



**UNIVERSITY
OF LATVIA**

**Summary
of Doctoral Thesis**

Rūta Ozola-Davidāne

**DEVELOPMENT AND
CHARACTERIZATION
OF CLAY-BASED COMPOSITES FOR
INNOVATIVE AND ENVIRONMENTALLY
FRIENDLY APPLICATIONS**

Rīga, 2022



UNIVERSITY OF LATVIA

FACULTY OF GEOGRAPHY AND EARTH SCIENCES
DEPARTMENT OF ENVIRONMENTAL SCIENCE

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DEVELOPMENT AND CHARACTERIZATION OF CLAY-BASED COMPOSITES FOR INNOVATIVE AND ENVIRONMENTALLY FRIENDLY APPLICATIONS

Summary of doctoral thesis

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INVESTING IN YOUR FUTURE

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The doctoral thesis and its summary are available at the Library of the University of Latvia, Raiņa bulvāris 19, Rīga.

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ABSTRACT

Chemicals Strategy for Sustainability, which is a part of the European Green Deal, highlights the importance of developing environmentally friendly technologies and increasing the usage of safe and sustainable materials that are not harmful to people and the environment. The solution suggested in the doctoral thesis is to replace synthetic and toxic substances in environmental technologies with natural, abundant and low-cost materials – clay minerals. The study aimed to develop and characterize clay minerals modified with organic and inorganic substances and experimentally test newly synthesized composite materials for applications in innovative and environmentally friendly technologies. Smectite type clay minerals were modified by two approaches: (1) covering clay with another inorganic material (iron oxy-hydroxides or hydroxyapatite) providing new sorption centres; (2) intercalating the organic modifiers (surfactants or ionic liquids) into the clay mineral interlayer space to provide hydrophobic properties. The clay-based composites were characterized by using multiparameter methods which included the analyses of the structural, morphological, and chemical composition of modified materials. Additionally, the sorption performance of newly developed materials was studied to investigate the application opportunities in environmental technologies.

The results reveal that modification methods provide possibilities for changing clay properties purposefully, including integrating new functional groups into their structure as well as changing physical and chemical properties thus supporting the development of new application prospects. Clay-hydroxyapatite and clay-iron oxy-hydroxide composites have high performance for removal of inorganic pollutants (arsenic), rare earth elements (lanthanum, neodymium, cerium) and other valuable elements (silver, aluminium). In turn, clay-surfactant and clay-ionic liquid materials showed high removal efficiency of toxic organic pollutants (Congo red, *p*-nitrophenol) due to provided hydrophobic properties. Consequently, it can be concluded that clay minerals modified with ionic liquids, surfactants, iron oxy-hydroxide and hydroxyapatite can be successfully used in solid-liquid sorption systems to remove pollutants or recover valuable elements from waste streams. Additionally, clay-anthocyanin composites were synthesized and suggested as freshness indicators for food quality control.

Keywords: clay; smectite minerals; clay modification; organic and inorganic modifiers; sorbents; organic and inorganic pollutants; elements recovery; water and wastewater treatment; freshness indicators.

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ABBREVIATIONS

AIPEA	Association Internationale pour l'Etude des Argiles
Bent clay	Bentonite, sodium form produced from Alfa Aesar
BET	Brunauer, Emmett and Teller method
BTMAC	benzyltrimethylammonium chloride
C ₁₂ mimCl	1-dodecyl-3-methylimidazolium chloride
C ₄ mimCl	1-butyl-3-methylimidazolium chloride
C ₈ mimCl	1-octyl-3-methylimidazolium chloride
CEC	cation exchange capacity
CMS	The Clay Minerals Society
CR	Congo red
DDAO	dimethyldodecylamine N-oxide
DTAC	dodecyltrimethylammonium chloride
FeOOH	iron oxy-hydroxide
FTIR	Fourier-transform infrared spectroscopy
Hap	hydroxyapatite
J clay	Jurassic System clay from the Legernieki deposit
LDH	layered double hydroxide
Mt clay	Montmorillonite K10 produced from Sigma-Aldrich
NMO	4-methylmorpholine N-oxide
PNP	<i>p</i> -nitrophenol
SEM	scanning electron microscopy
SSA	specific surface area
T clay	Triassic System clay from the Saltiski deposit
TG	thermogravimetry
XRD	X-ray diffraction

INTRODUCTION

There is a growing need for nature-based materials for applications in industry, environmental technologies and other fields to reduce the utilization of synthetic substances. For example, synthetic materials are increasingly used in environmental technologies as fillers, sorbents, materials for environmental remediation and other fields. One of such prospective material groups for applications in environmental technologies is clays (Sverdrup and Ragnarsdóttir, 2014).

According to the joint nomenclature committees of Association Internationale pour l'Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS) 'clay' is defined as "naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden, when dried or fired" (Guggenheim and Martin, 1995). In Latvia, there is a significant amount of different groups of clays found in 287 deposits (Stinkule, 2014; LEGMC, S.a.). However, clays have several major limitations related to their surface properties, physical shape and chemical composition. A solution to expand clay application potential is their modification using a targeted design approach in order to create materials that would have the necessary properties.

An example of such a modification method is the synthesis of organoclays (Guégan, 2019). Organoclays are prepared by modifying clay minerals (mainly smectites) with organic compounds (mainly surfactants) through the intercalation process and surface grafting (Park et al., 2011; He et al., 2014; Guégan, 2019). The modification changes the clay surface properties from hydrophilic to hydrophobic and increases the interlayer space of the clay mineral. The resulting materials can be effectively used as sorbents for the removal of organic and inorganic contaminants from soil and aquatic environments (Li and Bowman, 2001; Rodríguez-Cruz et al., 2007; Aftafa et al., 2014; Fiscal-Ladino et al., 2017).

Another method of clay modification is to use inorganic substances, such as iron-oxyhydroxide, as a coating agent for clay surfaces (Lenoble et al., 2002; Krauklis et al., 2017; Ozola et al., 2019b). Raw clays are widely used for the sorption of cationic pollutants, but the modification of clays with iron compounds also ensures the sorption of negatively charged pollutants, such as arsenic, phosphorus and antimony (Boujelben et al., 2008; Singh et al., 2015). The processes determining this ability are adsorption to surface hydroxyl groups, anionic exchange and coprecipitation (Smedley un Kinniburgh, 2002). However, other groups of properties can be of importance and thus the need for the development of clay modification methods and their applications to solve environmental problems are up-to-date.

The **aim** of this research work is to develop and characterize clay and clay minerals modified with organic and inorganic substances and experimentally test

newly synthesized clay composite materials for applications in innovative and environmentally friendly technologies. The current study has the following **tasks**:

1. To modify natural and manufactured clay samples with innovative modification approaches using organic and inorganic compounds.
2. To characterize properties of developed composite clay materials using the multiparameter method approach.
3. To analyse the sorption performance of newly developed materials under various conditions, e.g., the concentration of the sorbate, amount of sorbent, pH, temperature and contact time.
4. To investigate and discuss the opportunities for application in environmental technologies.

The **hypothesis** of this thesis states that the modification significantly increases the application possibilities of clay minerals for environmental technologies.

The novelty of the research

1. Innovative methods for clay modification are elaborated: smectite type clay modification with surfactants, ionic liquids and anthocyanins through an ion exchange reaction and modification with iron-oxyhydroxide and hydroxyapatite through the surface adsorption process.
2. The obtained hybrid materials are characterized using multiparameter analytical methods, convincingly proving the modification efficiency.
3. Possibilities to use design concept to develop materials for special applications to solve environmental problems, based on sorbent-sorbate interactions in combination with matrix impacts.
4. Modification establishes unique properties of clay materials: clay composites modified with ionic liquids, surfactants, iron-oxyhydroxide and hydroxyapatite can be used as effective sorbents in wastewater treatment; while clays modified with anthocyanins can be used in the food industry as intelligent sensors for spoiled food detection.

Practical applicability and significance of the research

1. Clay modification supports the development of innovative materials with broader scope and potential for environmental applications.
2. The modification of clay materials significantly expands the practical application of the natural resources of Latvia in various sectors, using approaches that are highlighted in the top emerging technology list (World Economic Forum, 2019).
3. The modified clay materials can be considered as prospective nature-based materials for applications in environmental technologies, at first as sorbents for the removal of pollutants from wastewaters.

Approbation of the results

The results of the study are published in 9 articles (6 of them are included in Web of Science and/or Scopus databases); in total, the author has 20 publications (17 of them are included in Web of Science and/or Scopus databases). The results of the research work were presented in 27 reports at international conferences and 18 reports at national conferences. The research results of the Paper VIII are briefly reported in the journal “Nature Sustainability” in the research highlights section (Burnside, 2018). The concept to use clay-anthocyanin composites in intelligent packaging for spoiled food detection won the European Institute for Innovations and Technology Regional Innovation Scheme Innovation Prize in Latvia (1st place) and the patent of the preparation method of freshness indicator is pending. The author of the thesis has supervised 2 bachelor's research works and has advised the preparation of 1 master's thesis on the topics related to her field of research. Furthermore, students were actively involved in the Latvian Clay Science Society events, including educational seminars about clay science, and were invited to participate in the international symposium “Clays & Ceramics”.

Scientific publications related to the thesis (note: as of 2020, the surname has been changed from ‘Ozola’ to ‘Ozola-Davidāne’):

1. **Ozola-Davidane, R.**, Burlakovs, J., Tamm, T., Zeltkalne, S., Krauklis, A. E., Klavins, M. 2021. Bentonite – ionic liquid composites for Congo red removal from aqueous solutions. *Journal of Molecular Liquids* 116373. (Web of Science/SCOPUS, Q2/Q1, IF₂₀₂₀ = 6.165) (further referred to as **Paper I**).
2. **Ozola, R.**, Burlakovs, J., Krauklis, A., Hogland, W., Klavins, M. 2019. Surfactant modified clay sorbents for the removal of p-nitrophenol. *Clays and Clay minerals*. 67(2), 132–142. (Web of Science/SCOPUS, Q3/Q2, IF₂₀₂₀ = 1.609) (further referred to as **Paper II**).
3. **Ozola, R.**, Krauklis, A., Leitietis, M., Burlakovs, J., Vircava, I., Anson Bertina, L., Bhatnagar, A., Klavins, M. 2019. FeOOH-modified clay sorbents for arsenic removal from aqueous solutions. *Environmental Technology & Innovation*. 13, 364–372. (Web of Science/SCOPUS, Q2/Q1, IF₂₀₁₉ = 3.356) (further referred to as **Paper III**).
4. **Ozola, R.**, Klavins, M., Burlakovs, J. 2018. Clays, intercalated with organic substances for environmental technologies. *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM*. 18(5.2), 197–202. (SCOPUS, Qn/a, IF₂₀₁₈ = 0.24) (further referred to as **Paper IV**).
5. Burlakovs, J., Jani, Y., Kriipsalu, M., Vincevica-Gaile, Z., Celma, G., **Ozola, R.**, Rozina, L., Rudovica V., Hogland, M., Viksna, A., Pehme, K. M., Hogland, W., Klavins, M. 2018. On the way to ‘zero waste’ management: Recovery potential of elements, including rare earth elements, from fine fraction of waste. *Journal of Cleaner Production*. 186, 81–90. (Web of Science/SCOPUS, Q1/Q1, IF₂₀₁₉ = 7.246) (further referred to as **Paper V**).
6. Krauklis, A., **Ozola, R.**, Burlakovs, J., Rugele, K., Kirillov, K., Trubaca-Boginska, A., Rubenis, K., Stepanova, V., Klavins, M. 2017. FeOOH and Mn₈O₁₀Cl₃ modified zeolites for As(V) removal in aqueous medium. *Journal of Chemical Technology and*

Biotechnology. 92(8), 1948-1960. (Web of Science/SCOPUS, Q2/Q1, IF₂₀₁₉ = 2.750) (further referred to as **Paper VI**).

7. **Ozola, R.**, Krauklis, A. Burlakovs, J. Vincevica-Gaile, Z., Rudovica, V. Trubaca-Boginska, A., Borovikova, D., Bhatnagar, A., Vircava, I., Klavins, M. 2017. Illite clay modified with hydroxyapatite – innovative perspectives for soil remediation from lead (II). *International Journal of Agriculture and Environmental Research*. 3(2), 177–189 (further referred to as **Paper VII**).
8. **Ozola, R.**, Burlakovs, J., Kļaviņš, M. 2016. Modified clay sorbents for organic and inorganic pollutants removal from aqueous solutions. *Publications of the International Scientific-Practical Conference "Modern Engineering Technologies and Environmental Protection"*. 1, 85 – 88 (further referred to as **Paper VIII**).
9. Burlakovs, J., **Ozola, R.**, Kostjukovs, J., Klavins, I., Purnmalis, O., Klavins, M. 2015. Properties of the Jurassic clayey deposits of southwestern Latvia and northern Lithuania. *Materials Sciences and Applied Chemistry*. 32, 5–12 (further referred to as **Paper IX**).

Other scientific publications (note: as of 2020 the surname has been changed from ‘Ozola’ to ‘Ozola-Davidāne’):

1. Krūmiņš, J., Kļaviņš, M., **Ozola-Davidāne, R.**, Ansone-Bērtiņa, L. 2022. The Prospects of Clay Minerals from the Baltic States for Industrial-Scale Carbon Capture: A Review. *Minerals*, 12(3), 349. (Web of Science/SCOPUS, Q2/Q2, IF₂₀₂₀ = 2.644).
2. Krauklis, A. E., Karl, C. W., Rocha, I. B. C. M., Burlakovs, J., **Ozola-Davidane, R.**, Gagani, A. I., Starkova, O. 2022. Modelling of Environmental Ageing of Polymers and Polymer Composites – Modular and Multiscale Methods. *Polymers*, 14(1), 216, doi:10.3390/polym14010216. (Web of Science/SCOPUS, Q1/Q1, IF₂₀₂₀ = 4.329).
3. Preisner, M., Smol, M., Horttanainen, M., Deviatkin, I., Havukainen, J., Klavins, M., **Ozola-Davidane, R.**, Kruopienė, J., Szatkowska, B., Appels, L. et al. 2022. Indicators for resource recovery monitoring within the circular economy model implementation in the wastewater sector. *Journal of Environmental Management*, 304, 114261, doi:10.1016/J.JENVMAN.2021.114261. (Web of Science/SCOPUS, Q1/Q1, IF₂₀₂₀ = 6.789).
4. Rudovica, V., Rotter, A., Gaudêncio, S., Novoveská, L., Akgül, F., Hoel, L., Alexandrino, D. A. M., Anne, O., Arbidans, L., Atanassova, M., Beldowska, M., Beldowski, J., Bhatnagar, A., Bikovens, O., Bisters, V., Carvalho, M. F., Catalá, T. S., Dubnika, A., Erdoğan, A., Ferrans, L., Haznedaroglu, B. Z., Setyobudi, R. H., Graca, B., Grinfelde, I., Hogland, W., Ioannou, E., Jani, Y., Katarzytė, M., Kikionis, S., Klun, K., Kotta, J., Kriipsalu, M., Labidi, J., Lukić, B. L., Martínez-Sanz, M., Oliveira, J., **Ozola-Davidane, R.**, ... & Burlakovs, J. 2021. Valorization of marine waste: exploitation of industrial by-products and beach wrack towards the production of high added-value products. *Frontiers in Marine Science*. 8, 1350 (Web of Science/SCOPUS, Q1/Q1, IF₂₀₂₀ = 4.912).
5. Obuka, V., Sinka, M., Nikolajeva, V., Kostjukova, S., **Ozola-Davidane, R.**, Klavins, M. 2021. Microbiological Stability of Bio-Based Building Materials.

- Journal of Ecological Engineering*. 22(4), 296–313. (SCOPUS, Q2, IF₂₀₁₉ = 1.27).
6. Burlakovs, J., Pilecka, J., Grinfelde, I., **Ozola-Davidane, R.** 2020. Clay minerals and humic substances as landfill closure covering material constituents: first studies. *Research for Rural Development*. 35, 219–226. (SCOPUS, Qn/a, IF = n/a).
 7. Anson-Bertina L., Jemeljanova M., Klavins M., **Ozola-Davidane R.**, Kviesis J. 2020. Clay-humic substance composites for removal of pharmaceuticals from water. *Key Engineering Materials*. 850, 28–34. (SCOPUS, Q3, IF₂₀₁₈ = 0.35).
 8. Burlakovs, J., Vincevica-Gaile, Z., Krievans, M., Jani, Y., Horttanainen, M., Pehme, K. M., Dace, E., Setyobudi, R. H., Pilecka, J., Denafas, G., Grinfelde, I., Bhatnagar, A., Rud, V., Rudovica, V., Mersky, R. L., Anne, O., Kriipalu, M., **Ozola-Davidane, R.**, Tamm, T., Klavins, M. 2020. Platinum Group Elements in Geosphere and Anthroposphere: The Interplay among the Global Reserves, Urban Ores, Markets and Circular Economy. *Minerals*. 10, 558. (Web of Science/SCOPUS, Q2/Q2, IF₂₀₁₉ = 2.38).
 9. Smol, M., Preisner, M., Bianchini, A., Rossi, J., Hermann, L., Schaaf, T., Kruopienė, J., Pamakštys, K., Klavins, M., **Ozola-Davidane, R.**, Kalnina, D., Strade, E., Voronova, V., Pachel, K., Yang, X., Steenari, B.-M., Svanström, M. 2020. Strategies for Sustainable and Circular Management of Phosphorus in the Baltic Sea Region: The Holistic Approach of the InPhos Project. *Sustainability*. 12(6), 2567. (Web of Science/SCOPUS, Q2/Q2, IF₂₀₁₉ = 2.576).
 10. Jemeljanova, M., **Ozola, R.**, Klavins, M. 2019. Physical-chemical properties and possible applications of clay minerals and humic acid composite materials. *Agronomy Research*. 17(S1), 1023–1032. (SCOPUS, Q3, IF₂₀₁₉ = 0.69).
 11. Lama, E., **Ozola, R.**, Rudovica, V., Bavrins, K., Viksna, A. 2018. Analytical studies on contents of essential and toxic elements in rice available in Latvian retail. *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM*. 18(3.2), 27–32. (SCOPUS, Qn/a, IF₂₀₁₈ = 0.24).

Patent: Ozola-Davidāne, R. 2022. Preparation method and application of freshness indicators for meat quality monitoring [pending] (further referred to as Patent).

Reports presented in international and national conferences (15 from 45) (note: from 2020 the surname has been changed from ‘Ozola’ to ‘Ozola-Davidāne’):

1. Burlakovs, J., **Ozola-Davidane, R.**, Klavins, M. 2021. Innovative composite sorbents for organic and inorganic pollutants removal from aqueous solutions in landfill leachates. *Book of Abstracts of the 22nd International scientific conference “EcoBalt 2021”*. Riga, Latvia, 20.
2. Burlakovs, J., **Ozola-Davidane, R.**, Vincevica-Gaile, Z., Hendroko Setyobudi, R., Zekker, I. 2021. Advanced studies of inert landfill fine fraction mass – hunting for values from waste. *2nd International Conference on Bioenergy and Environmentally Sustainable Agriculture Technology: ICoN-BEAT 2021*, Malang, Indonesia (hybrid: online and face to face).

3. **Ozola-Davidane, R.,** Kostjukova, S. 2021. Novel pH-sensitive composites containing clay minerals and anthocyanins to monitor meat freshness. *Nordic Clay Meeting/3rd Symposium Clays & Ceramics 2021. Book of Abstracts*. Riga, Latvia (Online), 36.
4. Burlakovs, J., **Ozola-Davidane, R.,** Kriipsalu, M., Klavins, M. 2021. Humic Substance – Clay Mineral Composites as Novel and Eco-Friendly Sorbents for Environmental Remediation. *Nordic Clay Meeting/3rd Symposium Clays & Ceramics 2021. Book of Abstracts*. Riga, Latvia (Online), 35.
5. Salmina, A., **Ozola-Davidane, R.,** Klavins, M. 2021. Composites of Clay Minerals and Natural Pigments: Their Synthesis, Characterization and Potential in Biocosmetics. *Nordic Clay Meeting/3rd Symposium Clays & Ceramics 2021. Book of Abstracts*. Riga, Latvia (Online), 45.
6. **Ozola-Davidane, R.,** Klavins, M. 2020. From research to management of phosphorus flows and implementation of circular economy concepts: case study in Latvia. *1st International Conference Strategies toward Green Deal Implementation. Conference proceedings*. (Online), 85.
7. **Ozola-Davidane, R.,** Klavins, M., Jemeljanova, M., Anson-Bertina, L. 2020. Humic substances for the removal of inorganic and emerging organic pollutants from wastewater. *1st International Conference Strategies toward Green Deal Implementation. Conference proceedings*. (Online), 118.
8. **Ozola-Davidane, R.,** Klavins, M. 2020. Wastewater management in Latvia: Success stories and challenges. *12th International conference of natural sciences and Tehnologies (EcoTech 2020). Book of abstracts: Linnaeus ECO-TECH '20*. Kalmar, Sweden (Online), n/a.
9. Burlakovs, J., Kriipsalu, M., Bhatnagar, A., Anson-Bertina, L., **Ozola-Davidane, R.,** Klavins, M. 2020. Modified clay composites as potential landfill covering material. *Goldschmidt 2020 Virtual Conference. Goldschmidt 2020 Abstract*, (Online), n/a.
10. **Ozola, R.,** Kostjukova, S. 2020. Montmorillonite-anthocyanin composites as sensors for monitoring food quality. *BIOR International Scientific Symposium “Science to Strengthen Sustainable and Safe Food Systems”*. *Book of abstracts*. Riga, Latvia, 79.
11. **Ozola, R.,** Klavins, M., Jemeljanova, M., Burlakovs, J. 2019. Clay minerals and ionic liquids or humic acids composites for applications in wastewater treatment. *International conference on clay science and technology (Euroclay 2019). Book of abstracts*. Paris, France, 483.
12. **Ozola, R.,** Klavins, M., Klavins, L., Jemeljanova, M., Burlakovs, J. 2019. Preparation and characterization of natural anthocyanin and montmorillonite composites. *International conference on clay science and technology (Euroclay 2019). Book of abstracts*. Paris, France, 484.
13. **Ozola, R.,** Klavins, M., Burlakovs, J. 2018. Modified clays for textile dyes and rare earth elements sorption and potential recovery. *11th International Conference of Natural Sciences and Tehnologies (EcoTech 2018). EcoTech 2018 Proceedings*. Kalmar, Sweden, 99.
14. **Ozola, R.,** Klavins, M., Burlakovs, J., Zicmanis, A., Klavins, L. 2018. Properties and applications of clay minerals modified with different organic/inorganic substances. *II*

- International Symposium "Clays and Ceramics". Book of Abstracts.* Riga, Latvia, 41.
15. **Ozola, R.**, Klavins, M., Zicmanis, A., Aboltina, E., Burlakovs, J. 2017. Clay minerals and ionic liquids composites as sorbents for emerging micro-pollutants removal. *XVI International Clay Conference (ICC 2017). Scientific Research Abstracts*, 7. Granada, Spain, 602.

Structure of the thesis

The thesis is based on 9 peer-reviewed articles and 1 patent. The interrelation among the articles and studied composite materials is represented in Table 1.

Table 1

Overview of the scientific papers related to the thesis					
Composite materials	Number of scientific papers	Covered sections in the thesis			
		Properties of clay and clay minerals	Modification methods	Characterization of composite materials	Study of the application of composite materials
Raw clay	IX	x			
Clay-surfactants	II		x	x	x
	IV	x			x
	VIII		x	x	x
Clay-iron oxy-hydroxide	III		x	x	x
	VIII		x		
	VI		x	x	x
Clay-hydroxyapatite	V				x
	VII		x	x	x
	Only in the thesis			x	x
Clay-ionic liquids	I		x	x	x
	IV	x			x
Clay-anthocyanins	Patent				x

The summary of the thesis consists of 37 pages and is supplemented with illustrations – 10 pictures and 4 tables.

LITERATURE REVIEW

1.1. Terminology for clay and clay minerals

In clay science, according to joint nomenclature committees of the Association Internationale pour l'Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS) 'clay' is defined as "naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired". Although clays mainly consist of phyllosilicates, other materials which harden when dried or fired and impart plasticity may comprise clays. Associated phases in clays can be minerals, such as calcite, quartz, feldspars, dolomite, oxides, hydroxides and organic phases (Guggenheim and Martin, 1995). According to this definition, synthetic clays are not considered as clays even though they may be fine-grained, hardening on drying/firing and plastic at appropriate water content (Bergaya and Lagaly, 2006; Christidis, 2010). Plasticity refers to the ability of the material to be moulded into any shape. The joint nomenclature committees also state that the plastic properties of clay do not require quantification since plasticity is affected by many factors, including chemical composition and particle aggregation. Furthermore, some non-plastic clays such as flint clays (consist of more than 95% of kaolinite) are still regarded as 'clay' because of past usage (Guggenheim and Martin, 1995; Bergaya and Lagaly, 2006). According to Guggenheim & Martin (1995), the definition of clay does not take into account the upper limit of particle size. This is because different disciplines consider different particle sizes for clays. In colloid science, the particle size limit is 1 μm , in geology and soil science 2 μm , but in sedimentology 4 μm (Moore and Reynolds, 1997). The International Organization for Standardization (ISO) uses < 2 μm as the upper limit for the fine fraction (Schroeder 2018). In the aforementioned definition 'fine-grained' refers only to the crystallite size (Guggenheim and Martin, 1995).

AIPEA and CMS nomenclature committees define 'clay minerals' as "phyllosilicate minerals and minerals which impart plasticity to clay when wet and which harden upon drying or firing" (Guggenheim and Martin, 1995). This definition does not include origin of the material (unlike 'clay' definition) and therefore clay minerals may be synthetic such as layer double hydroxides. Nor does the size of minerals feature as a criterion in the definition and therefore clay minerals can have any grain size (Bergaya and Lagaly, 2006; Christidis, 2010). Most clay minerals are found in nature with particle sizes in the less than 4 μm range (Schroeder, 2018). Also, according to Guggenheim & Martin (1995), non-phyllosilicate minerals which impart plasticity to clay and hardens upon drying or firing, can be defined as a clay mineral. The main difference between definitions of 'clay' and 'clay minerals' is shown in Table 2.

Table 2

Difference between definitions of ‘clay’ and ‘clay minerals’ (adapted from Bergaya and Lagaly, 2006)

	Clay	Clay minerals
Origin	Natural	Natural and synthetic
Classification	Phyllosilicates as principal constituents	May include non-phyllosilicates
Size	Fine-grained (< 1 µm, 2 µm or 4 µm)	No size criterion
Properties	Plastic (except flint clays), hardens on drying or firing	Plastic, hardens on drying or firing

1.2. Physical and chemical properties of clay minerals

The structural and composition features of particular clay minerals give them different physical and chemical properties. Clay minerals are characterized by the following physical and chemical characteristics: 1) particle size and shape; 2) specific surface area; 3) colour; 4) mineralogy; 5) ion exchange capacity; 6) rheology; 7) plasticity; 8) swelling; 9) surface electric charge (Murray, 2007). The most important property of clays in the environmental sector is the cation exchange capacity, which, together with the characteristic small particle size and relatively high specific surface area determines their effective sorption capacity (Brovkina et al., 2012).

Clay minerals have unique properties to sorb cations, anions, and polar molecules of inorganic or organic substances (Brovkina et al., 2012). In clay minerals, the active sites arise from (1) ‘broken edge’ sites and exposed surface aluminol and silanol groups, (2) isomorphous substitutions, (3) exchangeable cations, (4) hydrophobic silanol surfaces, (5) hydration shell of exchangeable cations, and (6) hydrophobic sites on adsorbed organic molecules (Figure 1) (Zhou and Keeling, 2013).

Anion exchange capacity is attributed to the charge of the edges of the crystals, which becomes positive by adsorption of hydrogen cation (H^+) at acidic pH, forming a water molecule. This molecule is weakly bonded, and thus can be easily displaced and exchanged by other anionic groups. Alternatively, anionic groups can replace OH groups located at crystal edges directly (Christidis, 2010). The smaller the particle size of the clay minerals, the more such sites there are and the higher the anion exchange capacity. In the case of kaolinite, the edge surface may contribute up to 15% of the total surface, whereas in smectites it is only 1%. Thus, kaolin group minerals display significant anion exchange capacity for anionic molecules such as phosphates (Christidis, 2010). The charged layers and ‘broken edge’ sites can be enhanced by chemical reactions such as acid activation (Zhou and Keeling, 2013).

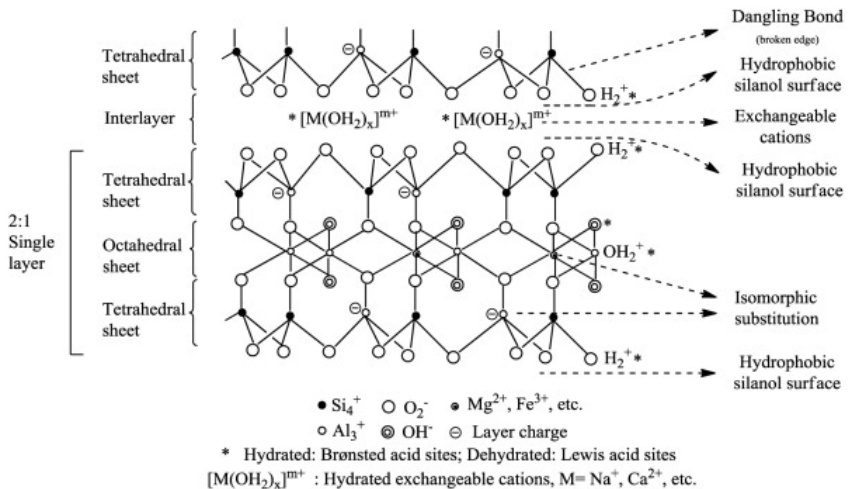


Figure 1. Schematic representation of 2:1-layer clay mineral showing active sites that provide ion exchange and sorption properties (Zhou and Keeling, 2013).

Cation exchange capacity is related to substitutions in the tetrahedral and/or the octahedral sheet which create a charge deficit. The layer charge is balanced by the interlayer cations such as potassium (K^+), sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) ions, which are exchangeable with guest molecules and ions (Lee and Tiwari, 2012; Zhou and Keeling, 2013). Cation exchange capacity is a characteristic property of all clay minerals but particularly notable in smectite group minerals (Christidis, 2010).

1.3. Modification methods of clay minerals and their applications

The physical and chemical properties of clay minerals, their availability, low cost, inertness and stability have led to numerous industrial applications (Zhou & Keeling, 2013; Rouquerol et al., 2013). For example, kaolin group minerals are traditionally used as fillers and coating materials in paper, fillers in paint, plastics, rubber, ink and applied in ceramics for the production of pottery, sanitaryware, insulators and refractories, while smectite group minerals are commonly used as liners and capping materials for landfill sites to isolate contamination from the surrounding environment, animal feed bonds, pet waste absorbents, carriers for agricultural insecticides, pharmaceutical and cosmetic products (Murray, 2000). Nevertheless, the applications in various advanced technologies of naturally occurring clay minerals are limited due to some of their characteristic features. For example, due to clays' hydrophilic nature, low interlayer spacing and high surface energy, they are inefficient adsorbents for the removal of organic pollutants including antibiotics, dyes, pesticides and biocides (Ismadji et al., 2015). However, modification or treatment of clay surface and/or interlayer structure is a technique to achieve certain properties such as

hydrophobicity, changed charge properties, enhanced pore volume, total surface area and available active sites that increases adsorption efficiency of clay mineral (Figure 2) (Sarkar et al., 2019).

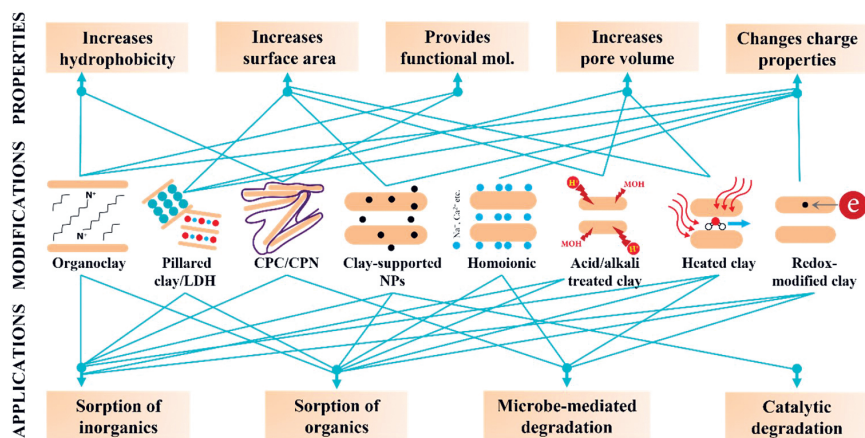


Figure 2. Scheme of potential networks showing modified clay minerals with their properties and environmental applications (developed from Biswas et al., 2019).

Modification of clays' minerals can be achieved through various processes, thus, the selection of modification techniques and materials used for the treatment is significant for achieving the desired properties for the intended purpose. The intended attributes can be achieved through heat, alkali and acid treatments, redox reactions, ion exchange, organic and polymer loading reactions (Figure 2) (Sarkar et al., 2019).

2. MATERIALS AND METHODS

2.1. Samples of clay and clay minerals used in this study

Natural origin and manufactured clay samples were chosen in this study: 1) smectite-dominated clay of Triassic System from the Saltiski deposit (Saltiski, Lithuania, coordinates: N 56°12'55", E 22°56'50") – further refers as T clay (Figure 3); 2) mixed content clay with organic matter of Jurassic System from the Legernieki deposit (Nikrace, Latvia, coordinates: N 56°32'37", E 21°59'53") – further called J clay (Figure 3); 3) Montmorillonite K10 industrially produced clay, purchased from Sigma-Aldrich (Germany) – further referred to as Mt clay; 4) Bentonite, sodium form industrially produced clay, purchased from Alfa Aesar (Germany) – further referred to as Bent clay.

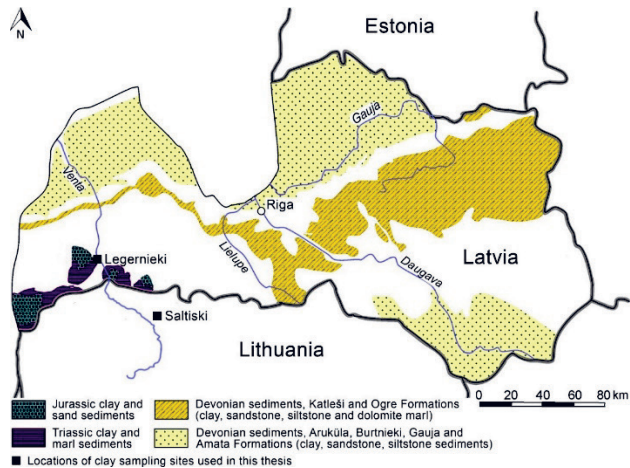


Figure 3. Deposits of natural clay samples used in the study (adapted from Stinkule, 2014).

The clays of natural origin before modification were purified from different matrix materials, such as carbonates, organic substances and quartz according to the method described in Karasa et al. (2012).

2.2. Clay mineral modification methods

Clay samples were treated using inorganic and organic modifiers. Iron oxyhydroxide (FeOOH) and hydroxyapatite (Hap) were chosen as inorganic modifiers, but ionic liquids and surfactants were chosen as organic modifiers. In addition, clay samples were treated with natural pigments – anthocyanins.

The modification method with iron **oxy-hydroxide (FeOOH)** is based on the impregnation of clay material with a precipitate of a mixture of 0.25 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 3M NaOH, based on the method described by Ozola et al.

(2019b). Similarly, for the modification of clay minerals with **hydroxylapatite (Hap)** ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), a precipitation method using 0.5 M CaCl_2 and 2 M KH_2PO_4 was used, where equimolar proportion of Ca/P is 1.6 (Ozola et al., 2017). Modification with **surfactants** was performed as described by Ozola et al. (2019a). The method is based on the exchange of inorganic ions in clay minerals with cationic surfactants (dodecyltrimethylammonium chloride (DTAC); benzyltrimethylammonium chloride (BTMAC)) or nonionic (dimethyldodecylamine N-oxide (DDAO); 4-methylmorpholine N-oxide (NMO)) molecules. The modification was performed at different proportions of the amount of surfactant and cation exchange capacity (CEC) of clay sample – 0.5; 1.0; 2.0 and 3.0. Desired amount of surfactant in the prepared solutions was calculated using the following equation:

$$m_s = m_c \cdot \text{CEC} \cdot 10^{-3} \cdot Q_{\text{CEC}} \cdot M \quad (1)$$

where m_s is mass of the surfactant (g), m_c is mass of the used clay sample (g), CEC is cation exchange capacity of the clay samples used (mmol/g), Q_{CEC} is a desired amount of added proportion of surfactant/CEC, and M is molecular weight of the surfactant (g/mol). The clay modification method with *ionic liquids* is described by Ozola-Davidāne et al. (2021) and is based on the exchange of inorganic cations in clay minerals with cations present in the ionic liquid structure. Imidazolium based ionic liquids with different alkyl chain lengths were used in the modification: 1-butyl-3-methylimidazolium chloride (Bent_C₄mimCl), 1-octyl-3-methylimidazolium chloride (Bent_C₈mimCl) and 1-dodecyl-3-methylimidazolium chloride (Bent_C₁₂mimCl). The proportion between the added ionic liquid and CEC of the clay sample was 1.0, calculated according to Equation No. 1. The modification method of clays with anthocyanins is not discussed in detail, as this method is being patented.

2.3. Sorption experiments

Sorption experiments were carried out to investigate the sorption capacity of raw and modified clay composites intended to remove model sorbates from aqueous solutions. Sorption experiments were performed using a batch system under various conditions, e.g., the concentration of the sorbate, amount of sorbent, pH, temperature and contact time. Clay-ionic liquids, clay-surfactant and clay-FeOOH sorption experiments are described in detail in Paper I, Paper II, and Paper III, respectively.

For the sorption studies, different quantities of sorbent were placed in a 100 mL glass vessel and supplemented with a certain volume of sorbate solution at various concentrations (Table 3). The obtained mixture was agitated continuously on the multi-functional orbital shaker Biosan PSU-20i (Riga, Latvia) for 24 h at room temperature. After shaking, the mixtures were centrifuged at 3000 rpm for 12 min. and filtered. To investigate pH influence on sorption capacity, pH of sorbate solution was adjusted in the range between 2 and 12 by adding either 0.1 M HCl or NaOH.

Table 3

Overview of materials and methods used in the thesis

Sorbent	Sorbate	Sorption conditions	Characterization methods	Number of scientific paper(s)
Mt/T/J clay – FeOOH	arsenic(V) silver(I), aluminum(III)	Ci = 5–400 mg/L; v = 40 mL; m = 0,5 g; t = 24 h; pH = 2–9; T = 24 °C Ci(Ag) = 422 mg/L; Ci(Al) = 3600 mg/L v = 10 mL; m = 0,5 g; t = 24 h; pH ~3; T = 24 °C	XRD, FTIR, SEM, SSA by BET, TGA, CEC, Content of Fe ₂ O ₃	Paper III n/a
Mt/T/J clay – Hap	lanthanum(III), neodymium(III), cerium(III) silver(I), aluminum(III)	Ci = 5–600 mg/L; v = 100 mL; m = 0,1 g; t = 24 h; pH = 6; T = 24 °C Ci(Ag) = 422 mg/L; Ci(Al) = 3600 mg/L v = 10 mL; m = 0,5 g; t = 24 h; pH ~3; T = 24 °C	XRD, FTIR, SEM, SSA by BET, TGA	Paper VII n/a
Mt/T/J clay – DDAO NMO BTMAC DTAC	<i>p</i> -nitrophenol	Ci = 5–25 mg/L; v = 20 mL; m = 0,3 g; t = 10–360 min, 24 h; pH = 2–12; T = 24 °C	XRD, FTIR, SEM, SSA by BET, TGA	Paper II
Bt/T clay – C ₄ mimCl C ₈ mimCl C ₁₂ mimCl C ₁₈ mimDMP C ₄ mmimDMP C ₈ mmimDMP C ₁₂ mmimDMP	Congo red	Ci = 0,5–100 mg/L; v = 25 mL; m = 0,01 g; t = 1–360 min, 24 h; pH = 2–10; T = 24 °C	XRD, FTIR, SSA by BET, TGA	Paper I
Mt clay – anthocyanins	Anthocyanin-rich extract from berry residues	Patent pending	Not included in this thesis	Patent (pending)

To undertake the sorption kinetics studies, the mixtures were agitated for 10–60 min. with 10 min. intervals and 120–360 min. with 60 min intervals. Standard deviations of the results were determined based on 3 experimental parallels.

In the case of clay-surfactant, clay-FeOOH, clay-ionic liquid and clay-Hap composite materials p-nitrophenol, arsenic, Congo red and rare earth elements (La, Ce and Nd) were chosen as model contaminants. In the case of p-nitrophenol (PNP) and Congo red (CR) the supernatants were analysed using a UV-Vis spectrophotometer (Shimadzu UV 1800, Kyoto, Japan) at 318 nm and 500 nm respectively. The concentration of As (V) in the filtrate was analysed using PerkinElmer AAnalyst 200 with flame atomization (FAAS – Flame Atomic Absorption Spectrometry). La (III), Ce(III) and Nd(III) concentrations in the filtrate were measured by iCAP7000 Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Thermo Scientific).

The quantity of the model contaminants sorbed on the clay composite material was calculated by using the following equation:

$$q_e = \frac{(C_i - C_e)}{m} \cdot v \quad (2)$$

where q_e is the amount of model contaminant sorbed on the sorbent (mg/g), C_i and C_e are initial and equilibrium liquid-phase concentrations of sorbate (mg/L), respectively, v is the volume of solution (mL), and m is mass of sorbent used (g). Determination of anthocyanin content was carried out by using the spectrophotometric pH differential method (Lee et al., 2005). The method is based on anthocyanin molecules' ability to change colour at different pH levels.

Langmuir and Freundlich isotherms were calculated to describe the relationship between the amount of sorbed sorbent and its equilibrium concentration in the solution. Lagergren's pseudo-first-order and pseudo-second-order kinetic models were used to analyse the relationship of sorption time and sorption capacity.

2.4. Characterization methods of clay composites

The physicochemical properties of clay composite samples were characterized by various multiproxy methods: 1) specific surface area and pore size were measured using the Brunauer, Emmett and Teller (BET) method; 2) the mineral composition and structural changes of the samples were identified by X-ray diffraction (XRD) method; 3) new functional groups in clay minerals were determined by Fourier-transform infrared spectroscopy (FTIR); 4) changes in surface morphology by scanning electron microscopy (SEM) and 5) changes in weight loss by thermogravimetry (TGA).

3. RESULTS AND DISCUSSION

3.1. Development and characterization of clay composites

3.1.1. Raw clay, clay minerals and the concept of their modification

In the study, clay samples of natural origin (samples from Latvia and Lithuania), as well as industrially produced mineralogically pure samples were used (see Chapter 2.1.). The characteristic parameters of used clay samples are summarized in Table 4. The selected samples were chosen considering prospects to develop new applications of clay resources topical for Latvia, as well as to test elaborated design concepts on mineralogically well-characterised clay samples.

Table 4

Characteristics of the selected raw clay samples in this thesis						
Clay sample	Dominant clay mineral group	CEC* (mmol/g)	d(001) (Å)	Interlayer spacing (nm)	SSA by BET method (m ² /g)	
Bt clay	Smectite	0.98 ± 0.03	12.63	0.30	45.21	
Mt clay	Smectite	0.50 ± 0.03	13.40	0.38	252.03	
T clay	Smectite, illite-smectite, illite	0.33 ± 0.03	12.08	0.25	57.29	
J clay	Smectite; illite; kaolinite; chlorite	0.25 ± 0.02	n/a	n/a	n/a	

*CEC was determined by methylene blue test

To develop new clay material application possibilities, modification of the selected clays was done with an aim to increase sorption capacity with respect to selected substances and considering prospects to develop new applications in environmental technologies and bioeconomy. The concept of design of clay composites is based on 2 principles (Figure 4):

1. Clay impregnation with another material (iron oxy-hydroxides or hydroxyapatite) providing new sorption capacities. Sorption capacities of the selected materials are widely studied (Ansone-Bērtiņa, 2015; Ozola et al., 2017; Ozola-Davidāne et al., 2019a) and the combination of the sorption profile of clays and modifiers provide possibilities to achieve new sorption profiles and thus increased application potential.
2. Modification of clay structure to enhance and modify clay sorption capacity oriented on intercalation of the modifier into the clay mineral interlayer space. In this study, clay modification is proposed with new groups of surfactants and ionic liquids (not previously used for clay modification). As a result, newly developed materials become hydrophobic with increased sorption capacity for the removal of organic substances.

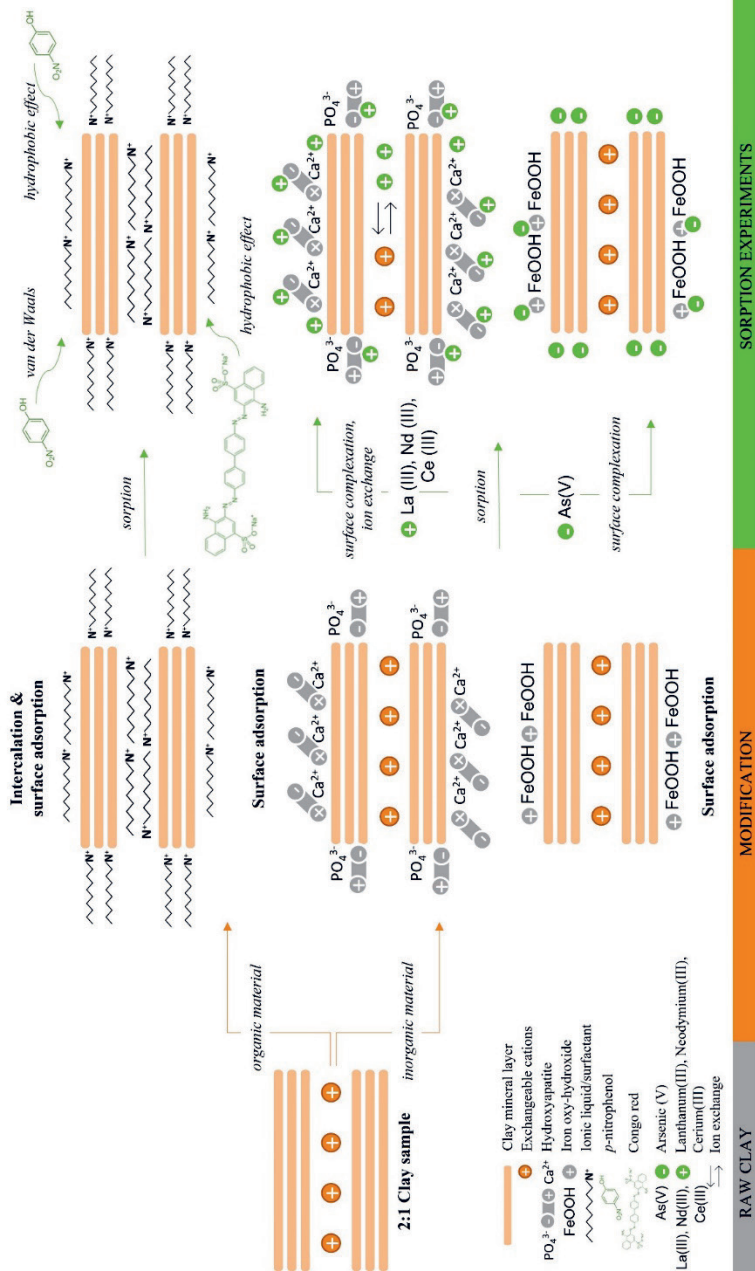


Figure 4. Schematic representation of modification methods used in this study and possible sorption mechanisms of model contaminants onto obtained sorbents.

3.1.2. Characterization of clay – iron oxy-hydroxide composite materials

Clay modification with iron oxy-hydroxide (FeOOH) was conducted as described in Ozola et al., 2019a. The method was based on the impregnation of the Mt, T and J clay with iron compounds to develop sorption sites for negatively charged pollutants, such as arsenic (As(V)) compound HAsO_4^{2-} , which is the dominant form in the media with pH 3–9 (Ansone-Bērtiņa, 2015). **SEM images** showed that the surface morphology of clay-FeOOH composites had changed compared to untreated clay samples (Figure 4).

For all composite materials, the characteristic smectite type mineral crystal shape was no longer visible, because the surface was coated with iron compounds. **XRD** diffractograms show a significant decrease in intensity and smoothing of basal peak of smectite (region of 15–15.5 Å) in clay samples modified with FeOOH. It was also found that diffractograms do not indicate new phases in modified materials compared to raw clays. This is consistent with expected results, as FeOOH phase is expected to be amorphous. Besides, the increased background noise of modified clays, while not unambiguous, is an indication of the increase in the amorphous phase. Additionally, the diffractograms suggested the presence of hematite (Fe_2O_3) for T and T-FeOOH samples, which could contribute positively to the sorption of As(V). According to **FTIR** data, the Mt-FeOOH composite were no new absorbance peaks. However, the FTIR spectra of the modified T and J clay indicated the occurrence of new absorbance peaks with wavenumber at $\sim 1400\text{ cm}^{-1}$ which is an indication of the presence of Fe–O functional group for maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (Khorshidi and Azadmehr, 2017).

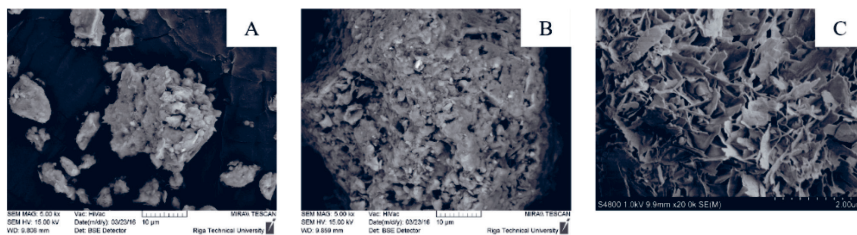


Figure 5. SEM images (5k magnification) of raw T clay (A), T clay modified with iron oxy-hydroxide (B) and hydroxyapatite (C).

TG analysis of FeOOH-modified clay samples showed weight loss observed for the modified materials at the temperature around 500°C and 800°C should be attributed to the partial transformation of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) phase to hematite ($\alpha\text{-Fe}_2\text{O}_3$) present in the composites (Wu et al., 2016). Total weight loss of Mt clay, Mt-FeOOH, T clay, T-FeOOH, J clay, J-FeOOH, which is attributed to the thermal dehydroxylation reactions and the γ to α phase transition, was 3.91%, 6.31%, 11.22%, 11.90%, 3.89%, 7.55%, respectively. These results are in accordance with the XRD and FTIR investigation. Additionally, the **SSA** values increased significantly after the modification of the clay materials, indirectly

indicating that the sorption capacity of the clay-FeOOH composites will be higher than those of the unmodified clay samples.

3.1.3. Characterization of clay – hydroxyapatite composite materials

Clay modification with synthetic Hap was carried out as described in Ozola et al., 2017. Based on the modification method, clay samples were impregnated with Hap to increase the sorption capacity of rare earth elements such as lanthanum(III), neodymium(III), and cerium(III). **SEM images** showed that after modification with Hap the morphology of the clay surfaces had changed – become completely covered with hydroxyapatite crystals (Figure 5). After modification with Hap, **SSA** of composite materials slightly decreased, for example, in the case of Mt-Hap from 252.03 m²/g to 121.53 m²/g. The decrease in the surface area of composite materials is attributed to attached hydroxyapatite particles on clay particles (El-Nagar et al., 2020). **XRD** data showed that the mineral composition is completely changed in modification processes of clays with hydroxyapatite. Characteristic peaks of chlorite, calcite, illite/smectite, feldspar and other mineral phases noticeably decreased in intensity or disappeared entirely. New peaks appear at ~26° and ~32° 2θ in the diffraction pattern, indicating the presence of hydroxyapatite in the modified samples. **FTIR spectra** for the newly developed composite material showed new functional groups at 1412 cm⁻¹ and 1450 cm⁻¹, indicating the presence of carbonate ions CO₃²⁻, and at 600 cm⁻¹ indicating the presence of phosphate ions PO₄³⁻ (Shaltout et al., 2011). The **TGA** results showed that after modification at 610° C, there was a new decomposition region indicating the release of carbon dioxide from apatite. Overall, the FTIR results are consistent with thermal analysis and confirm the presence of hydroxyapatite in the composite materials.

3.1.4. Characterization of clay – surfactant composite materials

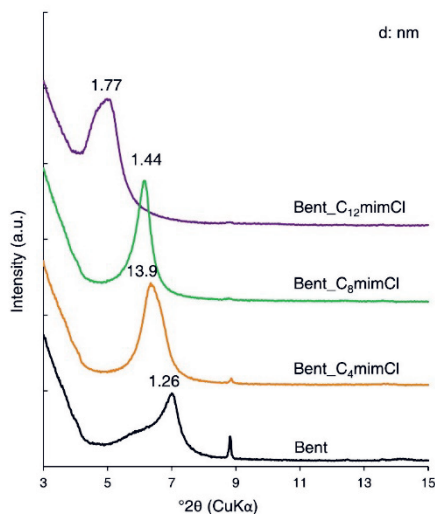
Clay modification with nonionic and cationic surfactants was carried out accordingly as described in Ozola et al., 2019. The method is based on the sodium ion exchange with surfactant ion within the interlayer space of clay minerals. Thus, the clay surface becomes hydrophobic and improves the sorption ability of organic pollutants, such as *p*-nitrophenol (PNP). **XRD** diffractograms showed that the interlayer space of clay minerals had significantly increased after the modification. The largest increase in interlayer spacing occurred with surfactant DDAO (0.46 nm), whereas a smaller change was observed with NMO (0.04 nm). These changes can be explained by the length of the surfactant alkyl chain or *n_c*, number of carbon atoms (He et al., 2014). The **SSA** of organoclays changed depending on the used proportion of added surfactant amount and CEC ratio. The SSA diminishes in the following order: Mt_Na > Mt_BTMAC_0,5 > Mt_BTMAC_1 > Mt_BTMAC_2 > Mt_BTMAC_3. The decrease of the SSA after modification is because surfactants arrange a monolayer on the outer surface of clay mineral, creating a ‘house of cards structure’, and occupying pores among the clay particles (Zhang et al., 2015). **SEM images** showed that

the morphology of the smectite-type mineral remained intact after modification with surfactants. After clay modification with surfactants, **FTIR** data showed new bands at 2930 cm^{-1} and 2854 cm^{-1} . This is assigned to the asymmetric and symmetric C–H stretching vibrations of the methylene groups. **TGA analysis** showed that after modification of montmorillonite, a new decomposition region appeared from $200\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$ due to the decomposition of surfactant molecules. Similar results were obtained in other organoclay studies (Taleb et al., 2018; Andrunik and Bajda, 2019)

3.1.5. Characterization of clay – ionic liquid composite materials

Clay modification with ionic liquids was conducted as described by Ozola-Davidane et al., 2021. The method was based on the intercalation of imidazolium-based ionic liquids with different lengths of alkyl chains in the interlayer space of bentonite via an ion exchange reaction. As a result of the modification, composite material becomes hydrophobic and improves the sorption ability of organic contaminants, such as Congo red. After modification of bentonite with ionic liquids, **FTIR** data showed new bands at 2927 cm^{-1} and 2847 cm^{-1} , which corresponded to asymmetric and symmetric C–H stretching vibrations of the methylene groups (Stuart, 2004). The presence of these bands in the range of 3000 cm^{-1} to 2840 cm^{-1} is an indication that the ionic liquid cations not only occupy clay surface but also are intercalated into bentonite structure (Sun et al., 2017). The **XRD** diffractogram revealed that after bentonite modification with ionic liquids the d_{001} peak shifted to lower angular values. The interlayer spacing was related to the length of the alkyl chain of the imidazolium cation – the longer the alkyl chain was, the larger the interlayer space expansion (Figure 6). Similar results have also been found in other studies (Nasser et al., 2016; Sun et al., 2017) confirming the successful intercalation of ionic liquids into the interlayer space of the bentonite. **TGA** data revealed that after modification with ionic liquids, a new decomposition region appears in the range of $480\text{ }^{\circ}\text{C}$ to $580\text{ }^{\circ}\text{C}$, indicating the decomposition of ionic liquids from the surface of the composite material and the interlayer space (Litefti et al., 2019).

The **SSA** values of clay-ionic liquid composite materials decreased with increasing alkyl chain length of the used ionic liquid. The SSA gradually diminish from $45.21\text{ m}^2/\text{g}$ to $29.83\text{ m}^2/\text{g}$, $18.80\text{ m}^2/\text{g}$, $6.89\text{ m}^2/\text{g}$ after modification with C_4mimCl , C_8mimCl , $\text{C}_{12}\text{mimCl}$, respectively.



Sample	$d_{(001)}$ (nm)	Interlayer space (nm)	Interlayer space expansion (nm)
Bent	1.26	0.30	-
Bent C ₄ mimCl	1.39	0.43	0.13
Bent C ₈ mimCl	1.44	0.48	0.18
Bent C ₁₂ mimCl	1.77	0.81	0.51

Figure 6. XRD diffractograms and interlayer spacing of modified Bent clay with imidazolium-based ionic liquids with different lengths of alkyl chains.

Obtained textural properties of the bentonite-ionic liquid composites show that ionic liquid cations not only have entered the bentonite interlayer space but also have adsorbed the exterior surface (Park et al., 2013).

3.2. Sorption studies of inorganic and organic ions

3.2.1. Sorption studies of arsenic (V)

Negatively charged arsenic (V) ions were selected as a model contaminant to study the sorption efficiency of aqueous solutions with raw clay and modified with iron oxy-hydroxide (FeOOH).

Effect of sorbent. The modification of clay materials with iron oxy-hydroxide improved the sorption capacity of studied sorbents in respect to As (V) more than six times. The highest sorption capacity was established for Mt-FeOOH, followed by J-FeOOH, T-FeOOH and raw Mt clay. The sorption capacity of Mt-FeOOH, J-FeOOH and T-FeOOH reached up to 15.62, 11.84 and 11.40 mg/g, respectively, which means that these sorbents are capable of removing more than 99% of As(V) at the initial As(V) concentration of 50 mg/L.

As(V) sorption capacity of Fe-modified clays is relatively high in comparison with other adsorbents described in the literature (Mohan and Pittman, 2007). **Effect of pH.** The highest sorption of As(V) on modified clays were at the initial pH of 2 and were 16.22 ± 0.91 , 16.22 ± 0.91 and 14.56 ± 0.82 mg/g for Mt-FeOOH, J-FeOOH and T-FeOOH, respectively. The maximum sorption capacity of FeOOH modified clays at pH 2-6 can be explained by the speciation forms of the As(V) and the changes in charged surface group concentrations of the sorbent. The sorption process may occur through the interaction of negatively charged As(V) speciation form H_2AsO_4^- and positively charged $\text{Fe}(\text{OH})_2^+$ surface groups, resulting in the formation of a surface complexes (Li et al., 2021). **Sorption isotherms.** Obtained correlation coefficient values (>0.89) indicated that almost for all sorbents (except T clay and Mt clay modified with FeOOH), both the Langmuir and Freundlich isotherms can describe sorption data adequately (Alkaram et al., 2009). The suitability of the two isotherm models for the investigated systems indicates that both monolayer and multilayer sorption exist under the experimental conditions studied. Thus, the sorption of As(V) onto these surfaces is a complex process, involving more than one mechanism (Freundlich, 1906; Langmuir, 1918; Febrianto et al., 2009).

3.2.2. Sorption studies of lanthanum(III), neodymium(III), cerium(III)

Positively charged lanthanum(III), neodymium(III) and cerium(III) ions were chosen as the model rare earth elements to investigate the removal efficiency from aqueous solution by raw Mt clay and modified with Hap.

Effect of sorbent. The sorption capacity increased more than 2 times after montmorillonite modification with hydroxyapatite and the highest sorption capacity was 284 mg/g for La(III). Modification with Hap increases sorption sites for positively charged elements. Based on previous studies, uptake mechanisms of La(III), Ce(III) and Nd(III) can include cations exchange with calcium ions and a surface complexation mechanism exerted by the surface phosphate anion groups (Ramakrishnan et al., 2016). **Sorption isotherms.** Obtained correlation coefficient values indicated that for raw Mt clay and Mt-hydroxyapatite composite, Langmuir isotherm model is the most suitable equation to describe the sorption behaviour. This indicates that for the studied sorbents, sorption of La(III), Nd(III), Ce(III) is a monolayer (Langmuir, 1918; Febrianto et al., 2009).

3.2.3. Sorption studies of p-nitrophenol

p-nitrophenol (PNP) was chosen as a model organic pollutant to investigate the removal efficiency from aqueous solution by raw Mt, T and J clays and modified with nonionic (DDAO, NMO) and cationic surfactants (BTMAC, DTAC) at various surfactant/CEC ratios.

Effect of surfactant loading. Obtained results revealed that the sorption capacity of raw Mt clay for PNP was negligible, but after modification of Mt clay with BTMAC, the sorption capacity increased at a surfactant/CEC ratio of 2.

However, the sorption capacity of the newly developed materials for PNP at surfactant/CEC ratios 0.5, 1.0, and 3.0 was relatively low. When surfactant loading exceeds the CEC of the clay, the surfactants occupy both the clay interlayer and the external space. Therefore, PNP sorption occurs not only due to hydrophobic interaction, but also through electrostatic interaction (Park et al., 2013). **Effect of sorbent.** The largest PNP sorption capacity was observed on Mt_DDAO_2 (0.36 mg/g) when the PNP concentration was 25 mg/L. X-ray diffraction results (see Chapter 3.1.4.) indicated that the increased interlayer space can be linked to the efficacy of PNP sorption (Park et al., 2013). **Effect of contact time.** Sorption capacity of the PNP onto Mt clay and T clay modified with dimethyldodecylamine N-oxide at surfactant/CEC ratio 2.0 (Mt_DDAO_2 and T_DDAO_2) reached a maximum within 60 min, after which no substantial changes were observed. This can be explained, in part, by the reduced number of available vacant sorption sites and increased contact time (Zhang et al., 2015). **Effect of pH.** The highest removal efficiency was obtained in an acidic environment, from pH 2 to 4. When the pH exceeded 6, the removal efficiency significantly decreased due to clay surface charge change and protonation of PNP. **Sorption isotherms.** The correlation coefficient values were >0.89 indicating that both the Langmuir and Freundlich isotherms can describe sorption data adequately (Alkaram et al., 2009). However, in the case of Mt clay modified with benzyltrimethylammonium chloride (Mt_BTMAC_2), R^2 is lower than 0.89, hence, sorption cannot be adequately described by these isotherms. The suitability of the two isotherm models for the investigated systems indicates that both monolayer and multilayer sorption exist under the experimental conditions studied. Thus, the sorption of PNP onto these surfaces is complex, involving more than one mechanism (Febrianto et al., 2009).

3.2.4. Sorption studies of Congo red

Congo red (CR) was chosen as a model organic pollutant to investigate the removal efficiency from an aqueous solution by raw Bt clay and modified with imidazolium-based ionic liquids with different lengths of alkyl chains.

Effect of sorbent. The sorption capacity significantly increased after Bent clay modification, and the highest sorption capacity was 150 mg/g for Bent clay modified with 1-dodecyl-3-methylimidazolium chloride (Bent_C₁₂mimCl), when CR concentration was 100 mg/L. According to sorption data and XRD results (see Chapter 3.1.5.), removal efficiency of CR is linked to the size of the interlayer space of modified Bent samples; the largest interlayer space sorbed the highest amount of dye molecules (Figure 7). **Effect on contact time.** At the initial stage, the removal of CR is relatively fast; with 10 mg of sorbents used, approximately 50% of dye molecules were sorbed in the first 30 minutes. Congo red sorption equilibrium time on raw Bent clay and modified with 1-dodecyl-3-methylimidazolium chloride (Bent_C₁₂mimCl) was 60 min. and 240 min., respectively. **Sorption kinetics.** Obtained correlation coefficient values indicated that for raw Bent clay and modified with ionic liquid 1-dodecyl-3-

methylimidazolium chloride (Bent C_{12} mimCl) the Lagergren pseudo-second kinetic model is the most suitable equation to describe the sorption mechanisms between the sorbent and sorbate. Thus, the sorption kinetics process is governed by the chemisorption mechanism (Alshammari et al., 2020). **Effect of pH.** The maximum equilibrium sorption capacity of 98 mg/g corresponding to 100% of removal efficiency was achieved at pH 2. At pH 4 both the removal efficiency and the equilibrium sorption capacity decreased to 70% and 76 mg/g, respectively. In the interval from pH 5 to pH 10, the removal efficiency slightly increased and was on average 80%. A decrease in the removal of CR by Bent clay with increasing pH is related to the dissociation of sulfonate groups of CR producing anionic dye ions. (Yang et al., 2021).

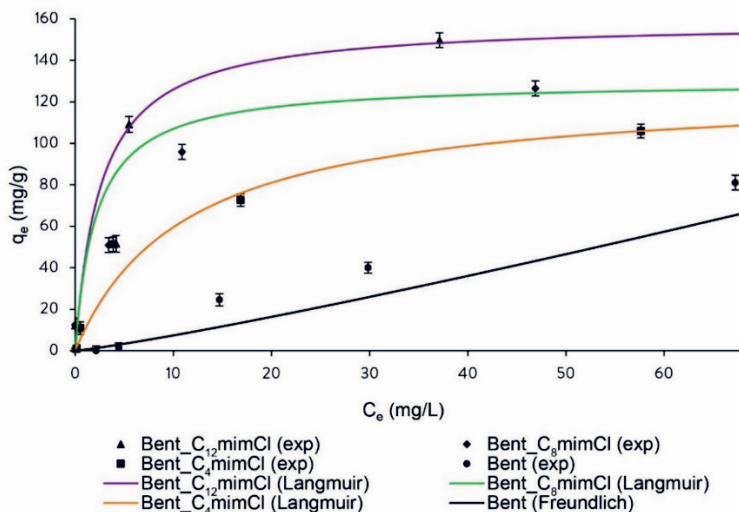


Figure 7. Effect of initial concentration on the removal of Congo red by raw Bent clay and modified with imidazolium-based ionic liquids with different lengths of alkyl chains (experimental conditions: $C_i = 0.5\text{--}50$ mg/L, pH = 5.5, contact time = 24 h, $T = 24$ °C).

Sorption isotherms. Obtained correlation coefficient values indicated that for raw Bent clay, Freundlich isotherm model is the most suitable equation to describe the sorption behaviour, whereas in the case of the Bent-ionic liquid composites Langmuir isotherm model is the most relevant. This suggests that for raw Bent clay sorption of CR is of a multilayer character, while for modified Bent samples sorption is of monolayer type (Freundlich, 1906; Langmuir, 1918; Alkaram et al., 2009).

3.3. Prospective applications of newly developed materials and future outlook

Sorbents are a group of materials with high application potential in solving environmental problems (remediation of contaminated areas), civil engineering (purification of drinking water), circular economy (recovery of valuable substances), bioeconomy (use of by-products to create high value-added materials) and many other fields. At the same time, commonly used sorbents are based on oil processing products (synthetic ion exchange resins, polyester, polypropylene and polyurethane and other materials), and despite their excellent performance, their use cannot be considered as sustainable (Fingas, 2011; Murray and Bugdayli, 2021). Additionally, the European Green Deal actions such as “Chemicals Strategy for Sustainability” highlight the importance of developing environmentally friendly technologies and increasing the usage of safe and sustainable materials which do not harm people and the environment (European Commission, 2020). Results of this study demonstrate that clay can be successfully used to replace synthetic sorbents. Clays are natural, abundant and low-cost material, while elaborated modified clay-based materials support possibilities to design sorbents with the properties needed to target the corresponding problem.

In this study, a targeted modification of clay minerals was conducted to change their physical and chemical properties and to design innovative materials for environmentally friendly technologies. Detailed characterization of the developed clay composites demonstrated alteration in interlayer space, specific surface area, pore volume, particle morphology, charge properties and new sorption centres (see Chapters 3.1. and 3.2.). Thus, modified clay materials viewed in this study can be used as efficient sorbents: 1) in environmental remediation by, e.g., removing inorganic and organic ions from water and wastewater; 2) in the circular economy by recovering valuable metals from waste; 3) in bioeconomy, using agricultural by-products to develop materials with high value-added materials, e.g., pH-sensitive indicators to monitor food freshness (Figure 8).

Materials elaborated in this study can find diverse application possibilities. Based on the discussion and results described in previous chapters, clays modified with ionic liquids, surfactants, iron oxy-hydroxide and hydroxyapatite can be successfully used in solid-liquid sorption systems, such as fixed-bed reactors and batch reactors. The main applications of clay sorbents include, but are not limited to the following water treatment systems: 1) the wastewater treatment plants for removal of emerging pollutants; 2) pre-treatment installations of industrial wastewaters; 3) constructed wetland treatment systems; 4) *in situ* filter system to remove pollutants from water streams.

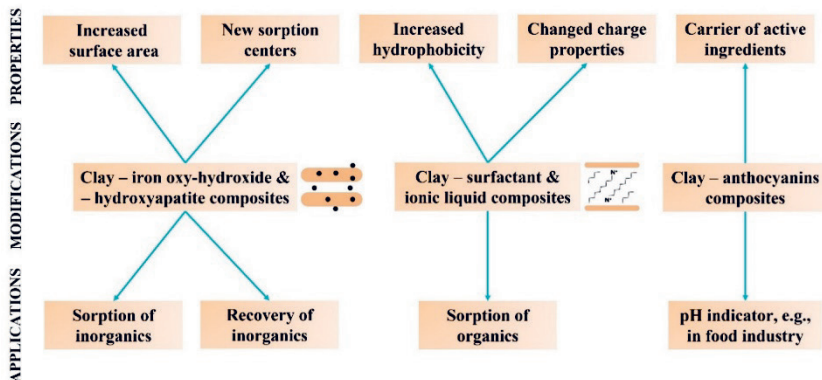


Figure 8. Scheme of modified clay composites' connections with their properties and environmental application prospects in this study.

For example, Heiderscheidt et al. (2020) has proposed an innovative purification system for mineral and biomass-based sorbent application in the pre-treatment installation of industrial wastewaters. In the study, a continuous-flow continuous stirred tank reactor, followed by a sedimentation unit for sorbent/water separation was designed (Figure 9). In the dosing tank, a slurry of the sorbent is prepared, and then the necessary concentration of suspension is pumped to the stirred tank where wastewater is being treated. The resultant suspension containing the wastewater and the dosed sorbent is transferred by gravity from the stirred tank reactor to the sedimentation unit to remove solid material from treated water. This example of purification installation solves one of the main challenges in the integration of clay sorbents in the WWTS – effective solid/liquid separation after the treatment process.

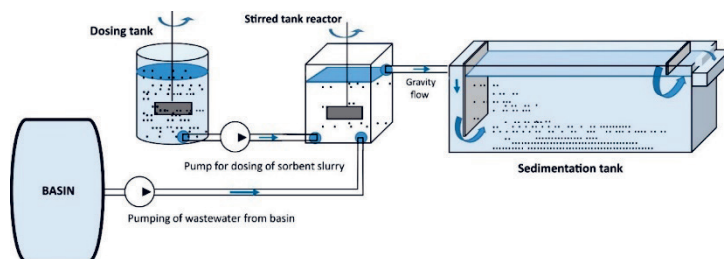


Figure 9. Visualization of the continuous-flow continuous stirred tank reactor system and sedimentation unit for mineral sorbents application in WWTS (Heiderscheidt et al., 2020).

Clay-anthocyanin composites are more appropriate for innovative application in the food industry as freshness indicators that detect perishable food

quality. Within the thesis, spoilage tests of fresh chicken fillets were conducted to evaluate clay-anthocyanin composites' performance as smart sensors in food packaging (Figure 10 A). The experimental results showed that the colour of the sensor changed from red to blue when organoleptic parameters were inadequate and changes in consistency, taste, odour and appearance of the meat product were not encouraging for consumption (Figure 10 B); and before bacterial contamination exceeded the threshold values set by the Commission Regulation on microbiological criteria for foodstuffs No. 2073/2005.

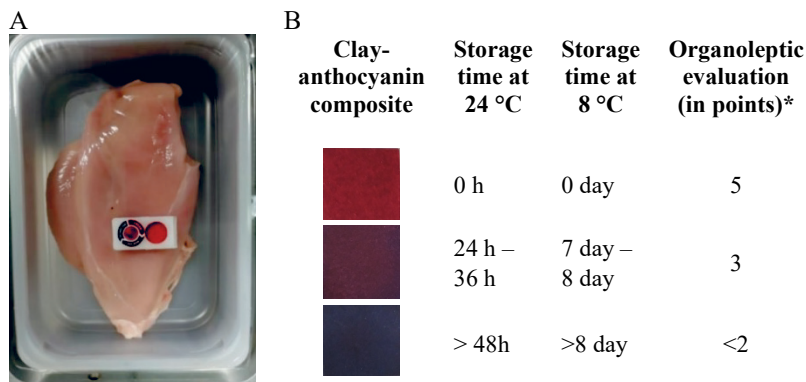


Figure 10. (A) Chicken fillet sample packaged with clay-anthocyanin composite sensor and (B) colour changes of clay-anthocyanin composite depending on the storage time and temperature in air atmosphere. *Organoleptic parameters are evaluated in points where 1 is inappropriate, and 5 is appropriate.

In the European Union, 8.8 million tons of food are wasted in the EU households every year, because customers have difficulties reading date labels (European Commission, 2018). Clay-anthocyanin composite solves the problem by offering complementary freshness sensors to date labels that are incorporated into standard food packaging. The simplicity of the colour change in the sensor will reduce avoidable food waste.

In future studies, prospective clay-based composites are planned to be tested not only in laboratory-scale experiments but also in pilot-scale experiments. Additionally, there are plans to explore new modification methods and application possibilities, e.g., sorption of greenhouse gases, i.e., carbon dioxide; drug carriers of clay-polyphenol composites with immuno-modulating properties, or magnetic clays in wastewater treatment.

CONCLUSION

The elaborated clay modification methods allow to purposefully change the clay properties by integrating into their structure new functional groups, as well as changing physical and chemical properties of the clay, thus supporting development of new application possibilities:

- Characterization methods (SEM, XRD, SSA by BET, FTIR, TG, CEC, content of Fe_2O_3) of the **clay-iron oxy-hydroxide** materials showed changed morphology of the clay particles, increased surface area, new Fe–O functional groups, the presence of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and other parameters indicating a successful clay modification with iron oxy-hydroxide.
- Characterization methods (SEM, XRD, SSA by BET, FTIR and TG) of the **clay-hydroxyapatite** materials showed the presence of hydroxyapatite precipitated crystals, new CO_3^{2-} groups by IR, significant changes in the mineral composition, decomposition region related to the carbon dioxide released from carbonated apatite and other parameters indicating a successful clay modification with hydroxyapatite.
- Characterization methods (SEM, XRD, SSA by BET, FTIR and TG) of the **clay-surfactant** materials showed new CH_2 groups by IR, interlayer space expansion, SSA and pore size decrease, larger particle agglomerations, hydrophobicity and other parameters indicating a successful clay modification with nonionic and cationic surfactants.
- Characterization methods (XRD, SSA by BET, FTIR and TG) of **clay-ionic liquid** materials showed new CH_2 groups by IR, the interlayer space expansion, pore volume increase, SSA and pore size decrease, hydrophobicity and other parameters indicating a successful clay modification with ionic liquids having different lengths of alkyl chains.

The modified clays obtained within this study demonstrate high performance and potential for solving environmental problems. Namely, the presence of specific substances cause undesirable effects in the environment, and the modified clays can be used for removal of the selected groups of substances:

- **Sorption studies of non-metals, for example, As(V)**, with clay-iron oxy-hydroxide sorbents under various environmental conditions revealed that the highest sorption capacity of As(V) can be achieved by modification of montmorillonite sorbent (Mt-FeOOH). The sorption capacity increases in an acidic environment through surface complexation, and Langmuir and Freundlich isotherm models are used to describe the monolayer and multilayer sorption. Therefore, the sorption studies indicate an efficacious modification of the clay-iron

oxy-hydroxide sorbent for the removal of negatively charged inorganic pollutants from aqueous solutions.

- **Sorption studies of REEs, for example, La(III), Ce(III), Nd(III)**, with clay-hydroxyapatite sorbents under various environmental conditions revealed that the highest sorption capacity of La(III), Ce(III), Nd(III) can be achieved by modification of montmorillonite sorbent (Mt-Hap), and Langmuir isotherm model is used to describe monolayer sorption. Therefore, the sorption studies indicate an efficacious modification of the clay-hydroxyapatite sorbent for the removal of positively charged inorganic elements from aqueous solutions.
- **Sorption studies of phenols, for example, *p*-nitrophenol (PNP)**, with clay-surfactant sorbents under various environmental conditions revealed that the highest removal of PNP can be achieved by modification of montmorillonite with dimethyldodecylamine N-oxide (DDAO) at surfactant/CEC ratio 2 (Mt-DDAO_2). The sorption capacity increases in acidic environment through hydrophobic interactions and Van der Waals force, and Langmuir and Freundlich isotherm models are used to describe monolayer and multilayer sorption. Therefore, the sorption studies indicate an efficacious modification of the clay-surfactant sorbent for the removal of organic pollutants (neutral molecules) from aqueous solutions.
- **Sorption studies of organic dyes, for example, Congo red (CR)**, with clay-ionic liquids sorbents under various environmental conditions revealed that the highest sorption capacity can be achieved by modification of bentonite with 1-dodecyl-3-methylimidazolium chloride (Bent_C₁₂mimCl) having the longest alkyl chain among the tested materials. The sorption capacity of CR increases in acidic environment through hydrophobic interactions, and Langmuir and Freundlich isotherm models are used to describe monolayer and multilayer sorption, while Lagergren's pseudo-second-order kinetic suggests that the sorption kinetics process is governed by the chemisorption mechanism. Therefore, the sorption studies indicate an efficacious modification of the clay-ionic liquid sorbents for the removal of negatively charged organic pollutants from aqueous solutions.

Clays modified with ionic liquids, surfactants, iron oxy-hydroxide and hydroxyapatite can be successfully used in solid-liquid sorption systems to remove pollutants or recover valuable elements from waste streams. The clay-anthocyanin composites, in turn, can be used in the food industry as freshness indicators that ensure quality of perishable food.

REFERENCES

- Aftafa, C., Pelit, F. O., Yalçinkaya, E. E., Turkmen, H., Kapdan, İ., & Nil Ertaş, F. (2014). Ionic liquid intercalated clay sorbents for micro solid phase extraction of steroid hormones from water samples with analysis by liquid chromatography–tandem mass spectrometry. *Journal of Chromatography A*, *1361*, 43–52.
- Alkaram, U. F., Mukhlis, A. A., & Al-Dujaili, A. H. (2009). The removal of phenol from aqueous solutions by adsorption using surfactant-modified bentonite and kaolinite. *Journal of Hazardous Materials*, *169*(1–3), 324–332.
- Alshammari, M., Al Juboury, M. F., Naji, L. A., Faisal, A. A. H., Zhu, H., Al-Ansari, N., & Naushad, M. (2020). Synthesis of a Novel Composite Sorbent Coated with Siderite Nanoparticles and its Application for Remediation of Water Contaminated with Congo Red Dye. *International Journal of Environmental Research*, *14*, 177–191.
- Andrunik, M., & Bajda, T. (2019). Modification of Bentonite with Cationic and Nonionic Surfactants: Structural and Textural Features. *Materials*, *12*(22), 3772.
- Ansone-Bērīņa, L. (2015). *V un VI grupas metaloīdu sorbcijas izpēte uz modificētiem biomateriālu sorbentiem* [Promcijas darbs, Latvijas Universitāte]. Latvijas Universitāte.
- Bergaya, F., & Lagaly, G. (2006). General introduction: clays, clay minerals, and clay science. In F. Bergaya, B.K.G. Theng and G. Lagaly (eds.), *Developments in Clay Science* (Vol. 1, pp. 1–18). Elsevier.
- Biswas, B., Warr, L. N., Hilder, E. F., Goswami, N., Rahman, M. M., Churchman, J. G., Vasilev, K., Pan, G., & Naidu, R. (2019). Biocompatible functionalisation of nanoclays for improved environmental remediation. *Chemical Society Reviews*, *48*(14), 3740–3770.
- Boujelben, N., Bouzid, J., Elouear, Z., Feki, M., Jamoussi, F., & Montiel, A. (2008). Phosphorus removal from aqueous solution using iron coated natural and engineered sorbents. *Journal of Hazardous Materials*, *151*(1), 103–110.
- Brovkina, J., Lakevičs, V., Stepanova, V., Ozoliņš, J., Bērziņa-Cimdiņa, L. (2012). Efektīvu sorbentu izstrāde uz Latvijas dabīgo mālu bāzes. *Material Science and Applied Chemistry*, *26*, 37–41.
- Christidis, G. E. (2010). Industrial Clays. In G. E. Christidis (ed.), *EMU Notes in Mineralogy. Advances in the Characterization of Industrial Minerals* (Vol. 9, pp. 341–414). European Mineralogical Union and the Mineralogical Society of Great Britain & Ireland.
- El-Nagar, D. A., Massoud, S. A., & Ismail, S. H. (2020). Removal of some heavy metals and fungicides from aqueous solutions using nano-hydroxyapatite, nano-bentonite and nanocomposite. *Arabian Journal of Chemistry*, *13*(11), 7695–7706.
- European Commission. (2018). *Market study on date marking and other information provided on food labels and food waste prevention: final report*. <https://data.europa.eu/doi/10.2875/808514>
- European Commission. (2020). *Final communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions Chemicals Strategy for Sustainability Towards a Toxic-Free Environment* (COM/2020/667 final). <https://ec.europa.eu/environment/pdf/chemicals/2020/10/Strategy.pdf>.
- Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y.-H., Indraswati, N., & Ismadji, S. (2009). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. *Journal of Hazardous Materials*, *162*(2–3), 616–645.
- Fiscal-Ladino, J. A., Obando-Ceballos, M., Rosero-Moreano, M., Montañó, D. F., Cardona, W., Giraldo, L. F., & Richter, P. (2017). Ionic liquids intercalated in montmorillonite as the sorptive phase for the extraction of low-polarity organic compounds from water by rotating-disk sorptive extraction. *Analytica Chimica Acta*, *953*, 23–31.
- Freundlich, H. M. F. (1906). Over the Adsorption in Solution. *The Journal of Physical Chemistry*, *57*, 385–471.
- Guégan, R. (2019). Organoclay applications and limits in the environment. *Comptes Rendus Chimie*, *22*(2–3), 132–141.
- Guggenheim, S., & Martin, R. T. (1995). Definition of Clay and Clay Mineral: Joint Report of the AIPEA Nomenclature and CMS Nomenclature Committees. *Clays and Clay Minerals*, *43*(2), 255–256.
- He, H., Ma, L., Zhu, J., Frost, R. L., Theng, B. K. G., & Bergaya, F. (2014). Synthesis of organoclays: A critical review and some unresolved issues. *Applied Clay Science*, *100*, 22–28.
- Heiderscheidt, E., Postila, H., & Leiviskä, T. (2020). Removal of metals from wastewaters by mineral and

- biomass-based sorbents applied in continuous-flow continuous stirred tank reactors followed by sedimentation. *Science of The Total Environment*, 700, 135079.
- Ismadjji, S., Soetaredjo, F. E., & Ayucitra, A. (2015). Natural Clay Minerals as Environmental Cleaning Agents. In S. Ismajji, F. E. Soetaredjo & A. Ayucitra (eds.), *Clay Materials for Environmental Remediation* (pp. 5–37). Springer, Cham.
- Karasa, J., Kostjukovs, J., Palasa, A., & Actins, A. (2012). Advanced Research of the Triassic Clay from the Baltic Region. *Latvian Journal of Chemistry*, 51(4), 376–382.
- Khorshidi, N., & Reza Azadmehr, A. (2017). Competitive adsorption of Cd(II) and Pb(II) ions from aqueous solution onto iranian hematite (Sangan mine): Optimum condition and adsorption isotherm study. *Desalination and Water Treatment*, 58, 106–119.
- Krauklis, A., Ozola, R., Burlakovs, J., Rugele, K., Kirillov, K., Trubaca-Boginska, A., Rubenis, K., Stepanova, V., & Klavins, M. (2017). FeOOH and Mn8O10Cl3 modified zeolites for As(V) removal in aqueous medium. *Journal of Chemical Technology & Biotechnology*, 92(8), 1948–1960.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40(9), 1361–1403.
- Latvian Environment, Geology and Meteorology Centre (LEGMC). (n.d.). *Register of mineral deposits*. Meteo. Retrieved on September 10, 2019, from <https://www.meteo.lv/apex/f?p=117>
- Lee, S. M., & Tiwari, D. (2012). Organo and inorgano-organo-modified clays in the remediation of aqueous solutions: An overview. *Applied Clay Science*, 59–60, 84–102
- Lenoble, V., Bouras, O., Deluchat, V., Serpaud, B., & Bollinger, J. C. (2002). Arsenic Adsorption onto Pillared Clays and Iron Oxides. *Journal of Colloid and Interface Science*, 255(1), 52–58.
- Li, B., Wei, D., Zhou, Y., Huang, Y., Tie, B., & Lei, M. (2021). Mechanisms of arsenate and cadmium co-immobilized on ferrihydrite inferred from ternary surface configuration. *Chemical Engineering Journal*, 424, 130410.
- Li, Z., & Bowman, R. S. (2001). Retention of inorganic oxyanions by organo-kaolinite. *Water Research*, 35(16), 3771–3776.
- Litefti, K., Freire, M. S., Stitou, M., & González-Álvarez, J. (2019). Adsorption of an anionic dye (Congo red) from aqueous solutions by pine bark. *Scientific Reports*, 9, 16530.
- Mohan, D., & Pittman, C. U. (2007). Arsenic removal from water/wastewater using adsorbents – A critical review. *Journal of Hazardous Materials*, 142(1–2), 1–53.
- Moore, D.M. & Reynolds, R.C. Jr (1997). *X-ray Diffraction and the Identification and Analysis of Clay Minerals* (2nd ed.). Oxford University Press.
- Murray, H. H. (2000). Traditional and new applications for kaolin, smectite, and palygorskite: a general overview. *Applied Clay Science*, 17(5–6), 207–221.
- Murray, H.H. (ed.). (2007). *Applied clay mineralogy: Occurrences, processing and application of kaolins, bentonites, palygorskite-sepiolite, and common clays. Developments in Clay Science* (Vol. 2.). Elsevier.
- Murray, M. L., & Bugdayli, K. (2021). Sustainable origin-sorbents for heavy metal contamination: Research progress within an Australian context. In A. Núñez-Delgado *Sorbents Materials for Controlling Environmental Pollution* (pp. 33–48). Elsevier.
- Nasser, M. S., Onaizi, S. A., Hussein, I. A., Saad, M. A., Al-Marri, M. J., & Benamor, A. (2016). Intercalation of ionic liquids into bentonite: Swelling and rheological behaviors. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 507, 141–151.
- Ozola(a), R., Krauklis, A., Burlakovs, J., Klavins, M., Vincevica-Gaile, Z., & Hogland, W. (2019). Surfactant-Modified Clay Sorbents for the Removal of p-nitrophenol. *Clays Clay Minerals*, 67, 132–142.
- Ozola(b), R., Krauklis, A., Leitietis, M., Burlakovs, J., Vircava, I., Ansone-Bertina, L., Bhatnagar, A., & Klavins, M. (2019). FeOOH-modified clay sorbents for arsenic removal from aqueous solutions. *Environmental Technology & Innovation*, 13, 364–372.
- Ozola, R., Krauklis, A., Burlakovs, J., Vincevica-Gaile, Z., Rudovica, V., Trubaca-Boginska, A., Borovikova, D., Bhatnagar, A., Vircava, I., Klavins, M. (2017). Illite clay modified with hydroxyapatite – innovative perspectives for soil remediation from lead (II). *International Journal of Agriculture and Environmental Research*, 3(2), 177–189.

- Ozola-Davidane, R., Burlakovs, J., Tamm, T., Zeltkalne, S., Krauklis, A.E., Klavins, M. (2021). Bentonite – ionic liquid composites for Congo red removal from aqueous solutions. *Journal of Molecular Liquids*, 116373.
- Park, Y., Ayoko, G. A., & Frost, R. L. (2011). Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media. *Journal of Colloid and Interface Science*, 354(1), 292–305.
- Park, Y., Ayoko, G. A., Kurdi, R., Horváth, E., Kristóf, J., & Frost, R. L. (2013). Adsorption of phenolic compounds by organoclays: Implications for the removal of organic pollutants from aqueous media. *Journal of Colloid and Interface Science*, 406, 196–208.
- Ramakrishnan, P., Nagarajan, S., Thiruvengadam, V., Palanisami, T., Naidu, R., Mallavarapu, M., & Rajendran, S. (2016). Cation doped hydroxyapatite nanoparticles enhance strontium adsorption from aqueous system: A comparative study with and without calcination. *Applied Clay Science*, 134, 136–144.
- Rodríguez-Cruz, M. S., Sánchez-Martín, M. J., Andrades, M. S., & Sánchez-Camazano, M. (2007). Modification of clay barriers with a cationic surfactant to improve the retention of pesticides in soils. *Journal of Hazardous Materials*, 139(2), 363–372.
- Rouquerol, J., Llewellyn, P., & Sing, K. (2013). Adsorption by Clays, Pillared Clays, Zeolites and Aluminophosphates. In F. Rouquerol, J. Rouquerol, K.S.W. Sing, P. Llewellyn & G. Maurin (eds.), *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications* (2nd ed., pp. 467–527). Academic Press.
- Sarkar, B., Rusmin, R., Ugochukwu, U. C., Mukhopadhyay, R., & Manjaiah, K. M. (2019). Modified clay minerals for environmental applications. In M. Mercurio, B. Sarkar & A. Langella (eds.), *Modified Clay and Zeolite Nanocomposite Materials: Environmental and Pharmaceutical Applications* (pp. 113–127). Elsevier.
- Schroeder, P. (2018). *Clays in the Critical Zone*. Cambridge University Press.
- Shaltout, A. A., Allam, M. A., & Moharram, M. A. (2011). FTIR spectroscopic, thermal and XRD characterization of hydroxyapatite from new natural sources. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 83(1), 56–60.
- Singh, R., Singh, S., Parihar, P., Singh, V. P., & Prasad, S. M. (2015). Arsenic contamination, consequences and remediation techniques: A review. *Ecotoxicology and Environmental Safety*, 112, 247–270.
- Smedley, P. L., & Kinniburgh, D. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17(5), 517–568.
- Stinkule, A. (2014). *Māli Latvijas zemes dzīlēs*. RTU publishing house.
- Stuart, B. (2004). *Infrared spectroscopy: fundamentals and applications*. John Wiley & Sons.
- Sun, K., Shi, Y., Xu, W., Potter, N., Li, Z., & Zhu, J. (2017). Modification of clays and zeolites by ionic liquids for the uptake of chloramphenicol from water. *Chemical Engineering Journal*, 313, 336–344.
- Sverdrup, H., & Ragnarsdóttir, V. K. (2014). Natural resources in a planetary perspective. *Geochemical Perspectives*, 3(2), 129–341.
- Taleb, K., Pillin, I., Grohens, Y., & Saidi-Besbes, S. (2018). Gemini surfactant modified clays: Effect of surfactant loading and spacer length. *Applied Clay Science*, 161, 48–56.
- World Economic Forum. (2019). *Insight Report: Top 10 Emerging Technologies of 2019*. Retrieved on December 9, 2019, from http://www3.weforum.org/docs/WEF_Top_10_Emerging_Technologies_2019_Report.pdf
- Wu, H., Xie, H., He, G., Guan, Y., & Zhang, Y. (2016). Effects of the pH and anions on the adsorption of tetracycline on iron-montmorillonite. *Applied Clay Science*, 119, 161–169.
- Zhang, L., Zhang, B., Wu, T., Sun, D., & Li, Y. (2015). Adsorption behavior and mechanism of chlorophenols onto organoclays in aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 484, 118–129.
- Zhou, C. H., & Keeling, J. (2013). Fundamental and applied research on clay minerals: From climate and environment to nanotechnology. *Applied Clay Science*, 74, 3–9.

