

9TH WORKSHOP OF SLOVAK CLAY GROUP



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

Book of abstracts



JUNE 26 – 28, 2023, TERCHOVÁ, SLOVAKIA



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ORAL PRESENTATIONS

STUDY OF ENHANCED FLUORESCENCE OF CATIONIC DYE CRYSTAL VIOLET AFTER INTERACTION WITH EITHER PRISTINE OR BY ETHYLENEAMINES MODIFIED MATRIX OF SYNTHETIC HECTORITE

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KEYWORDS: Crystal violet | Hybrid materials | Clay mineral | Fluorescence

Nowadays, considerable attention of scientific research is paid to the development of new fluorescent dyes. The plethora of already synthesized fluorophores do not possess satisfying quantum yields, moreover, insufficient mechanical and chemical stability are accompanied.

This work was aimed toward utilization of hectorite (HC) (from subgroup of smectite (SM)) which would act as supportive matrix for molecules of crystal violet (CV) with an option for additional modification by surfactants. With a goal of improvements of HC-CV hybrid systems, the modification by ethyleneamines had been conducted. Those modifiers were delicately selected with focus to gain the improvements of properties and practical usability in others SM-dyes systems. In general, the interaction of dye creates formation J-aggregates (lowering fluorescence intensities) and/or H-aggregates (causing quenching of fluorescence). Majority of similar research on preparation of SM-dye systems with a use cationic organic molecules as a modifier (seldomly anionic or neutral) usually helped to suppress formation aggregates. The concept of this work has been led towards using innovative modifiers with the focus onto mechanisms of action. The main investigation took into account five concentrations of CV incorporated into HC (0.001–0.01 mM·g⁻¹). The additional modification had been conducted with several ethyleneamines. However, by now, only samples modified by diethylenetriamine (DET) has been concluded therefore only certain data for others ethyleneamines-HC samples will be presented. CV encompasses noncentrosymmetric octupolar molecule belonging to the triphenylmethine dyes. CV dye in solvent undergoes ultrafast relaxation and is believed to be due to nonradiative relaxation induced by rotation or torsion of the phenyl rings. The molecule of CV had been purposefully chosen due to its high symmetry accompanied with optical nonlinearity. The fluorescent lifetimes of CV in solvents had been observed to be within range of 50 fs – 260 ps with almost imperceptibly low quantum yields (QY) [1]. By incorporation of CV in the HC with further modification by DET led to the improvements of lifetimes of CV to the nanosecond scale (max. 3.1 ns) with quantum yields reaching 30 %. The overall mechanism of improved fluorescent properties had been investigated by several other methodologies.

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References

- [1] R. B. Finkelman, 2019. The Influence of Clays on Human Health: A Medical Geology Perspective. *Clays and Clay Minerals*, 67, 1 – 6.

THEORETICAL STUDY OF THE STABILITY OF POLY(2-METHYL-2-OXAZOLINE) - SAPONITE HYBRID STRUCTURE

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KEYWORDS: Clay polymer nanocomposites | DFT-D3 | Saponite

Saponite, characterized by a 2:1 trioctahedral structure, consists of two tetrahedral sheets enclosing a central octahedral sheet. The introduction of trivalent cations, such as Al^{3+} and Fe^{3+} , into the tetrahedral sheet generates a negatively charged layer, which is balanced by exchangeable interlayer cations (Na^+ , NH_4^+ , K^+ , Li^+ , Mg^{2+}). The unique composition of saponite imparts it with remarkable properties, including high swelling capacity, thermal stability. The high swelling capacity of saponite allows efficient intercalation of polymers, resulting in well-dispersed and exfoliated hybrid structures. The hybrids exhibit enhanced mechanical strength, thermal stability, barrier properties, and flame retardancy, owing to the reinforcing effect of the saponite clay. Moreover, the unique layered structure of saponite enables tailored properties, such as controlled release of encapsulated substances and improved gas barrier performance [1].

In this work, a study of interaction of saponite clay mineral with the pentamer of poly(2-methyl-2-oxazoline) (PMeOX) by the DFT-D3 method is reported. The Perdew, Burke, and Ernzerhof (PBE) functional based on the generalized gradient approximation (GGA) theory was used for the description of exchange correlation energy. The structural stability of the studied model (saponite with the pentamer of poly(2-methyl-2-oxazoline) (Sap-PMeOX) was determined by hydrogen bond analysis and calculated intercalation energy. (Fig 1).

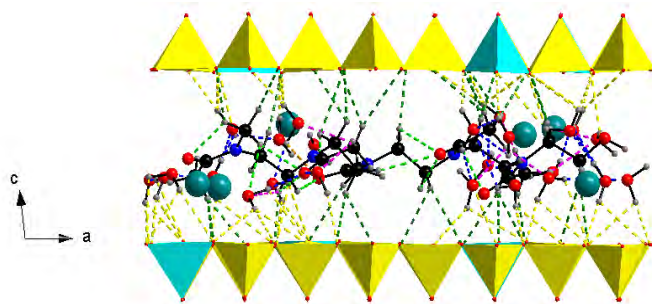


Fig 1. Optimized structure of saponite with the pentamer of poly (2-methyl-2-oxazoline) (Sap-PMeOX hybrid)

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References

- [1] C. Zhou, 2019. Modification, hybridization and applications of saponite: An overview, Applied Clay Science, 136-154.

PHOTOACTIVE HYBRID FILMS BASED ON CLAY MINERAL SAPONITE AND PHLOXINE B EFFECTIVELY ERADICATE STAPHYLOCOCCAL BIOFILMS

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KEYWORDS: Hybrid films | Nanomaterials | Antibiofilm | *Staphylococcus*

Staphylococcal biofilms formed on medical devices are responsible for life-threatening infections on over the world, especially biofilms formed by *Staphylococcus aureus*. Modifications of the surfaces can help prevent of formation of staphylococcal biofilms on medical devices. This research investigated the efficacy of polyurethane (PU) material modified with a hybrid film (HF) based on the clay mineral saponite (Sap) and poly(diallyldimethylammonium) (PDDA) and with functionalized phloxine B (PhB) [1] as a photoactive compound. The effectiveness of the material with HFs was tested before and after irradiation with a green laser ($\lambda = 532$ nm, 100 mW, duration of irradiation for 120 s).

Clinical isolate *S. aureus* L12 was confirmed to be resistant to oxacillin and fluoroquinolones such as ciprofloxacin and norfloxacin (MIC>256 $\mu\text{g/mL}$, MIC>32 $\mu\text{g/mL}$, MIC>256 $\mu\text{g/mL}$, respectively) using E-tests. The standard strain *S. aureus* CCM3953 was sensitive to tested drugs. The ethidium bromide agar screening method [2] showed a higher efflux activity for strain L12 compared to standard strain CCM3953. The results were confirmed by quantitative PCR (the $2^{\Delta\Delta}$ CT method) and demonstrated a 7.51 higher gene expression of the *norA* gene in 24-h biofilm of L12. The expression of the *norB* gene was not to be over-regulated in L12.

The preliminary test was performed only on strain CCM3953. The effectiveness was tested on polytetrafluoroethylene membranes covered with HFs prepared in different ratios of PhB/Sap ($n_{\text{PhB}}/m_{\text{Sap}}$: 0.5 mmol/g, 1.0 mmol/g, and 1.5 mmol/g). Results showed on a log scale: 2.03, 3.37, and 9.02 (100%) inhibition after irradiation. The efficacy of PU with modified surface containing PhB/Sap ratio ($n_{\text{PhB}}/m_{\text{Sap}}$) 1.5 mmol/g was demonstrated on a log scale 2.82 and 2.64 inhibition after irradiation for CCM3953 and L12, respectively.

Results claimed that PU material with modified surface containing HF with PhB can efficiently eradicate staphylococcal biofilms despite over-expressed the NorA efflux pump.

Acknowledgment:

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References

- [1] M. Pribus, Š. Budzák, L. P. Slušná, T. Š. Baranyaiová, Ľ. Jankovič, R. Mészáros, J. Bujdák, 2022. Luminescence of Reichardt's dye in polyelectrolyte-modified saponite colloids, *Colloids Surf A Physicochem Eng Asp.* 642, 128663.
- [2] M. Martins, M. P. McCusker, M. Viveiros, I. Couto, S. Fanning, J. M. Pagès, L. Amaral, 2003. A Simple Method for Assessment of MDR Bacteria for Over-Expressed Efflux Pumps, *Open Microbiol J.* 22;7:72-82.

POLYMER SURFACES MODIFIED WITH LAYERED SILICATES AND ORGANIC DYES

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KEYWORDS: Hybrid materials | Luminescence | Nanocomposite | Photosensitizers

The presentation is a summary and overview of the activities carried out within the project APVV-18-0075, which focused on polymer modified surfaces. Polymer modification was achieved by forming composite/nanocomposite phases using nanoparticles of layered silicate functionalized with organic dyes. The objective was to achieve nanocomposites with an increased particle concentration on the polymer surfaces. The results obtained in the different stages of the project are summarized here. The first stage of the project was related to the preparation of hybrid precursor nanoparticles pretreated with organic surfactants to achieve compatibility with the polymer, but also to activate efficient dye adsorption. Functionalization of the modified particles was another important task in this project. The methods had to be optimized and suitable precursors had to be selected to obtain functionalized systems exhibiting high photochemical and photophysical activities (Fig. 1). The last part of the project dealt with the formation of the composite materials themselves and the optimization of their properties in view of a suitable application. Versatile materials based on engineering polymers were designed and developed, using different types of organoclay precursors and photoactive dyes. Some systems achieved high photoactivity, luminescent and photosensitizing properties. Photodisinfectant and antimicrobial materials were also obtained, which could reduce the growth of bacterial biofilms.

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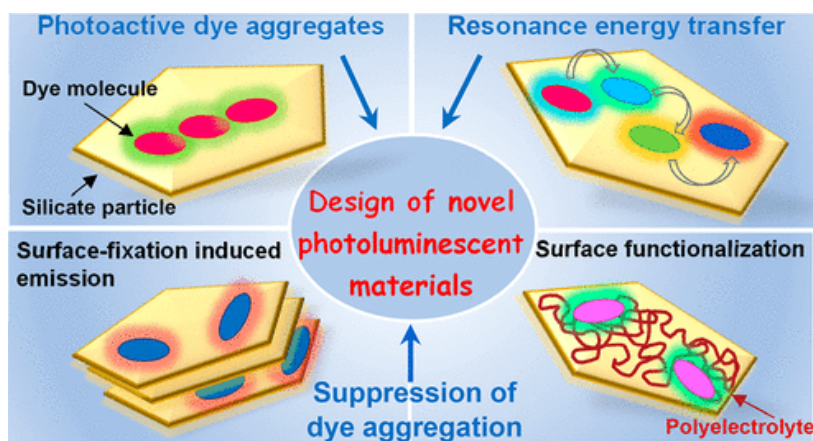


Fig. 1: Dye/silicate hybrid photoluminescent materials. "Reprinted with permission from J. Bujdák et al. J. Phys. Chem. B 2023, 127, 5, 1063–1073. Copyright 2023 American Chemical Society."

PRELIMINARY STATISTICAL ANALYSIS RESULTS OF THE MICHAĽANY-LASTOVCE BENTONITE DEPOSIT—SK

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KEYWORDS: Bentonite deposit | Smectite | Montmorillonite | Slovak bentonite

Michaľany–Lastovce deposit is one of the earliest discovered and studied bentonite deposits in Eastern Slovakia, comprises of Badenian–Sarmatian volcano-sedimentary assemblages, represented by various intensively argillitized rhyolite tuffs and tuffites, tuffitic clays and bentonites, scattered limnosilicite and diatomite and intercalated with marly calcareous clays [1]. This deposit has relatively appropriate properties on the point of the foundry industry and less favourable results as a bleaching clay [1, 2]. Sixteen samples were collected and investigated by different techniques to determine the petrographical and mineralogical characteristics. The studied samples exhibit varying amounts of smectite accompanied by almost the same quantity of opal-C/CT, as well as variable mineral admixtures such as feldspars, quartz, mica, kaolinite, and occasionally zeolite, carbonates, pyrite and marcasite [3]. The slightly higher pH values (more than 7) are due to the presence of carbonate phases, as confirmed by the correlation and regression analysis (74% at p-value 0.010, N=16). Montmorillonite and opal-C/CT were identified as the major components in the preponderance of the studied samples, with an amount between 38 to 45 wt.% and 33 to 44 wt.%, respectively, which reflects the almost 1:1 ratio between the two phases. It should, however, be emphasised that some samples contain less than 10% of both phases in the studied samples. This variable amount of the smectite and opal-C/CT content was also observed in the bentonite deposit of the same age in Northern Hungary [4]. The statistical results obtained so far indicate a slightly significant relation between the smectite content and opal-C/CT, depending on the depth; its content decreases with the depth and vice-versa with the opal-C/CT. The opal-C/CT displays a very significant negative correlation with the quartz (-93% at p-value 0.000, N=16). Moreover, a slightly considerable correlation (63% at p-value 0.008, N=16) was observed between the amount of opal-C/CT with the sand fraction (2–0.25 mm). However, further investigation is required to verify these results.

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References

- [1] J. Harcek, 1963. Závěrečná správa a výpočet zásob z ložiska Lastovce—bentonit. Archív. Geologický prieskum, n.p. Žilina, závod Spišská Nová Ves, 110.
- [2] I. Kraus, Z. Hroncová, S. Horský, A. Mihalic, 1989. Ložiská a výskyty bentonitov SSR, Mineralia Slovaca, 21, 525-531.
- [3] F.A. Gread, P. Uhlík, A. Biroň, M. Majdán, J. Šurka, J. Brčeková, O. Lintnerová, 2023. The Mineralogical Characterization of Michaľany-Lastovce Bentonite Deposit – East Slovakia, XXII International Conference of Young Geologists, Smolenice, Slovakia.
- [4] Z. Püspöki, M. Kozák, Á. Csámer, R. McIntosh, L. Vincze, 2003. Paleogeographic conditions and sequence stratigraphy of the Sarmatian sediment series in the Tardona Hills. Bulletin of the Hungarian Geological Society, 133, 191-210.

THE CHANGES OF RARE EARTH MODIFIED SILICATES UPON HEATING IN THZ REGION

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KEYWORDS: Smectites | THz-TDS spectroscopy | Refractive index | Dielectric properties

The rare earth elements (REE) promote materials research thanks to their interesting physical-chemical properties that affect material spectral properties in a various spectral region. However, there is less information available about the effect of REE on material properties in THz region and changes affecting the material refractive index (RI) with doping. The THz frequencies are currently considered in development of wireless communication by progress in 6G+ technologies at sub-THz frequencies e.g. above 100 GHz. These developments require dielectric resonators with high dielectric constant, high out-of-band suppression, low insertion loss, and high stability. The ceramic materials with dipole relaxations and dispersion of optical phonons are good candidates for materials with defined dielectric losses.[1] In our previous work by doping the lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$) with pyrochlore structure was found, that the doping by REE can enhance the dielectric permittivity of this material by 30%, if the lanthanum is replaced in the structure up to the 6%.[2] In the present work was investigated the effect of heating temperature used on silicate modified with REE affecting the change of its THz spectra in the range of 0.1-4.0 THz and refractive index compared at 1.5 THz. The heating of parent sample from room temperature 20 °C up to the 1200 °C resulted in high-temperature phase formation. The RI at 1.5 THz changed for non-modified material for 9.9%, while the modification with REE resulted in the RI change for 24% after sample heating to the temperature indicated.

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References

- [1] H. Elayan, O. Amin, B. Shihada, R.M. Shubair, M.-S. Alouini, 2019. Terahertz band: the last piece of RF spectrum puzzle for communication systems, *IEEE Open J. Commun. Soc.* 1, 1–32.
- [2] M. Janek, R. Klement, M. Naftaly, E. Trusova, A. Gatial, P. Veteška, Ľ. Bača, 2022. Terahertz response of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{La}_2\text{Zr}_2\text{O}_7$ synthesised using the sol-gel precipitation method, *Colloids Surfaces A: Physicochem. Eng.* 644, 128836.

HERBICIDES ADSORBED ON THE IMOGOLITE NANOTUBE

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KEYWORDS: Imogolite | Diuron | Atrazine | Molecular simulation methods

Imogolite mineral is an aluminosilicate that can be a promising sorbent for herbicides due to its nanotubular shape with two differentiated surfaces (an outer surface with hydroxyl groups, and an inner one with silanol groups). In the present study, the potential interactions of imogolite mineral with the herbicides diuron and atrazine have been investigated via theoretical approaches to characterise the mineral as a potential adsorbent for water or soil treatment applications.

The geometry optimisation and the molecular dynamics were performed using COMPASS force field [1]. The models with different ratios of herbicides on the inner/outer surfaces were prepared from the best initial models to study how the interactions between the herbicides and the imogolite vary. Furthermore, to consider the influence of a higher concentration in the interactions, three more herbicide molecules were added on the outer surface. Finally, the way of sorption/release of the herbicides was studied by preparing edge models from the periodical imogolite structure, adding a vacuum of 35 Å, and H atoms to the dangling atoms in the edges.

Force Field calculations showed stronger interactions between imogolite outer surface and herbicides. Otherwise, when herbicides interacted with the inner surface diuron molecules had a better adaptation to the nanotubular shape by torsion, unlike atrazine molecules due to their molecule length and rigidity. The release of the herbicides from the imogolite nanotube showed the unstable nature of both herbicides when they were loaded on the inner part of imogolite, which is in agreement with the sorption studies that proved the preference for herbicides on the outer surface and the edges of the minerals. Water molecules played a crucial role in the complexes related to imogolite properties as its inner surface is more hydrophilic. When herbicides were loaded on the outer surface, water molecules were the intermediate medium for the sorption of herbicides creating hydrogen bonds. In contrast, on the inner surface, the herbicide molecules had a competed behaviour to water. These results would be a first step to compare in future work the effect of the interactions of different polymers on imogolite surfaces to improve the adsorption capacity of herbicides.

Acknowledgment:

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References

[1] H. Sun, 1998. Compass: an ab initio force-field optimized for condensed-phase applications - overview with details on alkane and benzene compounds, J. Phys. Chem. B. 102, 7338–7364.

THE MECHANISM OF ADSORPTION-INDUCED EMISSION OF CATIONIC DYES IN SMECTITE COLLOIDS

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KEYWORDS: Molecular aggregation | TD-DFT | Spectral properties | Cationic dyes

The interaction between cationic dyes and the surface of clay minerals can lead to various phenomena that cause changes in their photoactive properties. They include molecular aggregation, resonance energy transfer, and Surface Fixation Induced Emission (S-FIE), which is the focus of our work.

When dye molecules are fixed onto the smectite surface, they undergo planarization, resulting in a shift of their absorption bands to longer wavelengths. Furthermore, this process inhibits molecular motion, and can thereby promote radiative deactivation processes such as fluorescence and phosphorescence [1].

In this work, we focused on the cationic dye pseudoisocyanine (PIC), which has been well studied in the past mainly because of unique photophysical properties of PIC J-aggregates. We present the phenomenon of the emission from monomeric PIC species adsorbed on smectite surfaces which has not been observed before.

Utilizing theoretical and computational chemistry methods, we analysed the vibronic structure of the spectra and provided an explanation for the strong luminescence observed in the PIC monomer. In an aqueous solution, the bending of the molecule promotes non-radiative deactivation of the excited state. However, the adsorption of PIC molecules onto smectite particles induces a change in the dihedral angle between the pyridine subunits, impeding the non-radiative deactivation pathways and promoting emission [2].

Ongoing research suggests that the S-FIE phenomenon can be expected for other types of dyes as well. The choice of smectite and the composition of the hybrid system are determining factors affecting this phenomenon.

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References:

- [1] J. Bujdák et al., 2023. Adsorption of Dye Molecules and Its Potential for the Development of Photoactive Hybrid Materials Based on Layered Silicates, *The Journal of Physical Chemistry B*, 127, 1063–1073.
- [2] P. Boháč et al., 2022. Adsorption-Induced Fluorescence of Pseudoisocyanine Monomers in Systems with Layered Silicates. *The Journal of Physical Chemistry C*, 126, 17255–17265.

ACTIVE POLYMER SURFACES FUNCTIONALIZED WITH PHLOXINE B

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KEYWORDS: Composites | Organoclay | Phloxine B | Photoactive surfaces

Lately there is a strong demand of novel polymers with active surfaces acting as photosensitizers. These materials they can be used for biomedical applications for disinfection and treatment. The photoactivity of these surfaces plays a key role to achieved these properties. A perfect candidate hybrid material suitable for this purpose, are the clay/dye particles. The clay minerals are used as a carrier for the photosensitizer organic dyes creating a more stable solid-state material. The modification of the polymer surface option for the improvement of the optical properties by the assembly of the clay/dyes nanoparticles located in the polymer surface [1].

In this work saponite nanoparticles were first organically modified by dimethyldioctadecylammonium bromide (DODA) surfactant and subsequently functionalized with phloxine B (PhB) organic dye in six different concentrations forming a solid film. Afterwards the organoclay film was deposit onto the poly(caprolactone) surface via melt fusion. The succesfull intercalation at the interface between the organoclay film and the poly(caprolactone) surface was confirmed from the XRD diffraction patterns. The increased of the interlayer space of saponite by 1 nm in relationship with the precursor organoclay film (d -spacing= 2.22 nm) means that the polymer chains were introduced into the saponite structure. The photoactivity of the sample were investigated by fluorescence spectroscopy. The optical properties of the samples were in a close relation with the final PhB concentration in the polymer surface. The sample with the highest photoactivity was for the sample with the lowest PhB concentration.

This novel technique for the development of new photoactive polymer surfaces can broadly be applied in other polymer surfaces as well. The organoclay solid film, with thickness of few micrometers, can also be tailored according with the requirements set for any application in the future.

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References

[1] E. Skoura et al., 2022. Modified Polymer Surfaces: Thin Films of Silicate Composites via Polycaprolactone Melt Fusion, *International Journal of Molecular Sciences*, 23, 9166.

STRUCTURAL CHARACTERIZATION AND PHYSICO-CHEMICAL PROPERTIES OF CLAY-BASED GEOPOLYMERS/ZEOLITES

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KEYWORDS: Geopolymers | Metabentonite | Metakaolin | Alkaline activator

Metakaolin and metabentonite were prepared by thermal treatment of the source clays, kaolin and bentonite, and their potential for geopolymer/zeolite formation was evaluated by FTIR, TGA/DSC, PXRD, HT PXRD, SEM, and BET analysis. For the preparation of geopolymers, the calcination temperature of 700, 750 and 800 °C with holding time 3 hours was used. The concentration of the alkaline activator (NaOH) was 5, 10 and 20 mass% and curing conditions 7 days at 80 °C. From FTIR results is clearly visible as the concentration of alkaline activator (5, 10, and 20 mass%) and calcination temperature (700, 750, 800 °C) increases, the band attributed to $\nu\text{Si-O}$ and $\nu\text{Al-O}$ gradually shifts to lower wavenumber. The shift is caused by the presence of non-bridging oxygen in the network, the incorporation of Si and Al into geopolymeric gel, and the state of hydration of the reaction products. The higher the NaOH concentration, the more promoted formation of hydrated aluminosilicates and the more enhanced Al^{3+} incorporation can be observed regardless of the initial material. The 10% NaOH seems to be the optimal concentration for alkali activation of metakaolin samples leading to the dominant geopolymer formation. Further increase in alkaline activator concentration resulted in a significant rise of zeolite ratio (predominant zeolite A and P). Following the bentonite character, the activity of metabentonite is much more strongly conditioned by temperature. Geopolymer formation was promoted mainly using 800 °C and 10% NaOH. The use of 800 °C and 20% NaOH seems to be the optimal concentration for alkali activation of metabentonite. From BET analysis, the value of $218.95 \text{ m}^2 \text{ g}^{-1}$, determined for metabentonite activated by 20 mass% NaOH seems to be very promising for adsorption processes. The opposite effect was observed for the metakaolin-based samples, and this result is caused by the increased formation of zeolite phases and corresponding changes in their channel dimensions.

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References

- [1] M. Slaný, E. Kuzielová, M. Žemlička, M. Matejdes, A. Struhárová, Martin T. Palou, 2023. Metabentonite and metakaolin-based geopolymers/zeolites: relation between kind of clay, calcination temperature and concentration of alkaline activator, *J. Therm. Anal. Calorim.*, <https://doi.org/10.1007/s10973-023-12267-1>.

STRUCTURAL CHARACTERISATION OF POLY(2-METHYL-2-OXAZOLINE)- AND TETRABUTHYLPHOSPHONIUM-MODIFIED MONTMORILLONITE AFTER ADSORPTION OF TOXIC HEXAVALENT SELENIUM OXYANIONS

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KEYWORDS: Hexavalent selenium | DFT-D3 | Modified montmorillonite

Selenium (Se) is a natural trace element naturally occurring in water, soils, and living organisms, including foods. It is also introduced into the environment by anthropogenic activities, such as mining and the combustion of fossil fuels [1].

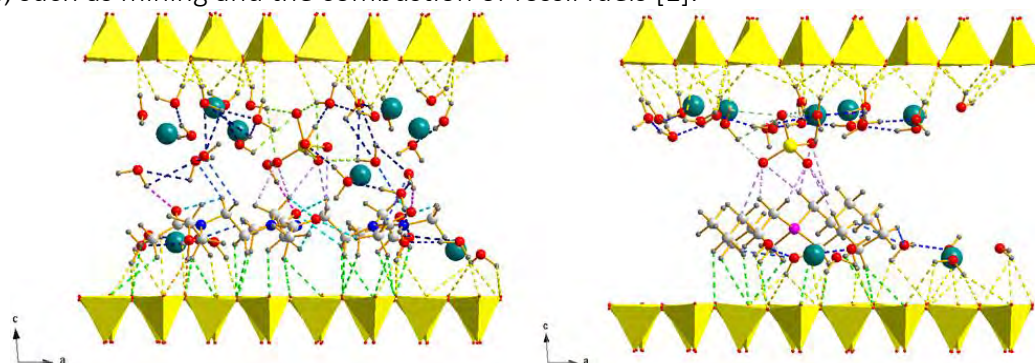


Fig. 1 Optimised structural models of Se-POx-Mt (left) and Se-TBP-Mt (right) with various types of HB interactions.

This work presents the study of the adsorption of toxic selenium oxyanions, specifically selenate (SeO_4^{2-}) anion, into the interlayer space of montmorillonite clay mineral modified by poly(2-methyl-2-oxazoline) polymer matrix and tetrabutylphosphonium (TBP) surfactant. The main goal of this research is to provide a comprehensive study of the structure of calculated models (Fig. 1). The structural stability of individual systems was determined by analysing the strength and number of hydrogen bond interactions in combination with the calculated intercalation energies. In addition, the vibrational density of states obtained from the calculated spectra using the ab initio molecular dynamics (AIMD) method were analyzed and compared with experimental FTIR spectra from the literature.

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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 Sci. Soc. Am. J.*, 70, 192–203.

POSTER PRESENTATIONS

ENHANCED SINGLET OXYGEN PHOTOSENSITIZATION VIA ADSORPTION-INDUCED EMISSION IN HYBRID SYSTEMS OF PORPHYRINS AND LAYERED SILICATES

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KEYWORDS: Singlet oxygen | Hybrid materials | Molecular aggregation | Adsorption induced emission

The ability of various dyes to sensitize highly reactive singlet oxygen is a useful tool with potential applications in synthetic photochemistry, environmental and medical fields, such as antibacterial materials. However, for many of these applications, it is necessary to immobilize the photosensitizers on solid carriers, which can pose a challenge due to molecular aggregation of the dye molecules, leading to reduced singlet oxygen production [1].

This study investigates the relationship between molecular aggregation of two metallo-porphyrin-based photosensitizers and singlet oxygen production efficiency in hybrid systems with synthetic saponite Sumecton SA. We controlled the molecular aggregation of porphyrins by varying the silicate/dye ratio ($n_{\text{dye}}/m_{\text{silicate}}$ - mmol/g) and/or by pre-modifying saponite with cetyltrimethylammonium cation [2].

Experimental results showed that the most effective production of singlet oxygen was observed in samples with the lowest loading of photosensitizer on smectite. We attribute this to the suppression of molecular aggregation of the dye, which can lead to a decrease in the efficiency of singlet oxygen production. In addition to loading, we found that premodification of smectite with a surfactant also had an effect on dye aggregation. The surfactant modification further suppressed molecular aggregation, leading to an increase in the efficiency of singlet oxygen production. Furthermore, the results confirmed the phenomenon of increasing the quantum yield of singlet oxygen due to adsorption-induced emission which is a consequence of the planarization of metallo-porphyrins on the smectite surface. This planarization suppressed the non-radiative deactivation of molecules.

These findings provide insights into optimizing singlet oxygen production in photosensitizer immobilization on solid carriers, which could have significant implications for the development of new applications in various fields.

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References

- [1] I. Pibiri, S. Buscemi, A. Palumbo Piccionello, A. Pace, 2018. Photochemically Produced Singlet Oxygen: Applications and Perspectives, *ChemPhotoChem.*, 2 (7), 535–547.
- [2] J. Bujdák, T. Baranyaiová, P. Boháč, R. Mészáros, 2023. Adsorption of Dye Molecules and Its Potential for the Development of Photoactive Hybrid Materials Based on Layered Silicates, *J. Phys. Chem. B.*, 127 (5), 1063–1073.

ADVANCED APPROACHES FOR TESTING ANTIMICROBIAL ACTIVITY OF HYBRID FILMS BASED ON CLAY MINERALS

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KEYWORDS: Clay-based film | Testing | Antimicrobial | Biocompatibility

The development of various nanomaterials with antimicrobial and anti-biofilm properties is an important part of current material research. While testing single-component materials is usually easy, testing composite systems is more complicated. This is because the possible effect of each component has to be tested alone to obtain accurate information on the possible contribution to the activity. Several methods are available, but they must be optimized concerning the system being tested.

Composite nanomaterials based on clay minerals with an immobilized photosensitizer (PS) represent complex systems, therefore optimization of methods focused on antimicrobial properties is not easy and requires a lot of experience. *In vitro* assays summarize the detection of cell survival based on the calculation of colony-forming units set at 1 ml. This technique is time-consuming and the human factor is not negligible, since the procedure involves many steps requiring precision. Therefore, the use of molecular biology techniques employing commercial kits should be simple and more accurate. One such technique is the determination of the number of genomic units using the propidium monoazide dye. This method seems to be more useful, especially in the study of multi-species biofilms, when the number of genomic units of all representatives of microorganisms can be determined in one sample. Microscopic techniques have an irreplaceable place in terms of determining the possible effect (electron microscopy) or direct detection of dead cells using propidium iodide staining (Confocal Laser Scanning Microscopy). The above techniques can be combined with molecular biology methods, for example, quantitative PCR to determine changes in gene expression of microorganisms forming biofilm on composite materials. This information provides insight into what is going on in the microbial cells. The effect of materials with immobilized PS can also be studied using biochemical methods to determine generated H₂O₂.

In addition, it is possible to study biocompatibility using *in vivo* models. Since the use of vertebrate models is governed by the strict rules of the EU Commission, non-vertebrate models are suitable for preliminary experiments. The greater wax moth *Galleria mellonella* is used as a model organism providing a lot of information compatible with the human response.

It can be summarized that there are several options for testing new materials, but the choice of approaches and their optimization must be adapted to the relevant nanomaterial.

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HYBRID SYSTEM BASED ON SMECTITE AND ANIONIC ORGANIC DYE PREPARED BY LAYER-BY-LAYER METHOD

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KEYWORDS: Layer by layer | Sumecton | Phloxine B | Plasma activation

Nanomaterials and hybrid materials with a controlled distribution of nanoscale components can exhibit unique physical, chemical, mechanical, and optical properties. One of the simplest methods used for the formation of hybrid materials with layered structure is layer-by-layer (LBL) deposition. It is a simple procedure, suitable for the construction of thin hybrid films at the molecular level with well-defined structures and compositions [1]. LBL assemblies are prepared by step-by-step molecular deposition, using a strategy of alternating the charge of the surface during the deposition. Deposited layers can be effectively manipulated using this technique, it provides a route for the formation of various layered structures at the molecular level [2]. The aim of this work was to perform a detailed investigation of the spectral changes taking place during the formation of LBL assemblies based on layered silicate (Sumecton – S), anionic organic dye (Phloxine B – PhB), and polycationic electrolyte (Poly(diallyldimethylammonium chloride) – PDDA). The polycarbonate glass (PCG), used as substrate for LBL films, was activated by plasma for 30 s at ambient air and dived to PDDA solution (1 wt. %). After the activation the PCG was dived to stock solutions of PhB ($5 \cdot 10^{-6}$ mol.dm⁻³), S (0.5 g.dm⁻³) and again PDDA and it was marked as the first layer of LBL film. Films were prepared by alternating layers of cationic PDDA molecules and negatively charged PhB and S until reaching of 10 layers of LBL film. The absorption and emission spectra were measured after each step of LBL assembly deposition. The absorption spectra exhibited maximum absorbance near 559 nm, which is similar to other PhB systems. As the number of PhB/S/PDDA layers increased, absorbance values progressively increased, which correlated with an increasing amount of PhB anions in the film. Although the deposition of each new S, resp. PDDA layer caused a significant decrease in the absorbance. The emission spectra exhibited maximum intensity near 570 nm. Similar to absorption spectra, the intensity values progressively increased with increasing number of PhB/S/PDDA layers. The deposition of each new PDDA layer caused increase in the intensity. A detailed study of this LBL system is necessary due to interesting preliminary results.

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References

- [1] J. Bujdák, 2014. Layer-by-layer assemblies composed of polycationic electrolyte, organic dyes, and layered silicates, *J. Phys. Chem. C*, 118, 7152–7162.
- [2] P. Boháč, R. Sasai, W. Soontornchaiyakul, A. Czímerová, J. Bujdák, 2021. Resonance energy transfer between cyanine dyes in hybrid films of layered silicate prepared by layer-by-layer method, *Appl. Clay Sci.*, 202, 105985-1-105985-9.

ANALYSIS OF INFRARED SPECTRA IN THE SYSTEMS CLAY MINERAL/ORGANIC SURFACTANT/DYE

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KEYWORDS: infrared spectroscopy | dye | organoclay | chemometric methods

The pigments exhibiting luminescent properties were analysed by evaluation of ATR (attenuated total reflectance) IR spectra. The aim of the study was to evaluate the relationship between individual components in the pigments, i.e. smectite (Sm), laser dye rhodamine 6G (R6G), and organic surfactant tetraoctylphosphonium. The amount of organic surfactants varied from 0-100 % with respect to the cation exchange capacity of smectite, and dye concentration was in the range of 0.001 to 0.08 mmol/g.

ATR infrared spectra in the middle IR (MIR) region displayed the absorption bands characteristic for smectites. Furthermore, the bands assigned to the C-H vibrations of both organic cations, with the shape of the bands depending on the type of organic surfactant appeared in the spectral region 3000-2800 cm⁻¹ and 1600-1300 cm⁻¹. The intensity of the bands within the series increased with the content of an organic phase. The presence of R6G was detectable in the spectra of Sm based on the bands assigned to the C=O and C-H vibrations of aromatic rings or methyl groups at 1717, 1650, 1610, 1533, and 1502 cm⁻¹ [1]. For organo-smectites, the absorption bands of R6G were detectable even for the samples with the highest loading of organic quaternary cations, i.e., for samples with pronounced overlapping bands of both organic molecules. Visibility of the bands decreased significantly with the dye amount of 0.005 mmol/g and the bands were not detectable directly in the spectra for the samples of the lowest R6G concentration (0.001 mmol/g). The chemometric and statistical analyses were used to evaluate components contributing to the spectral profiles and to discriminate individual components present in the spectra. Multivariate curve resolution (MCR) analysis of the complete series confirmed the presence of five components contributing to the spectra. Component attributed to Sm without (C1) and with (C2) organic phase contributed the most significantly to the IR spectra. MCR concentration of both individual components depended on the extent of surfactant loading, C1 decreased with increasing amount of TOP, while C2 showed an adverse trend. An interesting result is the observation of component Sm+R6G (C3) which also showed increasing MCR concentration with the amount of R6G present in the system. Applying chemometric methods can help to recognize and characterize relatively complex phases of hybrid or ternary organoclays.

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References:

[1] Majoube M., Henry M. (1991) Fourier transform Raman and infrared and surface-enhanced Raman spectra for rhodamine 6G. *Spectrochimica Acta Part A: Molecular Spectroscopy* 47, 1459-1466

PREPARATION OF ANTIMICROBIAL FILMS BASED ON LAYERED SILICATE AND PHOTOACTIVE DYE

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KEYWORDS: Phloxine B | Saponite | Composite nanomaterial | Antimicrobial material

The formation of microbial biofilms on medical devices is undesirable because it can cause serious infections. The use of antibiotics is usually not an effective option to prevent the formation of biofilms due to increasing antimicrobial resistance [1]. Hybrids based on nanoparticles of layered silicates modified with organic molecules are perspective materials for a wide range of medical applications, including antimicrobial treatment [2].

Particles of synthetic saponite - Sumecton (Sap), used as a carrier of phloxine B (PhB) molecules, had to be pre-modified due to their negative surface charge. For this purpose, a cationic polymer poly(diallyldimethylammonium) (PDDA) was used. Thus, the synthesis was carried out in two steps: modification with PDDA cations and adsorption of PhB anions. The final concentration of Sap in the prepared mixture was 0.1 g L⁻¹, and the loading of PDDAC and PhB was 1.5 mmol g⁻¹. The prepared mixture was stirred at room temperature and 20 mL was filtered through a Teflon filter and washed with distilled water to remove non-adsorbed PhB by vacuum filtration. A liquid precursor of transparent polyurethane (PU) was applied to the surface of the thin PhB/PDDAC/Sap films. Finally, the prepared polymer composites were air-dried and cured at room temperature.

The modified PU surface was characterized by physicochemical methods to determine the structure and photoactivity of the prepared materials. The PU disks with modified surfaces were also used in microbiological tests to characterize their efficiency in reducing the growth of biofilms.

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References

- [1] 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.
- [2] R. B. Finkelman, 2019. The Influence of Clays on Human Health: A Medical Geology Perspective. *Clays and Clay Minerals*, 67, 1 – 6.

ADSORPTION OF RIFAMPICINE DRUG ON MONTMORILLONITE

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KEYWORDS: Rifampicin | Montmorillonite | Adsorption | Computational method

Tuberculosis (TB), an infectious disease caused by *Mycobacterium tuberculosis*, is still a global health problem being the reason for over one million deaths every year worldwide [1]. Rifampin is a semi-synthetic derivative of rifamycin B. It inhibits DNA-dependent RNA polymerase of mycobacteria and other microorganisms by forming a stable drug-enzyme complex [2].

The synthesis and characterization of the hybrid material of montmorillonite (Mnt) as a possible suitable carrier and the rifampicin (RIF) drug was performed to clarify its structural stability. The density functional theory calculations with involved dispersion corrections (DFT-D3) were performed to characterize interactions acting in the interlayer space of montmorillonite intercalated with the rifampicin drug. The structure and stability of the RIF-Mnt intercalated complex were determined. Theoretical calculations revealed the deformation of the molecular structure of rifampicin after intercalation into the Mnt interlayer space due to the clay environment. The *ansa* chain of RIF was bent in the interlayer space compared with the structure of the RIF molecule in the monocystal structure. RIF was anchored on the Mnt surface via different hydrogen bonds of weak-to-moderate strength. The calculated vibrational spectrum from *ab initio* molecular dynamics (AIMD) agreed well with the FTIR measured spectra and helped to detect the overlapped vibrational bands in the experimental spectrum. Based on the analysis of the structural stability, theoretical calculations revealed that the Mnt clay is a suitable drug carrier for the postponed release of the RIF drug. Batch adsorption experiments showed the high adsorption capacity of montmorillonite for RIF. The further study of interactions of this hybrid structure with suitable polymers as coating materials for better postponed release is suitable.

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References

- [1] WHO, 2018. Global Tuberculosis Report 2018, Geneva, <https://apps.who.int/iris/handle/10665/274453>.
- [2] M. Hanumanaik, K.V. Kumar, G. Kiran, G.S. Rao, 2020. Formulation, characterization and evaluation of solid lipid nanoparticles of selected antitubercular agent, *International Journal of Pharmaceutical Sciences and Research*, 11(8), 3734-3744.

ADSORPTION OF CU(II) ONTO CLAY BASED GEOPOLYMERS

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KEYWORDS: Clay | Geopolymer | Adsorption | Cu(II)

Geopolymers are a favorable class of materials for the elimination of harmful substances from industrial and household liquid waste. The synthesis of geopolymers involved the reaction of solid precursor materials with an alkali activator. Three different systems were used, including metaphase of kaolinite of Serbian origin (GPS), metaphase of German clay (GPG), and a mixture of German clay and carbon cloth (GPGC). The carbon cloth was obtained through a carbonization process, and the metaphases were prepared by calcining kaolinite and clay at high temperatures. The alkaline activator solution was created by mixing solutions of Na_2SiO_3 and NaOH with specific concentrations. The different metaphases and alkaline activators were mixed, and the resulting pastes were poured into molds and allowed to cure. [1]

The geopolymer samples were then characterized using X-ray diffractometry (XRD), Diffuse Reflectance Infrared Fourier Transform (DRIFT) analysis, and Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS). XRD analysis confirmed the presence of sodium aluminosilicates in all geopolymer samples, and specific vibrational bands indicated the occurrence of geo-polymerization. SEM analysis revealed a dense, amorphous, porous structure suitable for adsorption.

The adsorption capacity of the geopolymers followed a specific trend, with the geopolymer containing carbon cloth showing the highest adsorption capacity. The adsorption capacity of used geopolymers followed the trend: GPGC > GPG > GPS. Isotherm studies indicated that the Langmuir isotherm model with maximum adsorption capacities of 72.86, 70.29 and 58.30 mg g^{-1} for Cu(II) on GPGC, GPG and GPS respectively, provided the best fit for the experimental data, and the adsorption equilibrium was well-described by this model. The experimental and theoretical data from the kinetics study supported the pseudo-second order of the adsorption process. The removal efficiency (*Ads. %*) were in accordance with this statement (96.92, 93.67 and 85.93 % for GPGC, GPG and GPS, resp.) for the initial concentration of Cu(II) $c_0 = 50 \text{ mg L}^{-1}$.

The results indicated that all investigated geopolymers were capable of immobilizing and adsorbing Cu(II) ions from aqueous solutions. The findings contribute to the development of cost-effective and environmentally friendly methods for removing toxic metal ions from water sources.

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References

- [1] L. M. Kljajević et al., 2017. Structural and Chemical Properties of Thermally Treated Geopolymer Samples. *Ceram. Int.* 43, 6700.
- [2] M. Ivanović et al., 2021. The Influence of Thermodynamic Parameters on Alkaline Activator of Geopolymers and Structure of Geopolymers, *Maced. J. Chem. Chem. Eng.* 40, 99.

COMPARISON OF CHEMICAL COMPOSITION OF BENTONITES, K-BENTONITE AND PERLITES FROM THE JASTRABÁ FORMATION (SLOVAKIA)

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Slovak deposits of perlite, bentonite and K-bentonite are related to Neogene volcanism. The most exploited bentonite and two most significant perlite deposits are located in the Central Slovakia Volcanic Field (CSVF) in Jastrabá formation. Jastrabá Fm. is represented by rhyolitic dykes, extrusive domes, cryptodomes, lava flows, related volcanoclastic rocks and lacustrine sedimentary rocks. The aim of the contribution is to compare the chemical composition of selected bentonites, K-bentonite (Dolná Ves) and perlites from Jastrabá Fm. Perlite is parental rock for most studied bentonite according to macroscopical, microscopical studies and application of computed tomography (CT). Our study tries to use the composition of major, minor and trace elements of bulk rocks and clay fractions for better understanding of the processes that accompanied the alteration of perlite volcanic glass to bentonite (montmorillonite) and K-bentonite (mixed layered illite-smectite). The comparison of major elements of perlites and bentonites shows that high-grade bentonites were affected by the same transformation mechanism. There was leaching of excess Si and alkali (Na and K), which were released during the transformation of volcanic glass into montmorillonite. Bentonites have higher content of Fe than perlites but this increase are only relative caused by releasing of Si and alkalies. An absolute increase in Mg content is observed in bentonites. A smaller absolute increase in Mg content was also observed in K-bentonites. Simultaneously, the area around the Kremnica is built by andesites that have 8-9-times higher MgO content than rhyolites. Practically the same proportions of non-mobile elements La/Yb, Nb/Ta and Zr/Hf of bentonites, K-bentonite and perlites from the Jastrabá Formation point to rhyolite (perlite) as the parent rock for bentonites. It looks, however, that alteration increased amount of REE in comparison with parent perlites (perlites: 171 ppm < K-bentonite: 247 ppm < bentonites: 249 ppm < clay fraction from bentonites: 318 ppm < clay fraction from K-bentonite: 392 ppm of REE).

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