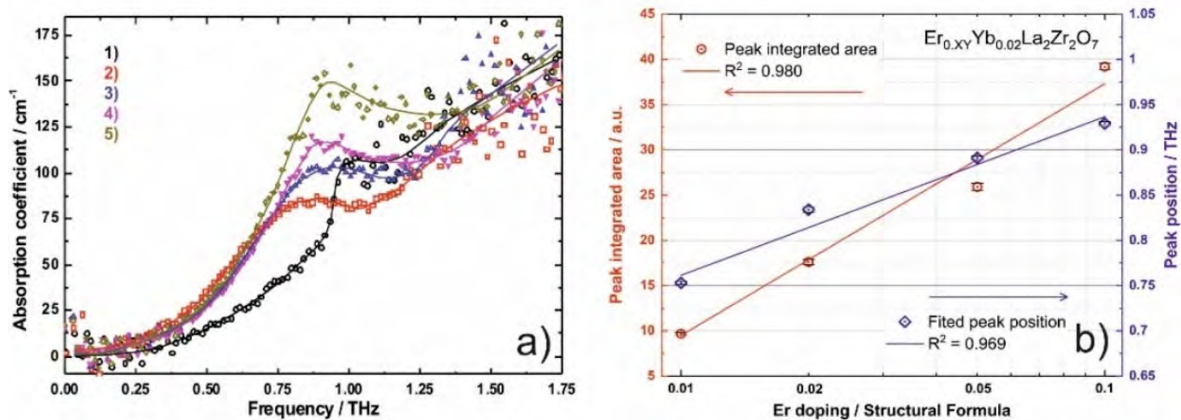


Fig. 1 Frequency dependence of absorption coefficient α_s for a) pure La₂Zr₂O₇ 1) and increasing ratio of Er³⁺/Yb³⁺ while Yb³⁺ was at the level 0.02 per structural formula and Er³⁺ 2) 0.01; 3) 0.02; 4) 0.05; 5) 0.10. Correlations of integrated peak areas and peak position b) found in THz region with increasing ratio of Er³⁺/Yb³⁺ as described above.

Acknowledgment:

The authors acknowledge financial support of Slovak Grant Agency VEGA (grant No. 1/0342/21, 1/0227/20, 1/0527/18) and of the support by the Slovak Research and Development Agency under the Contracts no. APVV-16-0341, APVV-18-0075, PP COVID 20 0025 and project Advancing University Capacity and Competence in Research, Development and Innovation ("ACCORD") ITMS2014+: 313021X329, co-financed by resources of European Regional Development Fund.

References

- [1] S.K. Gupta, M. Abdou, P. Garcia, J.P. Zuniga, M. Abdou, Y. Mao, 2019. Visible and ultraviolet upconversion and near infrared downconversion luminescence from lanthanide doped La₂Zr₂O₇ nanoparticles, *Journal of Luminescence*, 214, 116591-1-116591-8.
- [2] S.K. Gupta, M. Abdou, J.P. Zuniga, P.S. Ghosh, Y. Mao, 2020. Li⁺ co-doping induced phase transition as an efficient strategy to enhance upconversion of La₂Zr₂O₇:Er,Yb nanoparticles. *Journal of Luminescence*, 224, 117312-1-117312-9.
- [3] L. Bača, M. Janek, Z. Kováčová, J. F. Molloy, M. Naftaly, 2015: Dielectric properties of CaZrO₃ investigated by THz-TDS, 40th International Conference on Infrared, Millimeter, and Terahertz waves (IRMMW-THz), Hong Kong, 1–2.
- [4] G. Lan, B. Ouyang, J. Song, 2015. The role of low-lying optical phonons in lattice thermal conductance of rare-earth pyrochlores: A first principle study. *Acta Materialia*, 91, 304–317.

MINERALOGICAL AND CHEMICAL COMPOSITION OF MATURE FINE TAILINGS (MFT) FROM ALBERTA, CANADA

Y. Bai^{1*}, M. Osacký¹, P. Uhlík¹, H. Pálková², L. Puškelová³

¹ Department of Mineralogy, Petrology and Economic Geology, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15, Bratislava, Slovakia

² Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

³ Geological Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 840 05 Bratislava, Slovakia

* bai2@uniba.sk

KEYWORDS: Mature fine tailings | Mineralogy | Chemical composition

The water volatilization and complete solidification of mature fine tailings (MFT) take many years. Investigation of MFT is the key to solve the environmental and reclamation problems faced by oil sands tailings management. In the present research, the mineralogy and chemical composition of different size fractions for MFT solids were systematically characterized by several complementary techniques (X-ray diffraction, Fourier transform infrared spectroscopy, and Thermogravimetric analysis).

The as-received bulk MFT samples contained about 60 wt% of water and 40 wt% of solids. The amount of coarse fractions (>2 µm) and clay fraction (<2 µm) each accounted for about 50 wt% of the total MFT solid mass. The bulk MFT solids consisted mainly of quartz, clay minerals (kaolinite, illite, and illite-smectite), organic matter, and traces of TiO₂ minerals and pyrite. The clay mineral content gradually increased and the quartz content decreased as the size fraction of MFT decreased. The 0.2–2 µm size fractions contained the highest amounts of kaolinite, whereas the <0.2 µm fractions consisted mainly of 2:1 clay minerals (sum of discrete illite and illite-smectite). The 63–250 µm size fractions had the highest quartz content.

The FTIR results were consistent with QXRD. The FTIR bands at 2925 cm⁻¹ were related to stretching vibrations of CH₂ groups, while the bands at 2845 cm⁻¹ indicated stretching vibrations of CH₃ groups. These aliphatic CH groups indicated the presence of residual organic matter (bitumen) in MFT samples.

The weight loss was higher for the clay fractions (0.2–2 µm and <0.2 µm) in comparison with the coarse fractions of MFT. Such observations were consistent with the previously published data and were likely related to the stronger water holding capacity of clay minerals and amorphous Fe oxides which are preferentially accumulated in the clay-sized fraction [1]. DTG results showed that the residual organics displayed features characteristic of asphaltenes (300 ~ 500 °C) [2].

The obtained results may help to better understand the effect of mineralogical and geochemical factors on MFT settling and rheological behaviors, even, they can explain the interactions of the clays-organic matter during bitumen extraction.

Acknowledgment:

The authors gratefully acknowledge financial support from the Slovak Grant Agency (VEGA, projects no. 1/0196/19).

References

- [1] R.N. Yong, A.J. Sethi, 1978. Mineral Particle Interaction Control of Tar Sand Sludge Stability, *Journal of Canadian Petroleum Technology*, 17, 76–83.
- [2] W.I. Friesen, K.H. Michaelian, Y. Long, T. Dabros, 2005. Effect of solvent-to-bitumen ratio on the pyrolysis properties of precipitated Athabasca asphaltenes, *Energy and Fuels*, 19, 1109–1115.

APPLICATION OF ORGANO-MODIFIED LAYERED HYDROSILICATES FOR THE SYNTHESIS OF MATERIALS WITH LUMINESCENT PROPERTIES

M. Barlog^{1*}, H. Pálková¹, J. Bujdák^{1,2}

¹ Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

² Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovakia

* martin.barlog@savba.sk

KEYWORDS: Rhodamine 6G | Luminescence | Smectites | Surfactants

Smectites have been frequently investigated as suitable layered hosts for accommodating of dye molecules. The confinement of laser dye molecules intercalated in smectites and their distribution in interlayer spaces have significant effects on their photophysical properties. The dye molecules had tendency to spontaneously associate into supramolecular systems (aggregates) via electrostatic interactions on the smectite surface influencing thus spectral characteristics. In general, while the presence of monomers, J-dimers or J-aggregates enhance luminescent properties, the formation of H-aggregates often lead to their significant reduction [1]. Various methods have been proposed for suppressing or mediating the formation of dye aggregates, such as the use of cationic alkylammonium surfactants (Surf) or polymers producing hybrid pigments with enhanced luminescent properties [2,3].

The objectives of this work was to study how the extent of the modification with tetraalkylphosphonium and – ammonium surfactants affects the spectral properties, especially the fluorescence activity of R6G intercalated in smectites.

Two types of smectites with different configuration of octahedral sheets and different cation exchange capacities (CEC); montmorillonite (Mt) and saponite (Sap) were modified with the various amounts of organic cationic surfactants tetraoctylphosphonium (TOP⁺) and tetraoctylammonium (TOA⁺) with varying degrees of exchange 25%, 50%, 75%, 100% relative to CEC value of smectite as well as laser rhodamine 6G (R6G) dye in a ratio of 0.001; 0.005; 0.02 and 0.08 mmol·g⁻¹. Luminescent properties were analysed in dependence on various factors: amount of surfactant, dye concentration, type of hydrosilicate by using fluorescence spectroscopy.

The results confirmed that by using a suitable smectite, with a low concentration of dye in combination with a surfactant, an improvement in the luminescent properties was achieved. In samples based on saponite, an order of magnitude higher emission intensity was observed compared to montmorillonite, even without modification by organic cation. On the other hand, montmorillonite had to be modified with a surfactant to prepare a material with luminescent properties (Fig. 1). The fluorescence intensity increased already with the use of the amount of surfactant in the amount of 25% with respect to CEC. Increasing of dye concentration (0.02; 0.08 mmol g⁻¹) had adverse effect on activity as the formation of H-aggregates was more pronounced

for such conditions. By using surfactants for hybrid materials preparation, the amount of H-aggregates was reduced to some extent. The highest luminescence was observed for samples modified with surfactant loading between 50 – 75% CEC and a concentration of rhodamine 6G 0.005 mmol·g⁻¹.

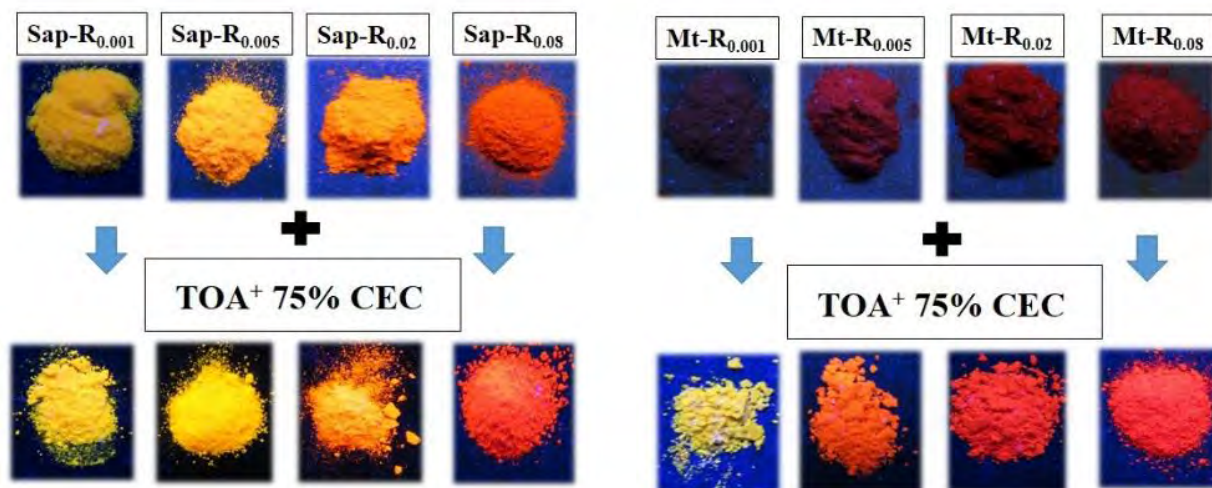


Fig. 1 Hybrid pigments based on saponite (Sap) and montmorillonite (Mt) modified with tetraoctylammonium cations and rhodamine 6G exposed to the light $\lambda = 254$ nm.

Chemometric and statistical analysis of fluorescence spectra were able to identify individual spectral components and evaluate the influence of individual factors on their formation. In addition to monomers, with maximum emission at about 570 nm, J-dimers and aggregates were identified, with emission at higher wavelengths (600–700 nm).

By a suitable choice of parameters, it was possible to prepare pigments that absorbed and emitted light at variable wavelengths. Interesting properties included the emission of light at the edge of the near-infrared region assigned to aggregates, which is an unusual property of this dye. The proportion of the individual spectral forms could be regulated by various factors, the most significant of which were the concentrations of the dye and surfactants. In this work we succeeded in preparation of new, fluorescently active materials (powder pigments) with potential use as fillers in polymer matrices.

Acknowledgment:

This work was supported by the Slovak Research and Development Agency under contracts No. APVV-19-0487, APVV-18-0075. The authors gratefully acknowledge financial support from the Slovak Grant Agency VEGA (project No. 2/0166/21, 2/0227/20).

References

- [1] J. Bujdák, 2017: Hybrids with Functional Dyes. In book: Inorganic Nanosheets and Nanosheet-Based Materials, Springer, 419-465
- [2] R. Sasai, R. Itoh, W. Ohmori, H. Itoh, M. Kusunoki, 2009. Preparation and characterization of rhodamine 6G/Alkyltrimethylammonium/Laponite hybrid solid materials with higher emission quantum yield. The Journal of Physical Chemistry C, 113, 415–421.
- [3] A. Czímerová, Ľ. Jankovič, J. Madejová, A. Čeklovský, 2013. Unique photoactive nanocomposites based on rhodamine 6G/polymer/montmorillonite hybrid systems. Journal of Polymer Science Part B: Polymer Physics, 51, 1672–1679.

ON THE MECHANISM OF ADSORPTION AND MOLECULAR AGGREGATION OF ORGANIC DYE ON LAYERED SILICATE PARTICLES

J. Bujdák^{1,2*}, and T. Šimonová Baranyaiová^{2,3}

¹ Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 842 15 Bratislava, Slovakia

² Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

³ Department of Chemistry, Faculty of Education, J. Selye University, Bratislavská cesta 3322, 945 01 Komárno, Slovakia

* juraj.bujdak@uniba.sk

KEYWORDS: Rhodamine 123 | Diffusion-controlled processes | Non-Arrhenius kinetics | Chemometry

Non-covalent interactions have been studied in chemistry and many other research fields. The objective of this work was to understand more about the mechanism of molecular aggregation of rhodamine 123 (R123) in dispersions of a layered silicate, montmorillonite (Mt). Although molecular aggregation includes neither decomposition nor formation of new covalent bonds, it is a relatively slow process indicating high activation energy [1]. On the other hand, similar processes occurring in homogeneous systems are extremely fast [2]. The reactions in colloids have not been fully understood and this mechanism remains to be explained.

Most of the papers dealing with these processes published so far do not provide sufficient evidence on the mechanism [3]. UV-Vis spectroscopy equipped with a stopped-flow device and diode array detector was used for fast spectra recording. Data processing was applied to separate the effects of light scattering to get a pure signal of light absorption. Chemometric analysis of thousands of recorded spectra eliminated the effect of instrumental noise.

The R123 adsorption on Mt particles is essentially an instantaneous process that is completed in a fraction of a second. Most of the initially adsorbed dye cations were in the form of monomers and the adsorption was followed by the slow process of molecular aggregation. The formation of aggregates logically requires desorption and release of at least a part of initially adsorbed R123 cations. They then migrated to the sites suitable for the formation of aggregates. The chemometric analysis of thousands of spectra identified three main spectral components: Monomers can be considered as reactants present in the systems at the beginning of the reactions. They converted slowly to J-aggregates of an oblique type. H-dimers were also identified as intermediates, but their concentration did not significantly alter during the reaction. The analysis was focused on the formation of J-aggregates.

The aggregation took up to hundreds of seconds. Two parallel reactions were identified and described by the two-phase exponential growth function. The faster process with the rate constant k_{fast} of the order of 10^{-2} s^{-1} was dominant at higher temperatures (T). The slow process had rate constants k_{slow} of an order of magnitude smaller compared to the fast process. Super-Arrhenius kinetics and linear growth of k with T were found for both processes. The Eyring-Polanyi model of the dependence of k on T confirmed a negligible influence of ΔH^\ddagger , and the key importance of entropic factors. ΔS^\ddagger reached similar values for both the processes ($\sim -250 \text{ J K}^{-1} \text{ mol}^{-1}$).

¹) and its negative values were consistent with an association mechanism. The ΔH^\ddagger played the role only at very low temperatures (<293.15 K), contributing to a nonlinear shape of the function at this range and k values close to zero when approaching $T=273.15$ K.

The functional relations of k to T revealed the mechanism based on diffusional processes, but could not provide much information on their identities. Other experiments shed more light on the interpretation of the fast and slow processes. As mentioned, the fast process prevailed at higher temperatures which could activate desorption of R123 cations to leave from the surface of the particle to diffuse to the bulk phase. Higher aggregation rates can be explained in terms of barrier-free diffusion of the dye cations through the bulk liquid phase. The fast process was also significantly suppressed at low silicate concentrations. At low concentrations, the distances between the neighboring particles in the colloids were too large and the probability of an inter-particle diffusion was rather low. Hence, $k_{\text{fast}}=k_{\text{inter-particle}}$.

The slow aggregation process was interpreted as the diffusion of dye cations but remaining on the surface of an individual particle. The lower rate is attributed to the inhibited migration of the adsorbed R123 cations due to the permanent electrostatic forces acting also during the diffusion process between cations and particle surface. These slow processes were unaffected by reducing the particle concentrations, which is another evidence that the diffusion process was limited between the sites of an individual particle.

The slow diffusion of R123 cations to the sites of molecular aggregation characterized by k_{slow} can be understood as the repeating desorption-readsorption process on the surface of an individual particle. The mechanism of repetitive dye desorption and subsequent readsorption can explain a slow character of the on-surface diffusion. It is not much influenced by the bulk concentration of silicate particles.

This is the first study, where both on-surface and inter-particle diffusion processes were clearly identified to occur in parallel [4]. Various factors can play the role in both processes, such as the interactions of dye molecules with present inorganic ions, collisions with water molecules, and even collisions between silicate particles can play a role. Although this study was based on the model system consisting of layered silicate and an organic dye, the knowledge about the mechanism and influence of reaction conditions on individual partial processes can be very important to interpret mechanisms of similar processes of quite different systems, such as adsorption/interaction with biopolymers as proteins, nucleic acids, biomembrane surfaces, cell surfaces, *etc.* The results of this study show the association of molecules is a rather complex phenomenon depending on the mechanism of partial processes and varying with reaction conditions.

Acknowledgment:

This work was supported by the Slovak Research and Development Agency under contract numbers APVV-18-0075, and APVV-19-0487. Supports from the VEGA grant agency (1/0227/20 and 2/0166/21) are also gratefully acknowledged. This publication was produced under the Operational Programme Research and Innovation for the project: "Support of research and development capacities in the area of nanochemical and supramolecular systems", code ITMS2014+ 313011T583, funded from the resources of the European Regional Development Fund.

References

- [1] T. Baranyaiová, J. Bujdák, 2018. Effects of dye surface concentration on the molecular aggregation of xanthene dye in colloidal dispersions of montmorillonite, *Clays and Clay Minerals*, 66, 114–126.
- [2] W. Inaoka, S. Harada, T. Yasunaga, 1980. Kinetic and Spectrophotometric Studies of Rhodamine 6G Dimerization in Aqueous Solution. *Bulletin of the Chemical Society of Japan*, 53, 2120–2122.
- [3] J. Bujdák, 2018. The effects of layered nanoparticles and their properties on the molecular aggregation of organic dyes, *Journal of Photochemistry and Photobiology C*, 35, 108–133.
- [4] T. Šimonová Baranyaiová, R. Mészáros, T. Sebechlebská, J. Bujdák, 2021. Non-Arrhenius kinetics and slowed-diffusion mechanism of molecular aggregation of a rhodamine dye on colloidal particles, *Physical Chemistry Chemical Physics*, 23, 17177–17185.

LAYERED SILICATES MODIFIED WITH RARE EARTH ELEMENT CATIONS

M. Čičkan^{1*}, M. Janek^{1,2}

¹ Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15, Bratislava, Slovakia

² Department of Inorganic Materials, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia

* cickan2@uniba.sk

KEYWORDS: Rare earth elements | Up conversion | Aluminosilicates

Layered aluminosilicates are inorganic materials with a well-defined structure. The basic building block in form of 1 nm thick layers is formed by the two tetrahedron networks that sandwich one octahedron networks. The single layers are separated by interlayer space containing interlayer cations. The presence of cations in the interlayers is required to compensate for the negative charge of the layers arising from the structural aliovalent substitutions [1]. Cations occurring naturally in the interlayer space with the valency $n+$ can be exchanged for other, charge-equivalent cations $m+$ by a cation exchange process at surface (*Surf*) solution (*Solv*) interface, preserving the charge equivalency $a \cdot |n+| = b \cdot |m+|$ e.g. shown in the reaction (1) and the (Fig.1) [2].



The total amount of cations that can be exchanged can be expressed by the cation exchange capacity [CEC] [3].

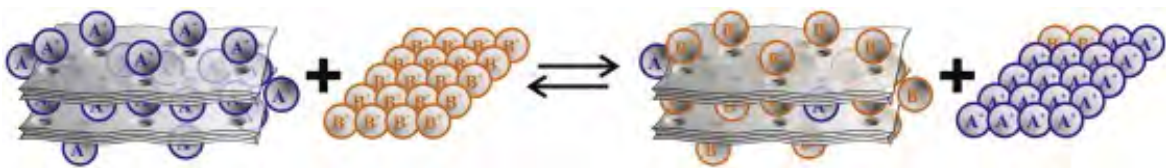


Fig.1 Principle of cation exchange [2].

The analyzed materials used in this work were created by modifying samples of aluminosilicates using trivalent cations of rare earth elements. A key feature of REE is the high density of energy levels of 4f electrons, allowing their excitation/de-excitations transfers and making them known phosphor elements [4]. By modifying the original aluminosilicates using trivalent REE cations, it is possible to obtain new materials with interesting optical and physicochemical properties.

From this material, thin-film plates could be prepared in the future, which would have up or down conversion properties. Up-conversion is a phenomenon in which, the light having less energy (longer wavelength) excites in multiple photon non-radiative energy exchange the electrons of REE element, resulting in the electron transfer from high excited orbital levels to the ground state, accompanied by the emission of photon having higher energy (shorter wavelength) than was used for excitation [5]. Down-conversion is the opposite phenomenon, and thus after the absorption of light radiation by the REE, the electron relaxation results in emission of photon with higher wavelength than used for the excitation, hence the photon energy decreases. The development of efficient up-conversion or down-conversion materials may enhance efficiency of solar panels operation, by the absorption of more energy from environmental radiation. This would have a positive impact on the solar energy production industry. In addition, such materials can be used for preparation of nanoparticles with light-conversion properties, that could be used in medical detection process [6-7].

Prepared materials were at first characterised by spectroscopic techniques such as Fourier-transform Infrared Spectroscopy [FTIR], X-ray powder diffraction [XRPD], thermal analysis [TA], the size of the material shrinkage on the temperature to which the materials were exposed was at the same time monitored, and the energy dispersive spectroscopy [EDX]. The results among original and modified materials were compared to follow the changes induced by REE after cation exchange. The samples modified at elevated temperatures were tested for the change of their optical properties.

Acknowledgment:

This work was supported by the Slovak Research and Development Agency under contract No. APVV-18-0075 and PP COVID 20 0025. Support from the VEGA grant agency 1/0227/20 and 1/0342/21, and grant UK/177/2021 are also gratefully acknowledged.

References

- [1] B. Čičel, I. Novák, I. Horváth, 1981: Mineralógia a kryštalochémia ťvov, 9-65.
- [2] M. Janek, D. Zich, M. Naftaly, 2014. Terahertz time-domain spectroscopy response of amines and amino acids intercalated smectites in far-infrared region, *Materials Chemistry and Physics*, 145 (3), 278-287.
- [3] N. Finck, K. Dardenne, H. Geckeis, 2015. Am(III) coprecipitation with and adsorption on the smectite hectorite, *Chemical Geologist*, 409, 12-19.
- [4] M. P. Bailey, B. F. Rocks, C. Riley, 1984. Terbium chelate for use as a label in fluorescent immunoassays, *Analyst*, 109, 1449-1450.
- [5] D. H. Weingarten, M. D. LaCount, J. Lagemaat, G. Rumbles, M.T. Lusk, S.E. Shaheen, 2017. Experimental demonstration of photon upconversion via cooperative energy pooling, *Nature Communications*, 8, 14808-1-14808-6.
- [6] J. C. G. Bünzli, 2019. Lanthanide photonics: shaping the nanoworld, *Trends in Chemistry*, 1(8), 751-762.
- [7] S. Kwon, H. S. Song, J. Conde, H. I. Kim, N. Artzi, J. H. Kim, 2016. Dual-Color Emissive Upconversion Nanocapsules for Differential Cancer Bioimaging In Vivo, *ACS Nano*, 10, 1512-1521.

ANTIBIOFILM ACTIVITY OF PHLOXINE B ENTRAPPED ON SAPONITE PARTICLES ON POLYURETHANE SURFACE

N.Ch.T. Dadi^{1*}, J. Bujdák^{2,3}, V. Medvecká⁴, H. Bujdáková¹

¹. Department of Microbiology and Virology, Faculty of Natural Sciences, Comenius University in Bratislava, 842 15 Bratislava, Slovakia

². Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, 842 15 Bratislava, Slovakia

³. Department of Inorganic Chemistry, Slovak Academy of Sciences, 845 36 Bratislava, Slovakia

⁴. Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava, 842 48 Bratislava, Slovakia

* d1@uniba.sk

KEYWORDS: Antibiofilm | Polyurethane | Saponite | Phloxine B

Clay minerals possess a wide range of medical applications such a drug delivery, cancer or antimicrobial treatment [1]. Microbial biofilm formed on medical devices is responsible for many nosocomial infections [2]. The excessive usage of antibiotics is no longer a feasible option concerning the development of antimicrobial resistance [3]. Several alternative strategies have been identified for tackling the microbial biofilm, among them, surface modification using clay minerals and photodynamic inactivation (PDI) is a prominent technique [4,5]. In this research, hybrid film based on clay mineral saponite (Sap) with functionalized photosensitizer (PS) phoxine B (PhB) was prepared and tested in prevention/eradication of microbial biofilm of *Staphylococcus aureus* using PDI.

Hybrid film was prepared on polyurethane (Pu) surface. A protocol in brief is summarized in (Fig. 1).

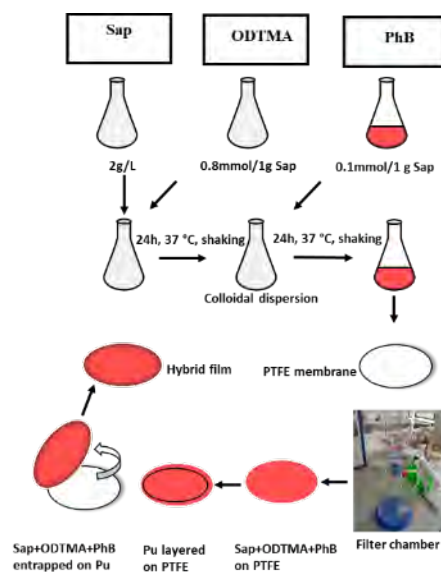


Fig. 1 Schematic diagram of preparation of hybrid film.

Hybrid film was characterized for their hydrophobic nature (water contact angle) and surface free energy (SFE). The WCA of Pu showed around 85° proving its very less hydrophilic nature or almost hydrophobic, whereas OTDMA, PhB and Sap films showed 30°, 40°, and 35°, respectively (high hydrophilic). The SFE of OTDMA and PhB hybrid films and Sap was about 65, 60, and 65 mJ/m², respectively, whereas Pu alone showed 30 mJ/m² (Fig. 2).

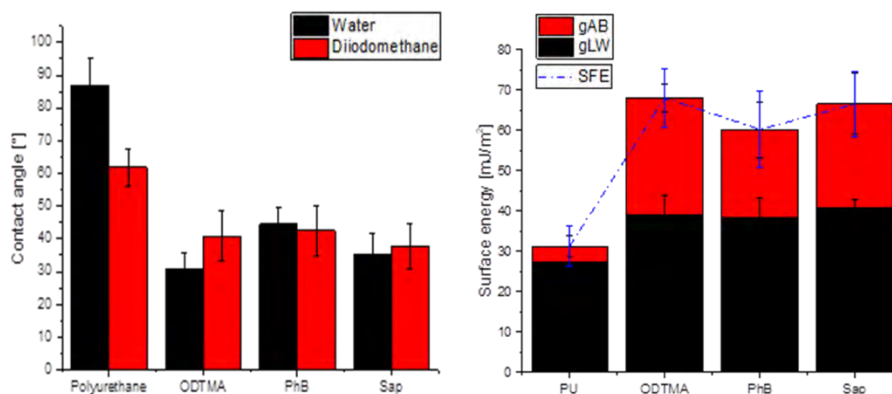


Fig. 2 Water contact angles and surface free energy of tested materials.

Already mentioned material was tested for antibiofilm properties. The PDI displayed reduction in survival of bacterial biofilms formed by standard strain of *S. aureus* and methicillin-resistant *S. aureus* from 4-log₁₀ to 3-log₁₀, when irradiated with green laser for 120 s compared to the control samples formed on Pu alone. Tested materials were assessed for antimicrobial effectiveness in the dark as well. It was surprising that Sap modified with OTDMA as well as hybrid film with PhB showed reduction from 3log₁₀ to 2log₁₀. This could be because of less hydrophilic nature of those material that probably prevent an attachment of bacteria.

Presented results showed that the surface properties of materials are crucial for antimicrobial effectiveness. Moreover, if nanomaterial contains PS, the antimicrobial effect is potentiated after PDI. Material such as hybrid film based on clay mineral particles with functionalized PS could be an excellent alternative with a potential of application in healthcare-associated infections.

Acknowledgment:

This research was supported by Slovak Grant Agency under the contract no. APVV-18-0075 and APVV-15-0347; Ministry of Education, Science, Research and Sport of the Slovak Republic under the contract no. VEGA 1/0227/20 and VEGA 1/0537/19.

References

- [1] R.B. Finkelman, R.B. 2019. The Influence of Clays on Human Health: A Medical Geology Perspective. *Clays and Clay Minerals*, 67, 1–6.
- [2] D. Koulenti, E. Tsigou, J. Rello, 2017. Nosocomial Pneumonia in 27 ICUs in Europe: Perspectives from the EU-VAP/CAP Study. *European Journal of Clinical Microbiology & Infectious Diseases*, 36, 1999–2006.
- [3] A. Bassegoda, K. Ivanova, E. Ramon, T. Tzanov, 2018. Strategies to Prevent the Occurrence of Resistance against Antibiotics by Using Advanced Materials. *Applied Microbiology and Biotechnology*, 102, 2075–2089.
- [4] C.S.A. Caires, C.M. Silva, A.R. Lima, L.M. Alves, T.H.N. Lima, A.C.S. Rodrigues, M.R. Chang, S.L. Oliveira, C. Whitby, V.A. Nascimento et al. 2020. Photodynamic Inactivation of Methicillin-Resistant *Staphylococcus Aureus* by a Natural Food Colorant (E-141ii). *Molecules*, 25, 4464-1-4454-11.
- [5] C. Adhart, J. Verran, N.F. Azevedo, H. Olmez, M.M. Keinänen-Toivola, I. Gouveia, L.F. Melo, F. Crijns, 2018. Surface Modifications for Antimicrobial Effects in the Healthcare Setting: A Critical Overview. *Journal of Hospital Infection*, 99, 239–249.

TAKING A LOOK AT THE INTERACTIONS BETWEEN DIURON AND SMECTITE

D. Moreno-Rodríguez^{1*}, Ľ. Jankovič¹, E. Scholtzová¹

¹ Institute of Inorganic Chemistry, Slovak Academy of Science, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

* daniel.moreno@savba.sk

KEYWORDS: Hydrogen-bonding | Diuron | Density functional theory | Smectites

Diuron (D) is a systemic broad-spectrum herbicide belonging to phenylurea herbicides (PUHs) having a hazardous effect in plants and animals [1]. Clay minerals, like smectites e.g., beidellite (Bd) and montmorillonite (Mt), being natural components of soils, are an interesting option to immobilize organic contaminants, improved by modifying the clay with organic surfactants (organoclays) [2].

To study the structural stability of the complexes, the density functional theory (DFT) method was used with DFT-D3 scheme [3] and the PBE functional [4]. The DDEC6 [5] method described the partial charges and bond order (BOs), that in conjunction with the atoms-in-molecules partitioning approach, the electron localization function (ELF) [6], provided a detailed view of the ρ in the diuron-smectite complexes. Four models were proposed: the Na-Bd/Mt with six $[\text{Na}(\text{H}_2\text{O})_4]^+$ with an intercalated diuron molecule forming the D-Bd and D-Mt complexes. Later, the Na-Bd/Mt were modified by the organic surfactant, tetramethylphosphonium cation (TMP) replacing one $[\text{Na}(\text{H}_2\text{O})_4]^+$ yielding the organoclays (D-TMP-Bd and D-TMP-Mt complexes).

The electron density mapping of the basal oxygens' surfaces (O_b) in the Bd displayed a better availability to form hydrogen bonds (H-bonds) than Mt's surfaces, even better using the TMP cation as a surfactant. The interactions among the diuron molecule and O_b were more dispersive in the chloro-phenyl fragment and the more electrostatic (forming more H-bonds) in the methyl groups of diuron molecule (Fig. 1).

Diuron showed better structural stability in both modified clays and particularly in the Bd structure, D-TMP-Bd ($-258.53 \text{ kJ mol}^{-1}$) and D-Bd ($-118.68 \text{ kJ mol}^{-1}$) versus D-TMP-Mt ($-204.22 \text{ kJ mol}^{-1}$), and D-Mt ($-107.79 \text{ kJ mol}^{-1}$) being in correlation with the strength of the H-bonds.

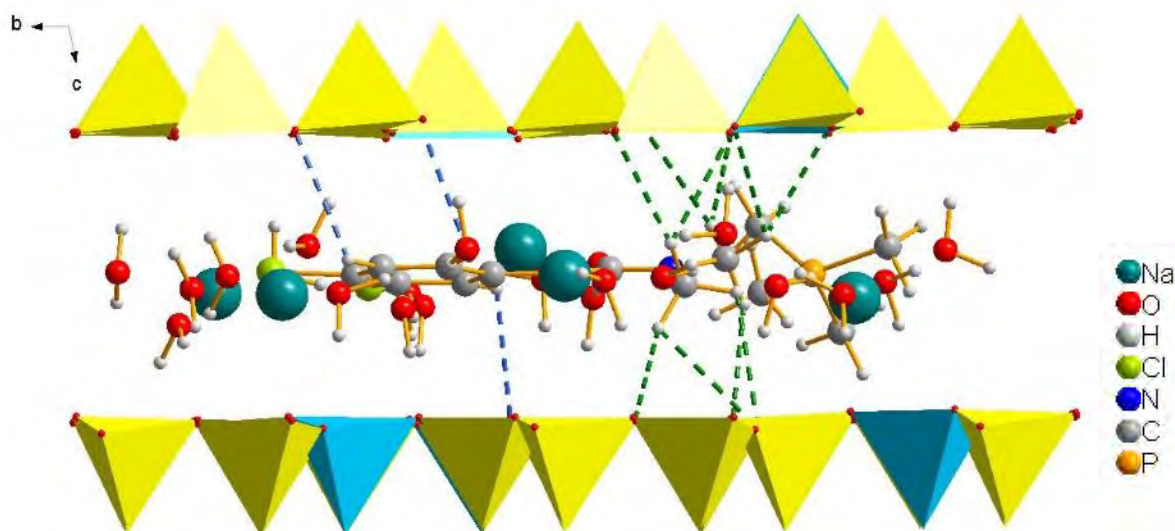


Fig. 1 The $C_D-H \cdots O_b$ H-bonds formed among the chloro-phenyl fragment and O_b basal oxygens (blue) and among the urea fragment and the O_b basal oxygens (green) in the D-TMP-Bd model.

Acknowledgments:

D. M-R., Ľ. J. and E. S. are grateful for the financial support by the Scientific Grant Agency (project No. VEGA 02/0021/19) and Slovak Research and Development Agency (project Nos. APVV-18-0075 and APVV-19-0487).

References

- [1] S. Giacomazzi, N. Cochet, 2004. Environmental impact of diuron transformation: a review. *Chemosphere*, 56, 1021–1032.
- [2] E. Grundgeiger, Y.H. Lim, R.L. Frost, G.A. Ayoko, Y. Xi, 2015. Application of organo-beidellites for the adsorption of atrazine. *Applied Clay Science*, 105–106, 252–258.
- [3] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, 2010. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *The Journal of Chemical Physics*, 132, 154104-1-154104-19.
- [4] J.P. Perdew, K. Burke, Y. Wang, 1996. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Physical Review B*, 54, 16533–16539.
- [5] T.A. Manz, N.G. Limas, 2016. Introducing DDEC6 atomic population analysis: Part 1. Charge partitioning theory and methodology. *RSC Advances*, 6, 47771–47801.
- [6] A.D. Becke, K.E. Edgecombe, 1990. A simple measure of electron localization in atomic and molecular systems. *The Journal of Chemical Physics*, 92, 5397–5403

UNUSUAL FLUORESCENCE OF REICHARDT'S DYE IN SAPONITE COLLOIDAL DISPERSIONS

M. Pribus^{1*}, T. Šimonová Baranyaiová^{1,2}, Ľ. Jankovič¹, J. Bujdák^{1,3}

¹ Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

² Department of Chemistry, Faculty of Education, J. Selye University, Bratislavská cesta 3322, 945 01 Komárno, Slovakia

³ Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovakia

* marek.pribus@savba.sk

KEYWORDS: Reichardt's Dye | Poly(diallyldimethylammonium chloride) | Saponite | Spectroscopy

Reichardt's dye (RD) is an organic dye notable for its solvatochromic properties. Solvatochromism is the phenomenon when changing the polarity of the medium causes a pronounced change in the position of a UV-Vis absorption band of the dye [1]. It can be visually observed as a change of color. RD belonging to the class of azomero-cyanine betaines has one of the largest solvatochromic effects ever observed [2], with the color varying across the entire visible spectrum [3]. Due to RD's solvatochromic properties, this compound is useful as a solvent polarity indicator. The structure of the RD molecule is shown in Fig. 1.

Sumecton is a commercial product of synthetic saponite (Sap) with the structural formula $(\text{Na}_{0.49}\text{Mg}_{0.14})^{+0.77}[(\text{Si}_{7.20}\text{Al}_{0.80})(\text{Mg}_{5.97}\text{Al}_{0.03})\text{O}_{20}(\text{OH})_4]^{-0.77}$ [4] and the cation-exchange capacity of $0.87 \pm 0.05 \text{ mmol}\cdot\text{g}^{-1}$ [5]. Saponite is a trioctahedral phyllosilicate belonging to the smectite group of clay minerals. It was used as a nanoparticle substrate for RD adsorption. Organic water-soluble polyelectrolyte – poly(diallyldimethylammonium chloride) (PDDAC) was used to modify the Sap surface. The modified particles exhibit some exceptional properties with respect to the interaction with organic dyes. The presence of polycations of different types can lead to either a partial change or complete reversal of the surface charge of silicate particles, which in some cases improved the adsorption of anionic dyes with respect to non-modified silicates [6]. Layered silicates in combination with polyelectrolytes and dyes have often been used in the synthesis of functional thin films exhibiting enhanced photoactivity [7, 8].

The first step of the sample preparation was the modification of the Sap surface with PDDAC macromolecules with an mass average molar mass of $200,000 - 350,000 \text{ g}\cdot\text{mol}^{-1}$. The final Sap concentration of in studied colloid systems was $0.1 \text{ g}\cdot\text{dm}^{-3}$. We studied two types of the systems – in the first case, samples had the same concentration of Sap ($0.1 \text{ g}\cdot\text{dm}^{-3}$) and loading of PDDAC ($0.5 \cdot \text{mmol g}^{-1}$), and the loading of RD was changed from $2.5 \cdot 10^{-3}$ to $0.25 \text{ mmol}\cdot\text{g}^{-1}$. In the second case, the samples had the constant concentration of Sap ($0.1 \text{ g}\cdot\text{dm}^{-3}$) and RD loading. In this case, the loading of PDDAC was changed (from 0.1 to $1.5 \text{ mmol}\cdot\text{g}^{-1}$).

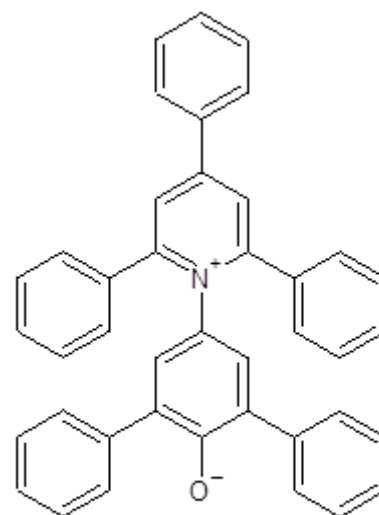


Fig. 1 Structural formula of Reichardt's dye.

The UV-Vis spectra of RD adsorbed on the organically modified Sap were similar to that of the dye solution. The absorbance maximum of the dye aqueous solution containing 2.5 vol. % ethanol (RD_{aq}) was at 305 nm. Upon the adsorption of RD on organoclay particles, the absorbance maximum shifted to 316 nm. Neither an RD ethanolic solution nor RD_{aq} exhibited any fluorescence. However, when the dye was adsorbed on the organoclay particles, a broad fluorescent band with the maximum at 500 nm was observed (the excitation wavelength was 330 nm) (Fig. 2). The luminescence was confirmed by the excitation spectrum with a profile similar to that of the absorption spectrum (Fig. 2). Luminescence of adsorbed RD molecules may bring new applications of this solvatochromic dye.

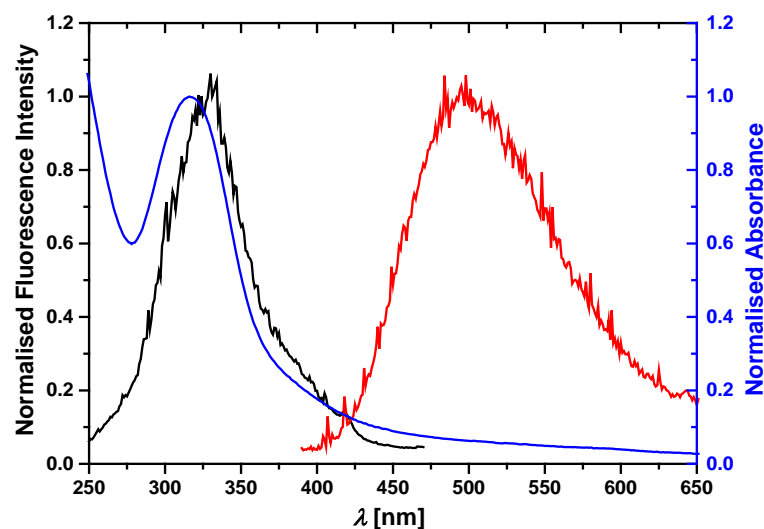


Fig. 2 Normalised excitation (black), emission (red) and absorption (blue) spectra of RD adsorbed on particles of Sap modified with PDDAC.

Acknowledgment:

This work was supported by the Slovak Research and Development Agency under contract numbers APVV-18-0075, and APVV-19-0487. Supports from the VEGA grant agency (1/0227/20 and 2/0166/21) are also gratefully acknowledged.

References

- [1] C. Reichardt, T. Welton, 2010: Solvents and solvent effects in organic chemistry (4th, updated and enl. ed.). Weinheim, Germany: Wiley-VCH. p. 360.
- [2] B. R. Osterby, R. D. McKelvey, 1996. Convergent Synthesis of Betaine-30, a Solvatochromic Dye: An Advanced Undergraduate Project and Demonstration, *Journal of Chemical Education*, 73, 260 – 261.
- [3] V. G. Machado, C. Machado, 2001. An Easy and Versatile Experiment to Demonstrate Solvent Polarity Using Solvatochromic Dyes, *Journal of Chemical Education*, 78, 649 – 651.
- [4] L. A. Utracki, M. Sepehr, E. Boccaleri, 2007. Synthetic, layered nanoparticles for polymeric nanocomposites (PNCs), *Polymers for Advanced Technologies*, 18, 1 – 37.
- [5] A. Czímerová, N. Iyi, J. Bujdák, 2007. Energy transfer between rhodamine 3B and oxazine 4 in synthetic saponite dispersions and films, *Journal of Colloid and Interface Science*, 306, 316 – 322.
- [6] H. Hata, Y. Kobayashi, T. E. Mallouk, 2007. Encapsulation of Anionic Dye Molecules by a Swelling Fluoromica through Intercalation of Cationic Polyelectrolytes, *Chem. Mater.*, 19, 79 – 87.
- [7] B. Van Duffel, T. Verbiest, S. Van Elshocht, A. Persoons, F. C. De Schryver, R. A. Schoonheydt, 2001. Fuzzy Assembly and Second Harmonic Generation of Clay/Polymer/Dye Monolayer Films, *Langmuir*, 17, 1243 – 1249.
- [8] J. Bujdák, 2014. Layer-by-Layer Assemblies Composed of Polycationic Electrolyte, Organic Dyes, and Layered Silicates, *The Journal of Physical Chemistry C*, 118, 7152 – 7162.

PHOTOACTIVE SURFACES OF POLYCAPROLACTONE NANOCOMPOSITES WITH SAPONITE AND METHYLENE BLUE

E. Skoura^{1*}, P. Boháč^{1,2}, M. Barlog¹, H. Pálková¹, J. Bujdák^{1,3}

¹ Institute of Inorganic chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36, Bratislava, Slovakia

² Centre of Excellence for Advanced Materials Application (CEMEA), Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovakia

³ Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, 842 15 Bratislava, Slovakia

* eva.skoura@savba.sk

KEYWORDS: Smectite | Organic dye | PCL nanocomposite | Photosensitizer

Clay/Polymer nanocomposites have been developed since 1980. Perfect candidates for being an inorganic filler are synthetic or natural layered silicates, such as smectites belonging to the expandable phyllosilicate family. The layered structure in combination with their chemical and physical properties makes them a suitable host material for many different molecules intercalated in the interlayer spaces, modifying their structure and properties [1]. The introduction of organic dyes into organoclays and further incorporation into the polymers can form nanocomposites promoting antimicrobial and optical properties, in particular fluorescence. There is a large list of dye molecules that have been used including methylene blue, cyanine, and rhodamine dyes. Particularly enhanced antimicrobial properties were observed in the case of hybrid materials with methylene blue [2].

In this work, the surface of polycaprolactone (PCL), a semi-crystal polymer, was modified by layered nanoparticles. An organoclay based on saponite (Sap) was firstly modified with a cationic surfactant hexadecyltrimethylammonium bromide (HDTMA) and subsequently functionalized with the cationic dye, methylene blue (MB). The intercalation of MB molecules into a clay mineral requires full delamination of the layers to increase the access to the surface and adsorption capacity of the inorganic host [3].

The activity of the nanoparticles is the key factor for the surface properties of the polymers for the nanocomposite to achieve the desired properties to get an active and antibacterial surface with MB to enable prospective applications of modified polymer surfaces to adopt photosensitizing and photoluminescent properties.

Saponite (Sap) was modified with hexadecyltrimethylammonium (HDTMA) cations. Subsequently, the organoclay was functionalized with ten different concentrations of methylene blue (MB1-MB10). The suspensions of Sap/HDTMA/MB were filtered through Teflon membranes to prepare thin films. The synthesis of nanocomposites with PCL with the functionalized organoclays was performed via melt diffusion at the interface of the film and the polymer.

The fluorescence spectra (Fig. 1a) 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. The presence of H-aggregates led to the quenching of fluorescence and to the shift of maximal emission to partially higher wavelengths.

Fluorescence was quenched completely for the samples of the highest MB concentrations (MB9 and MB10).

The XRD diffraction patterns of PCL nanocomposites (Fig. 1b) show that in the samples of PCL_Sap/HDTMA and PCL_Sap/HDTMA/MB10, the appearance of the characteristic peak of saponite at 6.2° (d -spacing = 1.47 nm) and 6° (d -spacing = 1.52 nm) indicates the presence of Sap/HDTMA and Sap/HDTMA/MB10 respectively, in the surface of PCL. The crystalline phase of PCL can be detected between the 2θ angles around 15° to 30° .

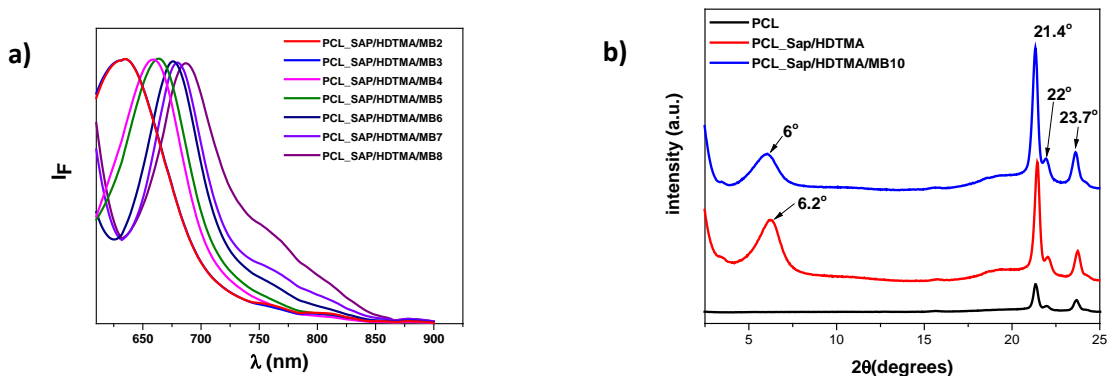


Fig. 1 Fluorescence spectra (a) and XRD diffraction patterns (b) of PCL nanocomposites.

Some of the prepared specimens exhibited high photoactivity. The optical properties and photoactivity of the dye reflected the concentration of the dye in the materials. The samples with a higher concentration of methylene blue exhibited a higher tendency to form H-aggregates which led to the quenching of luminescence. In the samples of lower concentrations of methylene blue, the formation of monomers is more likely to occur. The crystallinity of the PCL phase in the nanocomposites samples didn't alter after the modification. The samples with a high concentration of MB show antimicrobial activity against the strain of *S aureus* CCM 3953.

Acknowledgment:

This work was supported by the Slovak Research and Development Agency under contracts No. APVV-19-0487, APVV-18-0075. Supports from the VEGA grant agency (1/0227/20, 2/0166/21) are also gratefully acknowledged.

References

- [1] F. Wypych, F. Bergaya, R.A. Schoonheydt, 2018: From polymers to clay polymer nanocomposites, in *Developments in Clay Science*, Elsevier. 331-359.
- [2] J. Bujdák, J. Jurečková, H. Bujdáková, K. Lang, F. Šeršen, 2009. Clay Mineral Particles As Efficient Carriers of Methylene Blue Used for Antimicrobial Treatment, *Environmental Science & Technology*, 43(16), 6202 - 6207.
- [3] J. Bujdák, N. Iyi, T. Fujita, 2002. The aggregation of methylene blue in montmorillonite dispersions, *Clay Minerals*, 37(1), 121-133.

THE IMPACT OF THE ALKYL-AMMONIUM AND -PHOSPHONIUM CATIONS ON THE HYDRATION OF ORGANO-MONTMORILLONITE

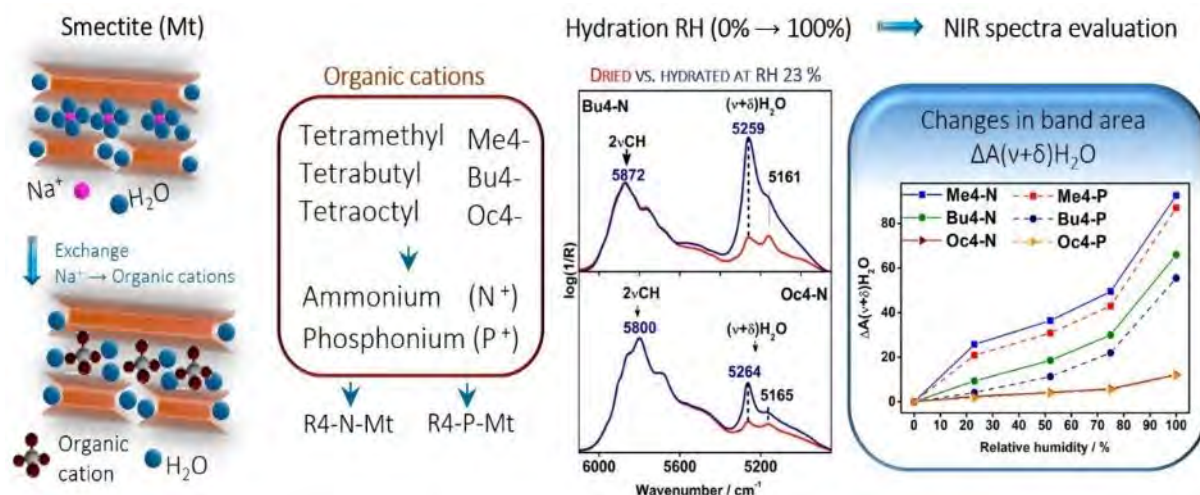
M. Slaný^{1*}, Ľ. Jankovič¹, J. Madejová¹

¹ Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

* michal.slany@savba.sk

KEYWORDS: Organo-montmorillonite | Alkyl-ammonium/phosphonium cations | Hydration | Near-infrared spectroscopy

Organo-montmorillonites (O-Mts) are attractive hybrid materials used in numerous industrial applications. In this work the adsorption of water molecules on montmorillonite saturated with alkylammonium and alkylphosphonium cations, tetramethyl-(Me₄-N/P⁺), tetrabutyl-(Bu₄-N/P⁺) and tetraoctyl-(Oc₄-N/P⁺) was studied. The effect of the organic cation size and predominantly type of the central atom of the organic cation head-group (N vs P) was followed at different relative humidities (RH). The samples were characterized using carbon analysis, N₂ adsorption, X-ray diffraction analysis, and infrared spectroscopy in the middle (MIR) and near (NIR) regions. Gravimetric analysis and NIR spectroscopy were used to monitor the hydration of the O-Mts. A gradual shift of the combination band of water molecules (ν+δ)H₂O to the lower wavenumbers with increasing amount of adsorbed water indicated a grow of the H₂O molecules involved in stronger hydrogen bonds. A shift of the 2νCH₃ band to higher wavenumbers with increasing RH, observed for Me₄-N/P-Mts and Bu₄-N-Mt, provided the evidence that water molecules interacted directly with methyl groups of the Me₄-N/P⁺ and Bu₄-N⁺ cations. Gravimetric and NIR analysis confirmed that at each RH the content of adsorbed water decreased in the direction Me₄-N/P-Mts ⇒ Bu₄-N/P-Mts ⇒ Oc₄-N/P-Mts due to the increasing hydrophobicity of the organic cations. Moreover, a higher hydrophobicity of O-Mts saturated with alkylphosphonium cations compared to their alkylammonium counterparts was found.



Acknowledgments:

The authors acknowledge the financial support of this research by the Slovak Grant Agency VEGA (Grant 2/0166/21) and the Slovak Research and Development Agency (APVV-19-0487 and APVV-18-0075).

References

- [1] J. Madejová, M. Barlog, Ľ. Jankovič, M. Slaný, H. Pálková, 2021. Comparative study of alkylammonium- and alkylphosphonium-based analogues of organo-montmorillonites. *Applied Clay Science*, 200, 105894-1-105894-10.
- [2] M. Slaný, Ľ. Jankovič, J. Madejová, 2019. Structural characterization of organo- montmorillonites prepared from a series of primary alkylamines salts: mid-IR and near-IR study. *Applied Clay Science*, 176, 11–20.
- [3] J. Madejová, Ľ. Sekeráková, V. Bizovská, M. Slaný, Ľ. Jankovič, 2016. Near-infrared spectroscopy as an effective tool for monitoring the conformation of alkylammonium surfactants in montmorillonite interlayers. *Vibrational Spectroscopy*, 84, 44–52.

REMOVAL OF TOXIC SELENIUM CONCENTRATIONS FROM WATER SOURCES BY MONTMORILLONITE MODIFIED WITH POLYMER MATRIX AND TETRABUTYLPHOSPHONIUM SURFACTANT

P. Škorňa^{1*}, S. Bashir¹, E. Scholtzová¹, D. Tunega^{2,3}

- ¹. Institute of Inorganic chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia
- ². Universität für Bodenkultur, Institut für Bodenforschung, Peter-Jordan-Strasse 82, A-1190 Wien, Austria
- ³. School of Pharmaceutical Science and Technology, Tianjin University, 300072 Tianjin, People's Republic of China

*peter.skorna@savba.sk

KEYWORDS: Selenium | Montmorillonite | DFT-D3 | Polymer

Selenium (Se) is a natural trace element found in bedrock, but it is also introduced into the environment by anthropogenic activities, such as mining and combustion of fossil fuels [1]. Therefore, water and soil contamination by selenium compounds has become a significant environmental problem all over the world [2]. In addition, the nuclear industry is another relatively large producer of radioactive selenium [2, 3]. Selenium is also naturally occurred in water, soils and living organisms, including foods. It forms an important part of nutrition as several Se-bearing proteins incorporate selenocysteine, recently known as the 21st essential amino acid [4]. The determination of the limit between toxicity and deficiency of selenium is one of the most important scientific challenges because it has very narrow margin between nutritionally optimal and potentially toxic dietary exposures for humans [5]. Selenium has also a wide range application in the industry such as the manufacture of ceramics, glass, photoelectric cells, pigments, rectifiers, semiconductors and steel, as well as the use in photography, pharmaceutical production and rubber vulcanizing [6].

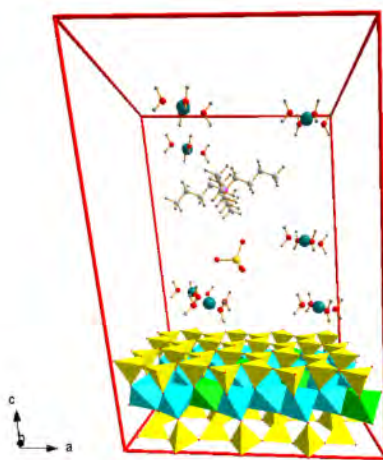


Fig. 1 Initial structural model of Se-TBP-Mt (3D), as an example.

Under aerobic conditions, the main forms of selenium are soluble oxyanions such as selenate (SeO_4^{2-}). Selenate is the dominant species of selenium in natural environments and its accumulation in soils and waters can threaten the health of humans [7]. Therefore, for the wide scientific community, it is very important to find the correct and low cost way for the removing of selenium pollutants from the environment. There are many techniques for removing of toxic selenate from water sources and soils, such as precipitation with ferrihydrite, membrane filtration, microbial reduction, anion exchange and adsorption [8].

The polymer-clay nanocomposites are materials of increasing interest of various scientific groups because of their excellent structural and functional behavior. Polyethyleneimine (PEI) is a typical polymeric amine and can exist as a linear and a branched structure. PEI has a different fields of application, e.g. as a chelating agent for metal ions, in waste water treatment, or as flocculation aid in the pulp and paper industry [9, 10].

This work introduces the study of the adsorption of toxic selenium oxyanions, specifically selenate (SeO_4^{2-}) anion, into the interlayer space of montmorillonite clay mineral intercalated by polymer matrix and tetrabutylphosphonium (TBP) surfactant. The main aim of this work is to provide detailed information about the structure of calculated models (Fig. 1). For the determination of the stability of individual systems, the strength and number of hydrogen bond interactions in combination with the calculated intercalation energies are analyzed. The vibrational modes obtained from the calculated spectra using the *ab initio* molecular dynamics (AIMD) approach are analyzed and compared with experimental FTIR spectra available from literature.

Acknowledgments:

Authors are grateful for the financial support by the Scientific Grant Agency VEGA (02/0021/19) and the Slovak Research and Development Agency (APVV-19-0487, APVV-18-0075). Part of the calculations are performed in the Computing Centre of the Slovak Academy of Sciences using the supercomputing infrastructure acquired in projects ITMS 26230120002 and 26210120002 (Slovak infrastructure for high-performance computing) supported by the Research & Development Operational Programme funded by the ERDF.

References

- [1] D. Peak, U.K. Saha, P.M. Huang, 2006. Selenite adsorption mechanisms on pure and coated montmorillonite: An EXAFS and XANES spectroscopic study, *Soil Science Society of America Journal*, 70, 192–203.
- [2] J.T. Olegario, N. Yee, M. Miller, J. Sczepaniak, B. Manning, 2010. Reduction of Se(VI) to Se(-II) by zerovalent iron nanoparticle suspensions, *Journal of Nanoparticle Research*, 12, 2057–2068.
- [3] B.D. Gibson, D.W. Blowes, M.B.J. Lindsay, C.J. Ptacek, 2012. Mechanistic investigations of Se(VI) treatment in anoxic groundwater using granular iron and organic carbon: An EXAFS study, *Journal of Hazardous Materials*, 241, 92–100.
- [4] L.S. Charya, 2017: Selenium Pollution in the Marine Environment and Marine Bacteria in Selenium Bioremediation, in: Naik, M.M., Dubey, S.K. (Eds.), *Marine Pollution and Microbial Remediation*. Springer Singapore, Singapore, 223–237.
- [5] Y.T. Chan, W.H. Kuan, T.Y. Chen, M.K. Wang, 2009. Adsorption mechanism of selenate and selenite on the binary oxide systems, *Water Research*, 43, 4412–4420.
- [6] D.G. Barceloux, 1999. Selenium, *Journal of Toxicology: Clinical Toxicology*, 37, 145–172.
- [7] T. Beauwens, P. De Canniere, H. Moors, L. Wang, N. Maes, 2005. Studying the migration behaviour of selenate in Boom Clay by electromigration, *Engineering Geology*, 77, 285–293.
- [8] N. Bleiman, Y.G. Mishaal, 2010. Selenium removal from drinking water by adsorption to chitosan–clay composites and oxides: Batch and columns tests, *Journal of Hazardous Materials*, 183, 590–595.
- [9] S. Deng, Y.-P. Ting, 2005. Characterization of PEI-modified biomass and biosorption of Cu(II), Pb(II) and Ni(II), *Water Research*, 39, 2167–2177.
- [10] I. Larraza, M. López-González, T. Corrales, G. Marcelo, 2012. Hybrid materials: Magnetite–Polyethylenimine–Montmorillonite, as magnetic adsorbents for Cr(VI) water treatment, *Journal of Colloid and Interface Science*, 385, 24–33.

POSTER PRESENTATIONS

ADSORBENTS OF ORGANIC POLLUTANTS BASED ON ORGANICALLY-MODIFIED HECTORITE-COATED SILICA PARTICLES

P. Boháč^{1,2,*}, K. Smutná³, S. Vallová^{3,4}, H. Pálková¹, J. Bujdák^{1,5}

¹. Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

². Centre of Excellence for Advanced Materials Application (CEMEA), Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovakia

³. Institute of Environmental Technology, VSB - Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic

⁴. Department of Chemistry, Faculty of Materials Science and Technology, VSB - Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic

⁵. Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, 842 15 Bratislava, Slovak Republic

* peter.bohac@savba.sk

KEYWORDS: Adsorption | Organic pollution | Organo-clay | Clay mineral synthesis

Contamination of the environment with various chemical substances is a serious environmental concern and represents one of the biggest challenges of the 21 century. The number of organic contaminants, including pharmaceutical and personal care products, pesticides, herbicides, dyes, and plastics and their additives, constantly increase and, due to their toxicity, endanger ecosystems as well as human health. One of the traditional methods of removing organic compounds from the water ecosystems is the adsorption using suitable adsorbent materials. Nanoarchitectonics of hybrid materials is an important concept, which allowed the preparation of novel materials with high-performance selective adsorption properties. Clay minerals are traditionally considered as a suitable building block due to their chemical and physical properties, layered structure, swelling properties, low cost, and wide variability. Clay minerals can be modified by various inorganic or organic modifiers to achieve the required properties. One of the traditional methods is a modification by amphiphilic compounds to achieved hydrophobic properties of materials. Such hydrophobic species have the ability to absorb and concentrate negatively charged organic compounds or compounds with poor polarity [1,2].

The disadvantage of using clay minerals and their hybrid materials in environmental technologies is the difficulty of the manipulation. In addition, the layered structure of the clay nanosheets and the formation of the gels in a higher concentration of suspensions complicates the use of clay mineral particles in the adsorption columns and complicated sedimentation and filtration process of dispersions during the various processes.

The goal of the presented work was to prepare the material with the high-performance adsorption properties of clay minerals, which will be easy to manipulate with. For this purpose, the hectorite-coated silica particles have been synthesized by hydrothermal synthesis following

the Tajima and Okada method [3]. As a core of materials, a microporous silica gel of approx. diameter of 300 μm has been used. The hectorite coatings have been synthesized for 48 h at 99.5°C using 25 ml hydrothermal synthesis reactors. The presence of hectorite coating has been confirmed by combining the IR spectroscopy, XRD, and SEM methods. Subsequently, prepared materials have been modified using cetyltrimethylammonium bromide (CS-CTM) or polydiallyldimethylammonium chloride (CS-PDDA) to achieve hydrophobic characters.

Prepared materials have been tested by adsorption experiments. The adsorption of three analgesics: paracetamol (PAR), ibuprofen (IBU-Na), and diclofenac (DCF-Na), two antibiotics: norfloxacin (NOR) and ofloxacin (OFL), and one pesticide metolachlor (MTZ) have been tested. Sample CS-CTM shows good adsorption of antibiotics NOR and OFL, as well as of the pesticide MTZ. The concentrations of antibiotics were decreased to the limits of detections. Sample CS-PDDA shows good adsorption properties of analgetics DCF-Na, IBU-Na and antibiotics NOR, and OFL. Thanks to their size, the prepared adsorbents are good to manipulate with and suitable for use in the adsorption columns. The low adsorption capacities q_e are caused by the bulk character of the core of the prepared materials. This can be increased by using smaller SiO_2 cores. Prepared materials represent very suitable materials with potential in the application in environmental remediation of some organic pollutants.

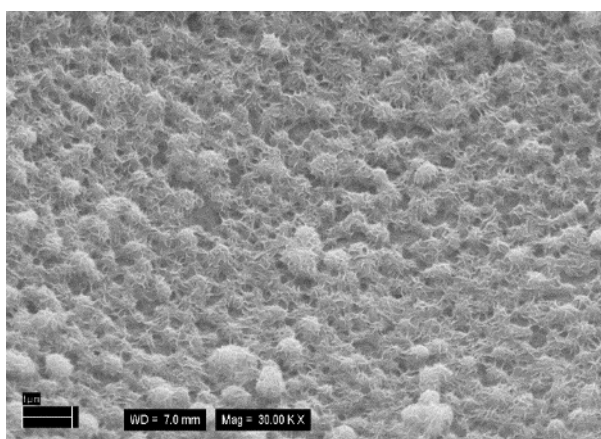


Fig.1 SEM of the surface of hectorite-coated silica particles

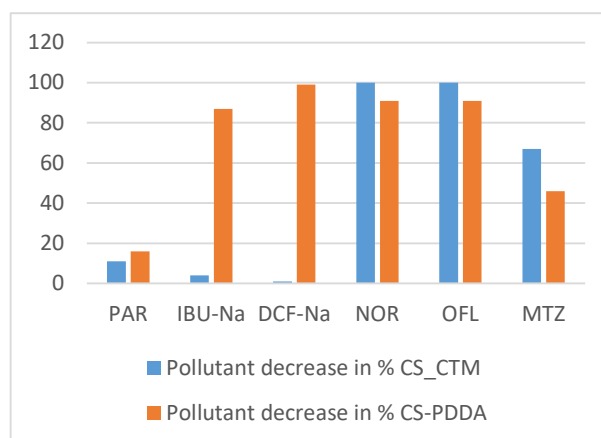


Fig.2 Adsorption efficiency of synthesized samples

Acknowledgment:

This work was supported by the Slovak Research and Development Agency under contract No. APVV-15-0347, APVV-15-0741, APVV-18-0075, ERDF "Institute of Environmental Technology – Excellent Research" (No. CZ.02.1.01/0.0/0.0/16_019/0000853), and by EU structural funding in Operational Programme Research, Development and Education, project No. CZ.02.1.01./0.0/0.0/17_049/0008419 „COOPERATION." Experimental results were accomplished using Large Research Infrastructure ENREGAT supported by the Ministry of Education, Youth and Sports of the Czech Republic under project No. LM2018098. The VEGA grant agency's support (1/0227/20, 2/0141/17) is also gratefully acknowledged.

References

- [1] E. Ruiz-Hitzky, P. Aranda, M. Darder, G. Rytwo, 2010. Hybrid materials based on clays for environmental and biomedical applications, *Journal of Materials Chemistry*, 20, 9306–9321.
- [2] A. Phuekphong, K. Imwiset, M. Ogawa, 2020. Designing nanoarchitecture for environmental remediation based on the clay minerals as building block, *Journal of Hazardous Materials*, 399, 122888-1-122888-41.
- [3] K. Tajima, T. Okada, 2019. A study of stereoselective adsorption in smectites using thin-layer chromatography, *Applied Clay Science*, 170, 13–20.

ASSAYS USED IN THE EVALUATION OF ANTIMICROBIAL PROPERTIES OF HYBRID MATERIALS

H. Bujdaková^{1*}, B. Radochová¹, N. Chandra teja Dadi¹, J. Vargová¹, M. Štefánek¹, S. Kendra¹

¹ Department of Microbiology and Virology, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovakia

* helena.bujdakova@uniba.sk

KEYWORDS: Methods | Microorganisms | Photosensitizer | Saponite

Testing the antimicrobial properties of biologically active molecules, materials, and their hybrid systems requires a multidisciplinary approach. For the determination of antimicrobial and antibiofilm properties, some *in vitro* techniques are the most common. *In vivo* tests are expensive, but there are several possibilities for simpler and cheaper alternatives using invertebrate models [1]. Hybrid films are usually complex systems consisting of several components. Therefore, not only the final system but also all components should be tested in biological experiments. Our hybrid film was based on nanoparticles of clay mineral saponite (Sap) functionalized with photosensitizer (PS) phloxine B (PhB) or methylene blue (MB). All components usually manifest antimicrobial properties when they are tested alone. In addition, Sap was modified with quaternary ammonium salts to achieve optimal interaction between Sap and PS. Such a hybrid film was fixed on the surface of the polyurethane (PU) membrane. Prepared PU nanocomposite was further used for *in vitro* testing to determine the antimicrobial properties of the material. In view of current knowledge, antimicrobial effectiveness is mainly focused on anti-biofilm activity [2]. Microbial biofilms are currently the main problem; not only in medicine but also in the food industry or wastewater treatment, and new materials with improved antimicrobial properties have a chance to be used in all these areas [3]. For *in vitro* testing, three basic sets of approaches are used; assay for determination 1) of microbial viability; 2) vitality; and 3) microscopy. While vitality documents metabolic activity and viability reflects the survival of microbes, microscopy can provide information in changes of morphology, but also in both, vitality or viability, depending on the type of a selected microscopic technique.

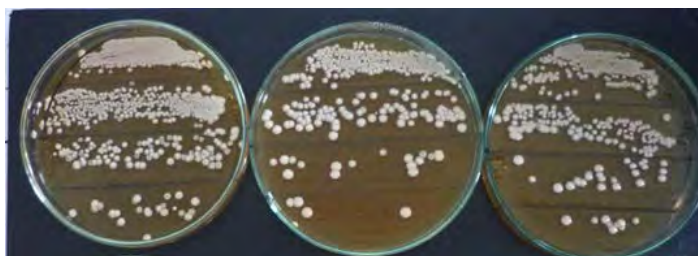
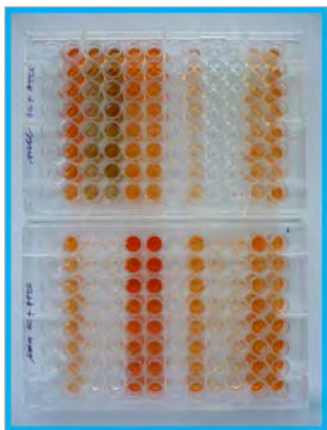


Fig. 1 (left) documents metabolic activity (vitality) of microbes determined by reduction of tetrazolium salt.

Fig. 2 (above) shows the determination of viability by growth of colony forming units.

Scanning Electron Microscopy (SEM) is suitable for detailed analysis of morphology or cell surface damage, while Confocal Laser Scanning Microscopy provides information in biofilm thickness and vitality or viability. Even more perfect and complex technique is Fluorescence *In situ* Hybridization. However, with such complex films as we are preparing, not all techniques are suitable, even many of them need to be modified.

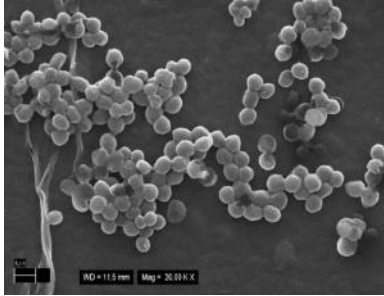


Fig. 3 (left) documents SEM of the effect of the hybrid film (Sap modified with trimethyl octadecyl ammonium and functionalized with PhB) on *S. aureus*.

For *in vivo* testing, invertebrate models are recently very popular due to their low cost, easy handling and do not require a permit to work with living organisms. An example is larvae of *Galleria mellonella* (the greater wax moth), which are suitable for testing the effect of individual components of hybrid films during infection by microorganisms, but also for biocompatibility testing.



Fig. 4 (left) documents the survival of larvae of *G. mellonella* after administration of 0.03 or 1 mM MB.

In summary, there are several options for testing the antimicrobial activity of hybrid materials. Their choice depends on the type of tested materials in order to achieve accurate and complex information.

Acknowledgment:

This research was supported by Slovak Grant Agency under the contract no. APVV-18-0075 and APVV-15-0347; Ministry of Education, Science, Research and Sport of the Slovak Republic under the contract no. VEGA 1/0227/20 and VEGA 1/0537/19.

References

- [1] J. Dekkerová-Chupáčová, E. Borghi, G. Morace, H. Bujdaková, 2018. Up-Regulation of Antimicrobial Peptides Gallerimycin and Galiomycin in *Galleria mellonella* Infected with *Candida* Yeasts Displaying Different Virulence Traits, *Mycopathologia*, 183(6), 935-940.
- [2] N. Ch. T. Dadi, M. Dohál, V. Medvecká, J. Bujdák, K. Kočí, A. Zahoranová, H. Bujdaková, 2021. Physico-Chemical Characterization and Antimicrobial Properties of Hybrid Film Based on Saponite and Phloxine B, *Molecules*, 26(2), 325-1-325-15.
- [3] A. Bianchera, F. Buttini, R. Bettini, 2020. Micro/nanosystems and biomaterials for controlled delivery of antimicrobial and anti-biofilm agents, *Expert Opinion on Therapeutic Patents*, 30(12), 983-1000.

SILICATES AND DRUG DELIVERY

D. Furka^{1,2*}, S. Furka^{1,2}, S. Slopovská^{1,2}, V. Heger³, J. Sokol⁴, R. Sokol⁴, M. Janek^{1,5}

- ¹ Comenius University, Faculty of Natural Sciences, Department of Physical and Theoretical Chemistry, Mlynská dolina, Ilkovičova 6, 84104-Bratislava, Slovakia
- ² Slovak Academy of Sciences, Department of cardiovascular physiology and pathophysiology, Centre of Experimental Medicine, Dúbravská cesta 9, 84005-Bratislava, Slovakia
- ³ Slovak Academy of Sciences, Institute of Experimental Pharmacology and Toxicology, Centre of Experimental Medicine, Dúbravská cesta 9, 84005-Bratislava, Slovakia
- ⁴ Private urologic ambulance, Piaristicka 257, 91101 Trenčín, Slovakia
- ⁵ Slovak University of Technology, Faculty of Chemical and Food Technology, Radlinského 9, 81237-Bratislava, Slovakia

* furka2@uniba.sk

KEYWORDS: Silicates | Medicine | Oncology

Due to their unique properties, clay minerals are widely used in modern medicine for drug delivery and diagnostics. They are mainly used as carriers of poorly soluble or low-bioavailability drugs, including antimalaritics, antipsychotics, antibiotics, and chemotherapy [1]. To reduce undesirable physicochemical parameters, it is necessary to design suitable hybrid carriers. The advantage of clay minerals as drug carriers is the high degree of biocompatibility, the layered structure able to intercalate drug molecules using cation exchange (montmorillonite) or in presence of nanotubes capability of capillary condensation (halloysite). However, some of the drugs are released relatively quickly from the clay matrix, which possibly reduces efficiency of treatment, and therefore in 2013 Oh et al. designed a hybrid clay matrix encapsulated in polyvinyl acetal diethylaminoacetate [2]. A hybrid inorganic-organic material based on montmorillonite encapsulated in a polymer reduced the amount of drug released up to 1% of the total (originally 70%) within 3 minutes of admission, and 95% of the total amount of intercalated drug being released after 2 hours. In the case of anti-cancer therapy, an intravenously applicable nanoparticulate form of Laponite or Double-layered -hydroxide (LDH) with a particle size of about 100 nm can be used. The advantage is biocompatibility and specific resorption by tumor tissue. Increased permeability of tumor cells to these nanocarticles is not due to the size effects, but due to their intrinsic cell targeting function known as the intracellular clatrin-mediated endocytosis. Hybrid LDH should be used as carrier for Methotrexate (therapy of osteosarcoma, cervical cancer, breast cancer), Mercaptoundecahydrochlorosododecaborate (diagnosis and neutron capture therapy for glioblastoma), Survivin siRNA (therapy of osteosarcoma, cervical cancer, breast cancer) gene therapy. Halloysite nanotubes can be utilized the transport of doxorubicin (breast cancer, bladder cancer, Kaposi's sarcoma, lymphoma, and acute lymphocytic leukemia).

Acknowledgment:

This work was supported by the Slovak Research and Development Agency under contract No. APVV-18-0075 and VEGA agency project 1/0227/20.

References

- [1] G. Choy, H. Piao, et al., 2019. Vectorized clay nanoparticles in therapy and diagnosis, *Clays and Clay Minerals*, 67, 25 – 43.
- [2] Y. Oh, G. Choi, 2013: Aripiprazole-montmorillonite: a new organic-inorganic nanohybrid material for biomedical applications, *Chemistry - A European Journal*, 19, 4869–4875.

SILICATES IN MODERN MEDICINE

S. Furka^{1,2*}, D. Furka^{1,2}, V. Heger³, M. Janek^{1,4}

¹ Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovakia

² Department of Cardiovascular Physiology and Pathophysiology, Centre of Experimental Medicine, Slovak Academy of Sciences, Dúbravská cesta 9, 841 04 Bratislava, Slovakia

³ Institute of Experimental Pharmacology and Toxicology, Centre of Experimental Medicine, Slovak Academy of Sciences, Dúbravská cesta 9, 841 04 Bratislava, Slovakia

⁴ Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia

* furka3@uniba.sk

KEYWORDS: Silicates | Medicine | Biocompatibility

Novel but also well-known silicate-based materials are widely used in modern medicine. While unmodified silicates are used primarily as carrier matrices in drug delivery systems, their modified or hybrid versions can be used in the development of antimicrobial surfaces and biocompatible materials. Physico-chemical and mechanical properties of silicates are suitable for the design of teeth, cartilage but also for bone tissues. Implantation of a bone prosthesis made of unmodified silicate leads to formation of a wide, scar-tissue zone with low elasticity. Currently available material for the production of bone tissue is hydroxyapatite (HAP). However, natural bone tissue differs from pure synthetic HAP, in the amount of natural substitution of CO_3^{2-} and biogenic elements. Thus, bone replacement made from pure HAP may be rejected by the original tissue several days after implantation, which may lead to permanent damage to the musculoskeletal system. In the case of a biocompatible composite material made of HAP, collagen and silicate modified by $\text{Ca}_3(\text{PO}_4)_2$, no inelastic tissue layer is formed. At the same time, the rate of absorption of such tissue by the original bone is several minutes [1]. In vivo and in vitro experiments of powdered forms of HAP and $\text{Ca}_3(\text{PO}_4)_2$ modified silicate (particle dimensions 150 nm - 600 nm) did not show a statistically significant effect of cytotoxicity in mice, in contrast to the strong cytotoxicity of crystalline quartz [2]. Hybrid materials based on biocompatible silicates containing collagen allow fibroblasts to adhere and migrate over the implant surface. This migration ensures the gradual overgrowth of the original bone into the implant. Over time, the implant can be completely replaced by the original bone, which represents a huge benefit for radical bone tumor resection, joint replacements, and rehabilitation.

Acknowledgment:

This work was supported by the Slovak Research and Development Agency under contract No. APVV-18-0075 and VEGA agency project 1/0227/20.

References

- [1] M. Sayer, A. Stratilatov, J. Reid, L. Calderin, M.J. Stott, X. Yin, M. MacKenzie, T.J.N. Smith, J.A. Hendry, S.D. Langstaff, 2003. Structure and composition of silicon-stabilized tricalcium phosphate, *Biomaterials*, 24, 369 – 382.
- [2] L. Hench, J. Wilson, 2007. Biocompatibility of Silicates for Medical Use, *Ciba Foundation Symposium 121 - Silicon Biochemistry: Silicon Biochemistry: Ciba Foundation Symposium 121*, 231 - 253.

INTERCALATION OF THE POLY(2-METHYL-2-OXAZOLINE) INTO MONTMORILLONITE

J. Madejová^{1*}, M. Barlog¹, Ľ. Jankovič¹, M. Slaný¹

¹ Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

* jana.madejova@savba.sk

KEYWORDS: Nanocomposites | Polycations | Montmorillonite

Clay minerals, mainly smectites, represent a special group of two-dimensional materials considered as suitable to form so-called hybrid materials via confining of organic moieties within the interlayer spaces of the inorganic carriers. In addition to quaternary alkylammonium cations, most frequently used to prepare organoclays, polycations (cationic polymers) are also prospective species used for modification of clay minerals. The aim of this study was to prepare and characterize nanocomposites based on montmorillonite (Mt) and poly(2-methyl-2-oxazoline) (PMeOx). Prepared materials were characterized by XRD, FTIR spectroscopy and TG analysis. XRD showed that degree of the intercalation depended on the concentration of the used polycation (85–680 mg per 1 g of Mt). A gradual increase of the interlayer space from 12.4 – 20.8 Å with increasing amount of used polycation was observed (Fig. 1). At low degree of the intercalation (85 – ~200 mg.g⁻¹) the polycations were arranged in monolayers. At higher amount of used PMeOx bilayers and transition to pseudotrilayer arrangement of the polycations within the Mt interlayer space was detected.

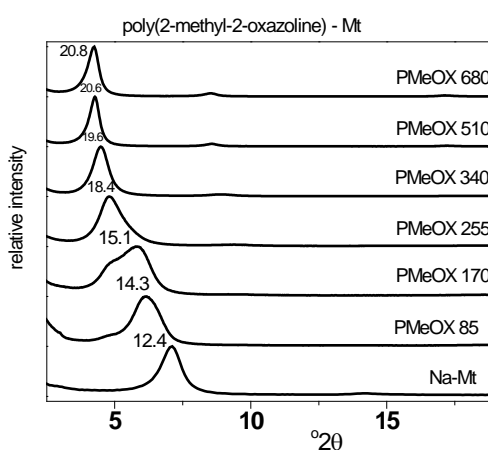


Fig. 1 XRD patterns of PMeOx-Mt prepared with different amount of polycation.

Presence of PMeOx in Mt interlayers was followed also by IR spectroscopy. In addition to the characteristic bands related to the stretching and bending OH (3623, 914, 842 cm⁻¹) and SiO (1030, 519, 465 cm⁻¹) vibrations of Mt, characteristic vibrations of the PMeOx cation were also observed, i.e. the intensive band at 1634 cm⁻¹ due to C=O and vibrations of CH₂ a CH₃ groups near 2937 cm⁻¹ (stretching) and 1480 – 1200 cm⁻¹ (bending).

TG curves allowed comparing the thermal stability of PMeOx-Mt with Na-Mt (Fig. 2). Dehydration of Na-Mt occurred up to about 300°C, dehydroxylation took place at higher temperatures. The intercalation of polycations induced alterations in TG profile. The content of water in PMeOx-Mt was lower (8%) than in Na-Mt (12%). The most significant change was the increase of the mass loss due to the polycation degradation. Concurrently with dehydroxylation of the Mt structure, decomposition of the organic phase continued even after temperatures above 600°C.

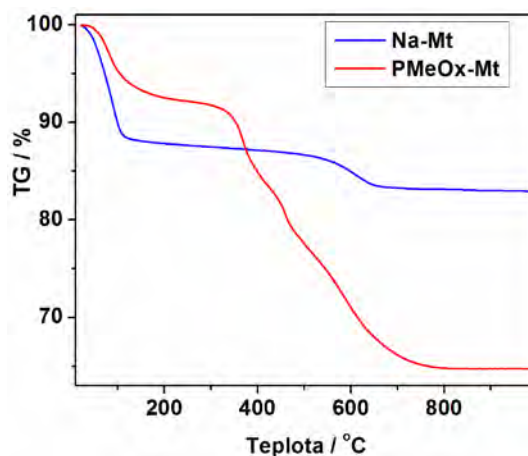


Fig. 2 TG profiles of Na-Mt and PMeOx-Mt

Acknowledgment:

The authors acknowledge the financial support of the Slovak Grant Agency VEGA (2/0166/21) and the Slovak Research and Development Agency (APVV-19-0487, APVV-18-0075).

STRUCTURAL CHANGES IN MECHANOCHEMICALLY TREATED SMECTITES INVESTIGATED BY INFRARED SPECTROSCOPY

H. Pálková^{1*}, M. Barlog¹, J. Madejová¹, E. Šimon^{2,3}, M. Zimowska⁴

¹ Institute of Inorganic Chemistry, SAS, Dúbravská cesta 9, SK-845 36 Bratislava, Slovakia

² Centre of Excellence for advanced materials application SAS, Dúbravská cesta 5807/9, 845 11 Bratislava, Slovakia

³ Institute of Materials and Machine Mechanics, SAS, Dúbravská cesta 9, 845 13 Bratislava, Slovakia

⁴ Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Kraków, Poland

* helena.palkova@savba.sk

KEYWORDS: Infrared spectroscopy | Structure modification | Grinding

Mechanochemical activation (MA) has frequently been applied to clay minerals in order to enhance their application potential in the field of materials engineering, to be used e.g. as adsorbents in the waste treatment process, in agriculture for fertilizer preparation or for preparation of clay mineral based hybrid materials. MA of solid-state samples involves the application of mechanical energy to solids, resulting in their physical and chemical changes in the near-surface regions generating a number of defects in structures, dislocations and different levels of materials transformation [1]. Upon MA the layered structure of clay minerals undergoes alteration, starting with breakage of the particles at the beginning of the process, then with the changes in their size and shape, followed by disruption of the bonds between the principal structural units in the clay mineral structure. The amorphous phase is considered the final product of this process. All stages of the process are accompanied by changes in the surface area, surface activity and layer charge [2].

The main goal of this work was to analyse the influence of the short-duration mechanochemical activation process on the structure of smectites with differing octahedral sheet configuration by infrared (IR) spectroscopy in the middle (MIR) and near (NIR) regions. For this purpose, several smectites - dioctahedral and trioctahedral, were selected for the study. Trioctahedral smectites, natural and synthetic hectorites, HcS and HcL (SHCa-1, California, USA, Laponite, RD, Rockwood Additives, UK), synthetic saponite, SpS (Sumecton, Kunimine Industries, Japan) and dioctahedral montmorillonites, MtK and MtJ (Kunipia, Kunimine Industries, Japan, and Jelšovský potok, Slovakia) were subjected to a short period (2, 4, 6 min) of high energy grinding (HIG) and IR spectra were analysed.

The perturbation of the chemical bonds in the studied smectites upon grinding was reflected in the qualitative changes in their MIR and NIR spectra. The most extensive changes were detected for MtK and MtJ, showing alteration of the spectra even after 2 min of grinding. With increasing duration of treatment, the sharp bands νOH and $2\nu\text{OH}$ around 3630 cm^{-1} and 7074 cm^{-1} were transformed into wide, complex bands overlapping with a wide water band, as a result of the disruption of the bonds in the octahedral sheets of the montmorillonites. The corresponding δOH bands between $920 - 840\text{ cm}^{-1}$ disappeared from the spectra of MtK-6 and MtJ-6, while $(\nu+\delta)\text{OH}$ at 4528 cm^{-1} was transformed into a wide band attributed to $(\nu+\delta)\text{OH}$ for OH

groups at the surface of the amorphous phase [3]. The formation of the amorphous phase was performed by analysing the MIR spectra focused on the changes in the absorption bands connected with SiO₄ or AlO₄. The complex ν SiO band for MtK and MtJ ground for 4 and 6 min showed significant widening on the higher wavenumber side (near 1200 cm⁻¹), a shift of the maximum from ca. 1038 to 1050 cm⁻¹, and increasing intensity of the band near 800 cm⁻¹ which resulted from the increasing contribution of the absorption band of the amorphous three-dimensional SiO₂ phase. The intensity of the δ Al^{VI}OSi band diminished with the length of grinding indicating the almost complete disappearance of the Al-O-Si bonds between AlO₆ and SiO₄. For MtK-6 this band was not possible to detect in the spectra indicating high disintegration of the octahedral from tetrahedral sheet. Shape of the spectra in this region for MtJ-6 indicated that δ AlOSi band is still present. An increase in the intensity for the band near 720 cm⁻¹ was attributed to the formation of an amorphous phase consisting of the AlO₄ units [3].

In contrast, the structural OH groups were less affected in the trioctahedral samples. A decrease of the structural OH bands (stretching and bending) was clearly visible, but the bands around 7190, 4320, 4181, 3680 and 670 cm⁻¹ persisted in the spectra of SpS, HcL and HcS even after treatment of the samples for the longest selected time (6 min). The preservation of all bands related to octahedral Mg proved that the decomposition of the layers was less pronounced than for Mt despite the same treatment conditions being used. The trioctahedral samples, on the other hand, showed only a small broadening of the ν SiO (1012 cm⁻¹) band and a negligible shift in its position, thus reflecting only a low degree of amorphization for HcS, HcL and SpS.

Results obtained by analysis of the spectra showed that MIR spectra are very useful to follow formation of amorphous phase in mechanochemically treated smectites while analysis of NIR spectra provide information on changes in the structural OH groups and water molecules. Structural changes observed in the IR spectra were also confirmed by other methods, such as MAS NMR spectroscopy, thermal analysis and XRD analysis [4].

Acknowledgment:

The authors acknowledge financial support from the Slovak Grant Agency VEGA (project No. 2/0166/21), Slovak Research and Development Agency (project Nos. APVV-18-0075 and APVV-19-0487). This work was also the results of the implementation of the project Buildingup Centre for advanced materials application of the Slovak Academy of Sciences (ITMS project code 313021T081) which is supported by the Research & Innovation Operational Programme funded by the ERDF.

References

- [1]. P. Baláž, M. Achimovič, M. Baláž, P. Billik, Z. Cherkezova-Zheleva, J.M. Criado, F. Delogu, E. Dutková, E. Gaffet, F.J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletski, K. Wieczorek-Ciurowam, 2013. Hallmarks of mechanochemistry: from nanoparticles to technology. *Chemical Society Reviews* 42, 7571–7637.
- [2]. G.E. Christidis, F. Dellisanti, G. Valdrè, P. Makri, 2005. Structural modifications of smectites mechanically deformed under controlled conditions. *Clay Minerals* 40, 511–522.
- [3]. J. Madejová, H. Pálková, 2017. NIR contribution to the study of modified clay minerals. In: Gates, W.P., et al. (Eds.), *Developments in Clay Science 8. Infrared and Raman Spectroscopies of Clay Minerals*, Elsevier, Amsterdam, pp. 447–481.
- [4]. H. Pálková, M. Barlog, J. Madejová, V. Hronský, L. Petra, E. Šimon, P. Billik, M. Zimowska, 2021. Structural changes in smectites subjected to mechanochemical activation: The effect of the occupancy of the octahedral sites. *Applied Clay Science* 213, 106214.

THEORETICAL STUDY OF INTERACTIONS IN THE POLYCATION-MONTMORILLONITE – ADVANCED HYBRID MATERIAL

E. Scholtzová^{1*}, S. Bashir¹

¹ Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

* eva.scholtzova@savba.sk

KEYWORDS: Montmorillonite | DFT-D3 | Polycation | Polymer

Intense research in the field of the advanced layered hybrid materials is based on the use of various types of clay minerals mainly from the smectites group, e.g., montmorillonites, providing their layered structure to accommodate various guest species.

The layered structure of smectites consists of the tetrahedral (T) and octahedral (O) sheets linked together through apical oxygens of tetrahedra forming a TOT layer. Due to the layer thickness of ~1 nm, they are considered as nanomaterials. The isomorphous substitutions in the T sheets (e.g., Al³⁺/Si⁴⁺) and O sheet (e.g., Fe²⁺, Mg²⁺/Al³⁺) generate a negative net charge which is compensated by exchangeable hydrated inorganic cations (e.g., Ca²⁺, Na⁺, Li⁺) in the interlayer space. The presence of these exchangeable cations is often a key factor for further easy modification with organic surfactants (e.g., quaternary cations or polycations – cationic polymers).

Design of the polycation-clay hybrid materials was targeted to prepare, e.g., the effective sorbents of organic pollutants, clay-based nanocomposites with antibacterial properties or advanced materials with photoactive properties [1].

Detailed knowledge on the binding interactions and intercalation energies as a measure of the structural stability of the polycation-clay hybrid structures in this work is studied employing DFT method in solid state using PBE functional together with D3 scheme for dispersion corrections [2] on the models based on the hybrid structures of montmorillonite and pentaethylenimine, PEI-Mt (Fig. 1), and Mt with penta(2-oxazolines), POX-Mt (Fig. 2), respectively. The properties of the hybrid structures based on the montmorillonite and cationic (PEI) and neutral (POX) polymers will be compared.

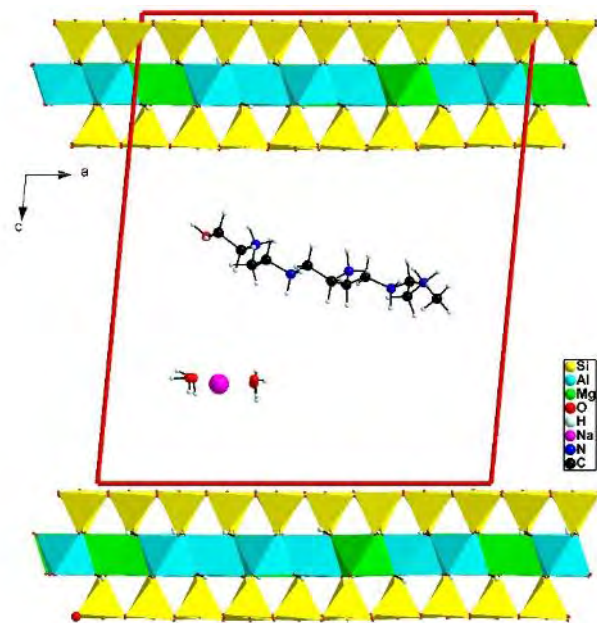


Fig. 1 Starting model of the Mt-PEI hybrid material.

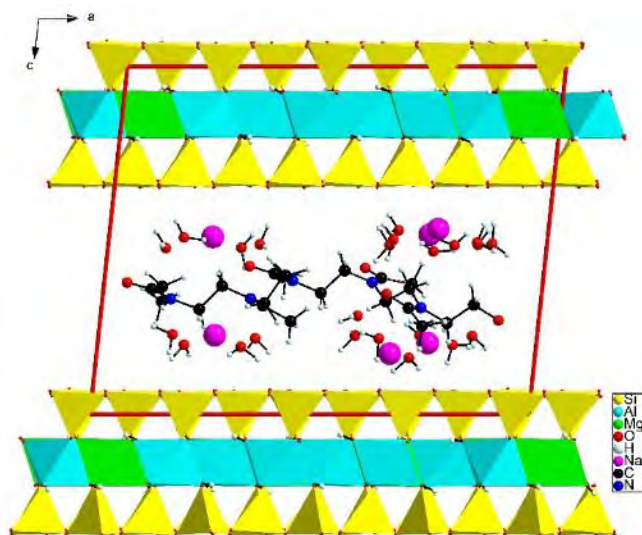


Fig. 2 Pre-optimized structure of the Mt-POX hybrid material.

Acknowledgments:

Authors are grateful for the financial support by the Scientific Grant Agency (project No. VEGA 02/0021/19) and Slovak Research and Development Agency (projects No. APVV-18-0075 and APVV-19-0487).

References

- [1] D. Johec-Mošková, I. Janigová, Z. Nógellová, M. Sedničková, L. Jankovič, P. Komadel, M. Šlouf, I. Chodák, 2018. Prediction of compatibility of organomodified clay with various polymers using rheological measurements, *Polymer Testing*, 69, 359–365.
- [2] S. Grimme, J. Antony, S. Ehrlich., H. Krieg, 2010. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *The Journal of Chemical Physics*, 132, 154104-1-154104-19.

BASIC CHARACTERISATION OF SELECTED BENTONITES FROM KREMICKÉ VRCHY – PRELIMINARY RESULTS

P. Uhlík^{1*}, Y. Bai¹, O. Lintnerová¹, M. Osacký¹, M. Rybárik¹

¹ Department of Mineralogy, Petrology and Economic Geology, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15, Bratislava, Slovakia

*peter.uhlik@uniba.sk

KEYWORDS: Bentonite | Grain size | Kremnické vrchy | Montmorillonite

With the annual production of more than 200 kt and total reserves more than 55 000 kt, Slovakia belongs to world's leading countries in bentonite exploitation (Kúšik et al., 2019). In Slovakia, bentonites are among the strategic industrial raw materials. Bentonite exploitation has increased significantly over the past 10-15 years. Currently, the annual domestic bentonite production belongs to the world's TOP 15. The most important bentonite deposits in Slovakia are located in the Central Slovakian Neovolcanites, predominately in Kremnické vrchy Mts. (near Stará Kremnička, Lutilla and Kopernica villages). The bentonites associated with rhyolitic volcanism of the Jastraba formation. The aim of the study is determined a degree of homogeneity in the frame of selected deposits and mutually between them base on basic characterisation (colour, texture, grain size, water content, pH, swelling, mineralogy). The samples were collected just in July 2021 therefore the presented results are only preliminary.

Studied bentonites are variable coloured, even in one deposit. The selected bentonites are light and dark rose, green, yellow to ocre, light grey to white. Evenly distributed biotite indicated the original rhyolite texture in most of the studied bentonites. Pieces of rocks were also occasionally observed in some deposits. One sample with green color was macroscopically significantly fine-grained. It was confirmed by grain size analysis (> 90 wt. % of fraction < 63 µm). Grain size distribution was identified by wet sieving. Predominant fraction is < 63 µm, mostly between 70-80 wt. %. Portion of clay fraction (< 2 µm) is ranged from 10 to 40 wt. % from whole sample. It shows to still significant aggregation even after 24 hours stirring of bentonite with water. Natural moisture of natural bentonites (pieces of bentonites directly from deposit with size less than 1 cm) after drying at laboratory temperature was from 14 to almost 30 wt. %. Amount of water in dry bentonites (dried at laboratory temperature) was from 2.29 to 6.45 wt. % after drying at 90 °C (45 min) and from 2.8 to 10.47 after drying at 105°C (4 hours).

Quartz is dominant mineral in observed fractions > 63 µm. It is accompanied by biotite and feldspars. Feldspars and/or biotite are sporadically more abundant than quartz.

The presented results shows to partly heterogeneity. Lately, we will compare these results with amount of montmorillonite. The results are also initial data to optimize the industrial quality control procedure of bentonites in company ROMIN Slovakia spol s r.o. and for characterisation bentonite properties in order to find their best possible use.

Acknowledgment:

The authors gratefully acknowledge financial support from the Research and Development Agency (project APVV-20-0175). Companies: REGOS s.r.o., Kremnická banská spoločnosť, s.r.o., KOPEREKOMIN, s.r.o. are acknowledged for provision of bentonite samples. B. Uhlíková is acknowledged for help at laboratory works.

References

[1] D. Kúšik, S. Šoltés, J. Mižák, 2019: Slovak Minerals Yearbook 2018. State geological institute of Dionyz Štúr, 141.

SURFACE SEGREGATION OF THE Mg SPECIES AS A RESULT OF CHEMICAL AND HYDROTHERMAL TREATMENT OF THE LAPONITE-BASED NANOCOMPOSITES

M. Zimowska¹, M. Śliwa¹, R. P. Socha¹, H. Pálková²

¹Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Kraków PL-30 239, Poland

²Institute of Inorganic Chemistry, SAS, Bratislava 845 36, Slovakia

* e-mail nczimows@cyf-kr.edu.pl

KEYWORDS: Laponite | Porous Heterostructured Composites (PCH) | Sorption Properties |

Preparation of suitable supports for sorption of post-combustion effluents is nowadays very active research area. It is the scientific answer on the development of modern civilization, progressing industrialization, exploitation of fossil deposits, resulting in generation of environmental pollution, as their harmful side aspect of global development. Especially the new solutions enable to minimize the level of CO₂ emission are being sought. The high demand for efficient, stable, and cheap CCS nanosorbents has drawn our attention to the clay minerals, attractive from the point of view of sorption properties and abundance. The features of layered silicates particularly from the smectite group, dispose them into a first group of such supports particularly due to the specific composition, structure and ion exchange properties.

The objective of this work was to investigate properties of porous heterostructured composite materials (PCH) based on Laponite, towards their application as sorption materials. We focus on the development of the surface basicity by application of chemical (A), sonochemical (S1, S2) and hydrothermal activation (H) of synthesised PCH. In order to obtain of highly porous heterostructured crystalline - amorphous nanocomposites the templating method, with the synthetic trioctahedral hectorite Laponite RD (Lap) consisting of octahedral sheet (occupied by MgII) sandwiched between two tetrahedral sheets (occupied by Si atoms) as a platform was used. To get insight into detailed characterization of surface species generated upon treatment, the X-ray diffraction (XRD) method, scanning electron microscopy (SEM), advanced FTIR and X-ray photoelectron spectroscopy (XPS) techniques as well as TPD temperature programmed CO₂ sorption were used.

The applied treatment affected the structure of the Laponite component in the composite in a different manner and resulted in some rearrangement of PCH structure. XPS study showed that the composites activated by ultrasounds or with pressure assistance are characterized by higher amount of Mg on the surface than only activated in the acidic environment. It was the result of slight dissolution of Mg²⁺ cations from octahedral sheets of the Laponite component.

FTIR analysis supported that data and indicated the decrease of the band intensities at 668 cm⁻¹ attributed to the bending vibrations of structural OH groups (δ Mg₃OH) and Mg-O_{ap} groups found at 535 cm⁻¹ within octahedral sheets of Laponite. This effect was pronounced in the

ultrasounds treated samples. It was stated that the PCH precursor approach influenced the Mg content exhibited to the surface.

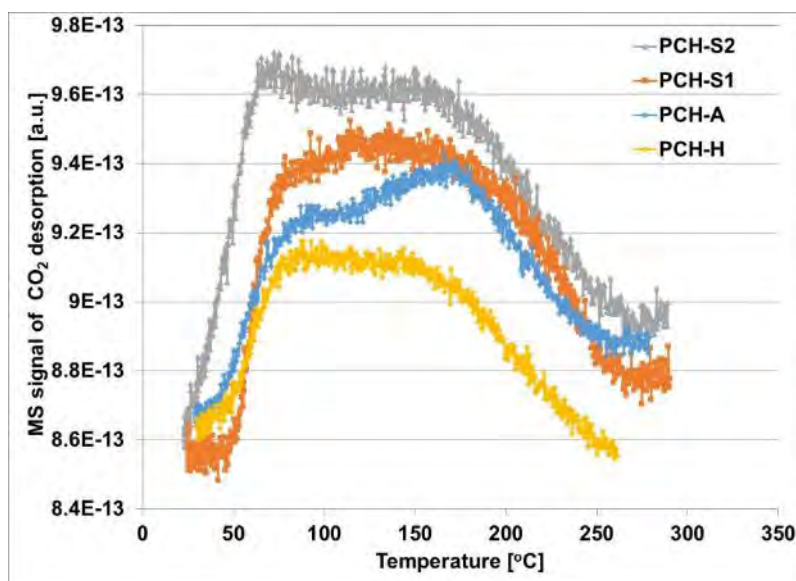


Fig. 1 Temperature-programmed CO₂ desorption profiles of Laponite based PCH composites.

Segregation of the Mg cations caused slightly basic character of the composite surface. The basicity of the catalysts and the sorption properties were assessed by the TPD temperature programmed CO₂ technique. The results of sorption properties of synthesized catalysts are presented in the Fig 1. Above investigations indicated that modification of porous composites based on synthetic hydrous magnesium silicate may cause same rearrangements in the Laponite structure forcing the migration of Mg cations from octahedral sheets of used clay mineral and enriched the surface of composites into base properties.

Summarizing, the synthesized materials serve as promising materials for CO₂ sorption however, further investigation into modification of clay derived composite materials should be undertaken.

LIST OF PARTICIPANTS

1.	BAI Yuqing	Department of Mineralogy, Petrology and Economic Geology, Faculty of Natural Sciences, Comenius University, Bratislava, SVK
2.	BARLOG Martin	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
3.	BOHÁČ Peter	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
4.	BUJDÁK Juraj	Department of Physical and Theoretical Chemistry, Faculty of Natural Science, Comenius University in Bratislava, SVK
5.	BUJDÁKOVÁ Helena	Comenius University in Bratislava, Faculty of Natural Sciences, Department of Microbiology and Virology, Bratislava, SVK
6.	ČIČKAN Michal	Comenius University, Department of Physical and Theoretical Chemistry, Bratislava. SVK
7.	FURKA Daniel	Comenius University, Department of Physical and Theoretical Chemistry, Bratislava. SVK
8.	FURKA Samuel	Comenius University, Department of Physical and Theoretical Chemistry, Bratislava. SVK
9.	DADI Nitin	Comenius University in Bratislava, Faculty of Natural Sciences, Department of Microbiology and Virology, Bratislava, SVK
10.	MADEJ Ján	
11.	MADEJOVÁ Jana	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
12.	MORENO RODRIGUEZ Daniel	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
13.	PÁLKOVÁ Helena	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
14.	PRIBUS Marek	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
15.	MORENO RODRIGUEZ Daniel	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
16.	OSACKÝ Marek	Department of Mineralogy, Petrology and Economic Geology, Faculty of Natural Sciences, Comenius University, Bratislava, SVK
17.	SCHOLTZOVÁ Eva	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
18.	SLANÁ Marica	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
19.	SLANÝ Michal	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
20.	ŠKORŇA Peter	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
21.	SKOURA Eva	Institute of Inorganic Chemistry Slovak Academy of Sciences, Bratislava, SVK
22.	UHLÍK Peter	Department of Mineralogy, Petrology and Economic Geology, Faculty of Natural Sciences, Comenius University, Bratislava, SVK
23.	UHLÍKOVÁ Juraja	
24.	ZIMOWSKA Małgorzata	Jerzy Haber Institute of Catalysis and Surface Chemistry, PAN, Krakow, Poland

8th Workshop of Slovak Clay Group

Book of abstracts

September 6-8, 2021 Habovka, Slovakia

Publishers: Slovak Clay Group
Dúbravská cesta 9
845 36 Bratislava

Edited by: H. Pálková, T. Šimonová

ISBN 978-80-972367-5-5

