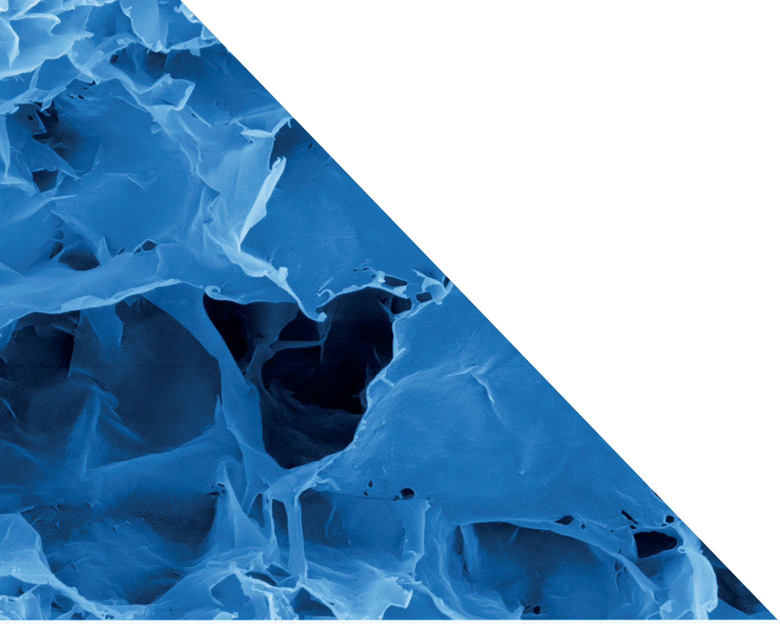

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Rūta
Ozola-Davidāne

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

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MĀLA KOMPOZĪTMATERIĀLU IZSTRĀDE UN
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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

AEC	anion exchange capacity
AIPEA	Association Internationale pour l'Etude des Argiles
Bent clay	Bentonite, sodium form produced from Alfa Aesar
BET	the Brunauer, Emmett and Teller method
BTMAC	benzyltrimethylammonium chloride
C_{12}mimCl	1-dodecyl-3-methylimidazolium chloride
C_{12}mmimDMP	1-dodecyl-3-methylimidazolium dimethyl phosphate
C_1mmimDMP	1,3-dimethylimidazolium dimethyl phosphate
C_4mimCl	1-butyl-3-methylimidazolium chloride
C_4mmimDMP	1-butyl-3-methylimidazolium dimethyl phosphate
C_8mimCl	1-octyl-3-methylimidazolium chloride
C_8mmimDMP	1-octyl-3-methylimidazolium dimethyl phosphate
CEC	cation exchange capacity
CMS	The Clay Minerals Society
CPC/CPN	clay–polymer composite / clay–polymer nanocomposite
CR	Congo red
CW	constructed wetland
DDAO	dimethyldodecylamine N-oxide
DTAC	dodecyltrimethylammonium chloride
DTGA	differential thermogravimetry analysis
DWT	drinking water treatment
EEE	electrical and electronic equipment
FAAS	flame atomic absorption spectrometry
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
NPs	clay-supported nanoparticles
PNP	*p*-nitrophenol
PZC	point zero charge

REEs	rare earth elements
SEM	scanning electron microscopy
SSA	specific surface area
T clay	Triassic System clay from the Saltiski deposit
TG	thermogravimetry
TWW	treated wastewater
WWT	wastewater treatment
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.

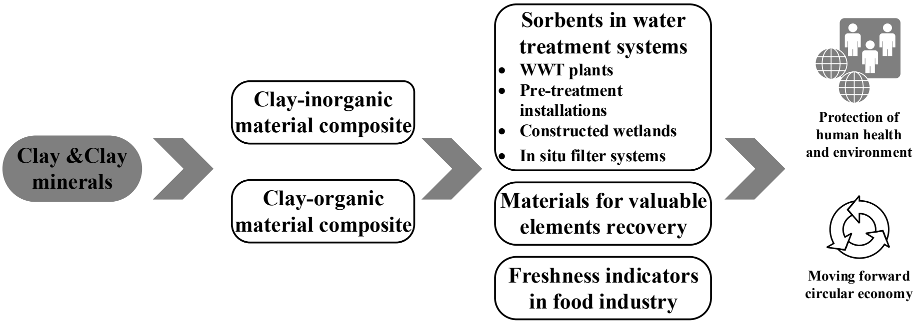

Figure I. **Schematic representation of the study tasks** (WWT – wastewater treatment).

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, IF_{2020} = 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, IF_{2020} = 1.609) (further referred to as **Paper II**).
3. **Ozola, 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. (Web of Science/SCOPUS, Q2/Q1, IF_{2019} = 3.356) (further referred to as **Paper III**).
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Journal of Cleaner Production. 186, 81–90. (Web of Science/SCOPUS, Q1/Q1, IF_{2019} = 7.246) (further referred to as **Paper V**).

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(note: as of 2020, the surname has been changed from 'Ozola' to 'Ozola-Davidāne')

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Patent

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

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(note: as of 2020, the surname has been changed from 'Ozola' to 'Ozola-Davidāne')

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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 I. Three scientific articles are included in the Appendices (A–C).

Table I

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	×			
Clay-surfactants	II		×	×	×
	IV	×			×
	VIII		×	×	×
Clay-iron oxy-hydroxide	III		×	×	×
	VIII		×		
	VI		×	×	×
Clay-hydroxyapatite	V				×
	VII		×	×	×
	Only in the thesis			×	×
Clay-ionic liquids	I		×	×	×
	IV	×			×
Clay-anthocyanins	Patent				×

The structure of the thesis includes an introduction, three main chapters and appendices. In the first part of the thesis, the definition of clay and clay minerals are reviewed; structural differences, classification and properties of clay minerals are described; information on clay mineral distribution in the world and in Latvia is aggregated; as well as the compilation of scientific literature on clay modification methods and their application in environmentally friendly technologies is presented. The second part comprises information about the clay samples, the methodology of the clay modification and characterization. The third part focuses on the results of physical and chemical properties of clay minerals, the removal efficiency of organic and inorganic substances as well as application potential for newly developed clay composite materials.

The thesis consists of 106 pages and is supplemented with illustrations – 45 pictures and 8 tables. The Paper I, Paper II, and Paper III are included in the appendices.

Author’s contribution

R. Ozola-Davidāne developed all modification methods, carried out most of the experiments, analysed and interpreted data as well as wrote the major part of the papers under the supervision of *prof., Dr. habil. chem*. Māris Kļaviņš and *Dr. geogr.* Juris Burlakovs. In the preparation of papers V and VI the main contribution was from *Dr. geogr.* Juris Burlakovs and *Dr.* Andrejs E. Krauklis, respectively. Detailed author's contribution in preparing scientific papers related to the thesis is as follows:

- **Paper I**. Conceptualization 90%; Methodology 90%; Experimental work 100%; Data analysis 100%; Writing (original draft preparation, review, and editing) 90%; Visualization 100%.
- **Paper II**. Conceptualization 90%; Methodology 90%; Experimental work 100%; Data analysis 90%; Writing (original draft preparation, review, and editing) 90%; Visualization 100%.
- **Paper III**. Conceptualization 90%; Methodology 90%; Experimental work 100%; Data analysis 70%; Writing (original draft preparation, review, and editing) 70%; Visualization 60%.
- **Paper IV**. Conceptualization 80%; Methodology 100%; Experimental work 100%; Data analysis 80%; Writing (original draft preparation, review, and editing) 60%; Visualization 100%.
- **Paper V**. Conceptualization 10%; Methodology 10%; Experimental work 20%; Data analysis 20%; Writing (original draft preparation, review, and editing) 20%; Visualization 10%.
- **Paper VI**. Conceptualization 10%; Methodology 10%; Experimental work 10%; Data analysis 10%; Writing (original draft preparation, review, and editing) 40%; Visualization 10%.
- **Paper VII.** Conceptualization 50%; Methodology 50%; Experimental work 50%; Data analysis 50%; Writing (original draft preparation, review, and editing) 50%; Visualization 40%.
- **Paper VIII**. Conceptualization 100%; Methodology 100%; Experimental work 100%; Data analysis 80%; Writing (original draft preparation, review, and editing) 70%; Visualization 100%.
- **Paper IX**. Conceptualization 60%; Methodology 70%; Experimental work 80%; Data analysis 70%; Writing (original draft preparation, review, and editing) 70%; Visualization 70%

1. LITERATURE REVIEW

1.1. Terminology for clay and clay minerals

According to the joint nomenclature committees of Association Internationale pour l'Etude des Argiles (AIPEA) and Clay Minerals Society (CMS) for the scientific purposes '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. The 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. The reason for this is that various disciplines consider different particle sizes for clays. In colloid science, the particle size limit is 1μm, in geology and soil science 2 μm and 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 the origin of materials (unlike 'clay' definition) and therefore clay minerals may be synthetic such as layer double hydroxides. Also size of minerals does not serve as a criterion in the definition, thus the clay minerals can have any grain size (Bergaya and Lagaly, 2006; Christidis, 2010). Most of the clay minerals found in nature are with a particle size range less than 4 μm (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 differences between definitions of 'clay' and 'clay minerals' is shown in Table 1.1.

In Latvia 'clay' is defined as 'fine grained sedimentary rock, in which the main component is clay minerals – hydrated aluminosilicates – giving specific properties to clay' (Kuršs and Stinkule, 1999; Stinkule, 2014). As natural clay is a mixed rock with foreign material (such as sand, carbonates, and silt), its granulometric composition is characterized by the relative proportions of three fractions in the content:

Table 1.1.

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

clay (<2 μm), silt (2–50 μm), and sand (50–2000 μm). The Figure 1.1. shows detailed representation of the subdivision of soil granulometric composition groups in Latvia (the Regulation of the Cabinet of Ministers No. 804, 2005), which is the same as in the United States (the United States Department of Agriculture (USDA) soil texture triangle) (Groenendyk et al., 2015).

1.2. Structure of clay minerals

Clay minerals have layered structure where each layer consists of two main building blocks: a silica tetrahedral [SiO_4] sheet and a metal oxide, hydroxide octahedral [Me (O, $OH)_6$] sheet, linked together in certain proportions (Schulze, 2005; Theng, 2012; Ismadji et al., 2015).

A tetrahedron consists of central silicon (Si_4^+) cation surrounded by four oxygen atoms (Figure 1.2. A). A tetrahedral sheet is formed when three out of four oxygen ions, known as basal oxygens, of each tetrahedron are shared with three nearest tetrahedra.

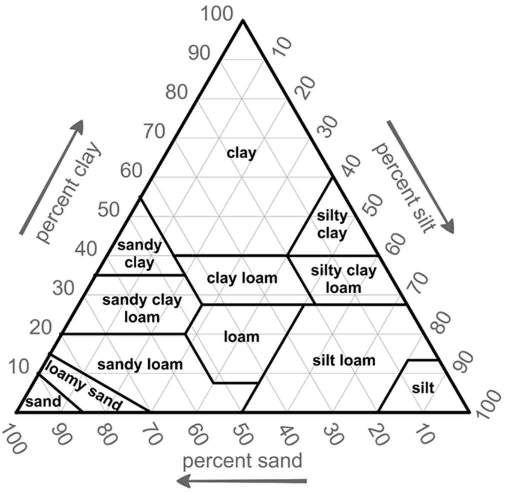


Figure 1.1. **Nomograph for determination of soil and ground texture**
(Groenendyk et al., 2015).

In the result, corner-linked tetrahedra form an infinitive two-dimensional hexagonal mesh pattern (Figure 1.2. B). The fourth oxygen ion, apical oxygen, points in a direction normal to the sheet and at the same time it is a part of the adjacent octahedral sheet. Unshared oxygen atoms are present in hydroxyl form (Schulze, 2005; Christidis, 2010).

An octahedron consists of a central cation (mainly, aluminum (Al_3^+) or magnesium (Mg_2^+)) surrounded by six oxygen or hydroxyl atoms (Figure 1.2. C, E). An octahedral sheet is formed when adjacent octahedrons share two oxygens with one another. The edge-shared octahedra form a sheet of hexagonal or pseudo-hexagonal symmetry. The smallest structural unit contains three octahedra. When bivalent cation, such as Mg^{2+} or Fe^{2+}, is the central molecule, all three octahedral positions are occupied to produce an electrically neutral structure (Figure 1.2. F).

The resultant sheet structure is termed as 'trioctahedral' and it is typical for the mineral brucite. When trivalent cation, such as Al^{3+} or Fe^{3+}, is the central molecule, only two of every three octahedral sites are filled in order to maintain electrical neutrality (Figure 1.2. D). The resultant sheet structure is termed as 'dioctahedral' and it is typical for the mineral gibbsite (Figure 1.3. A) (Schulze, 2005; Christidis, 2010; Theng, 2012; Schoonheydt et al., 2018).

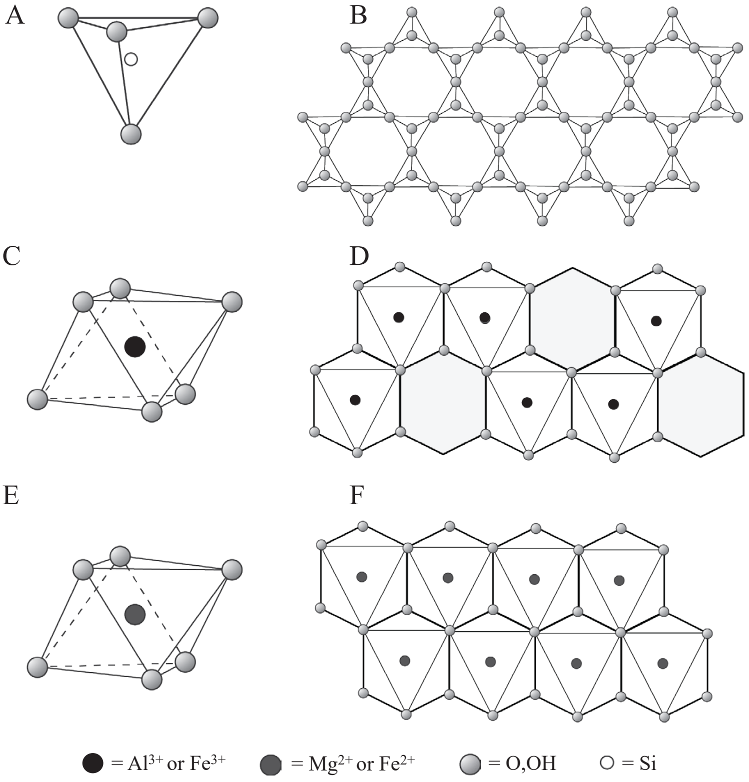


Figure 1.2. **Schematic representation of Si tetrahedron (A) and tetrahedral sheet (B), Al octahedron (C) and dioctahedral sheet (D), Mg octahedron (E) and trioctahedral sheet (F)** (adapted from Yariv and Cross, 2002).

1.3. Classification of clay minerals

The classification of clay minerals was firstly proposed by Grim (1962), which has become a basis for outlining the nomenclature and differences between the various clay minerals (Murray, 2007). Martin et al. (1991) introduced classification with modifications made by international nomenclature committee, which is currently

Table 1.2.

Classification of clay minerals based on a scheme for planar and modulated hydrous phyllosilicate structures (adapted from Guggenheim et al., 2006 and Schroeder, 2018)

Layer type	Interlayer material[1]	Group	Octahedral character[2]	Mineral species[3]
1 : 1	None/H_2O (X = 0)	Serpentine	tri	Chrysolite, lizardite
		Kaolin	di	Kaolinite dickite, nacrite, halloysite
2 : 1	None (X = 0)	Talc	tri	Talc
		Pyrophyllite	di	Pyrophyllite
	Hydrated exchangeable cations and small polar organic compounds (X = 0.2–0.6)	Smectite	tri	Saponite, hectorite, sauconite, stevensite
			di	Montmorillonite, beidellite, nontronite
	Hydrated exchangeable cations (X = 0.6–0.9)	Vermiculite	tri	Trioctahedral vermiculite
			di	Dioctahedral vermiculite
	Non-hydrated monovalent cations (X = 0.6–0.85)	True micas	di	Illite, glauconite
	Non-hydrated monovalent cations (X = 0.85–1.0)		tri	Phlogopite, biotite
			di	Muscovite, celadonite, paragonite
	Non-hydrated divalent cations (X = 1.8–2.0)	Brittle micas	tri	Clintonite
			di	Margarite
	None (X = 0)		tri (mod.)	Sepiolite, palygorskite
2:1:1	Hydroxide sheets (X = 1)	Chlorite	tri	Clinochlore, chamosite
			di	Donbassite
			di-tri	Cookeite, sudoite
1:1 2:1 2:1:1	Randomly ordered mixed layers. Hydrated exchangeable cations and small polar organic compounds (X = 0–1.0)	Mixed layer		Chlorite-smectite, chlorite-vermiculite, illite-smectite, kaolinite-illite, serpentine-chlorite

[1] X – net negative layer charge per formula unit, expressed as a positive number

[2] tri – trioctahedral; di – dioctahedral; mod. – modulated

[3] this list includes only some common clay mineral species

used (Guggenheim et al., 2006). In this classification planar hydrous phyllosilicates, firstly, are divided by layer types or tetrahedral and octahedral sheet combinations:

a. 1 : 1 (tetrahedral: octahedral) or (TO);
b. 2 : 1 (tetrahedral: octahedral: tetrahedral) or (TOT);
c. 2 : 1 : 1 (tetrahedral: octahedral: tetrahedral): octahedral or (TOT:O).

Then within each layer type charge per formula unit, dioctahedral or trioctahedral character and chemical composition are used as the criteria for classification (Table 1.2) (Guggenheim et al., 2006; Schroeder, 2018). Few commonly known clay mineral species with different layer types are detailed described below.

1 : 1 layer silicates: kaolin group minerals

A 1 : 1 layer type mineral structure is composed of one alumina octahedral sheet and one silica tetrahedral sheet stacked one above the other (Figure 1.3. B, C) (Yariv and Cross, 2002; Schulze, 2005). The layers are kept together by hydrogen bridges between basal oxygen atoms on the tetrahedral sheet and surface hydroxyl groups on

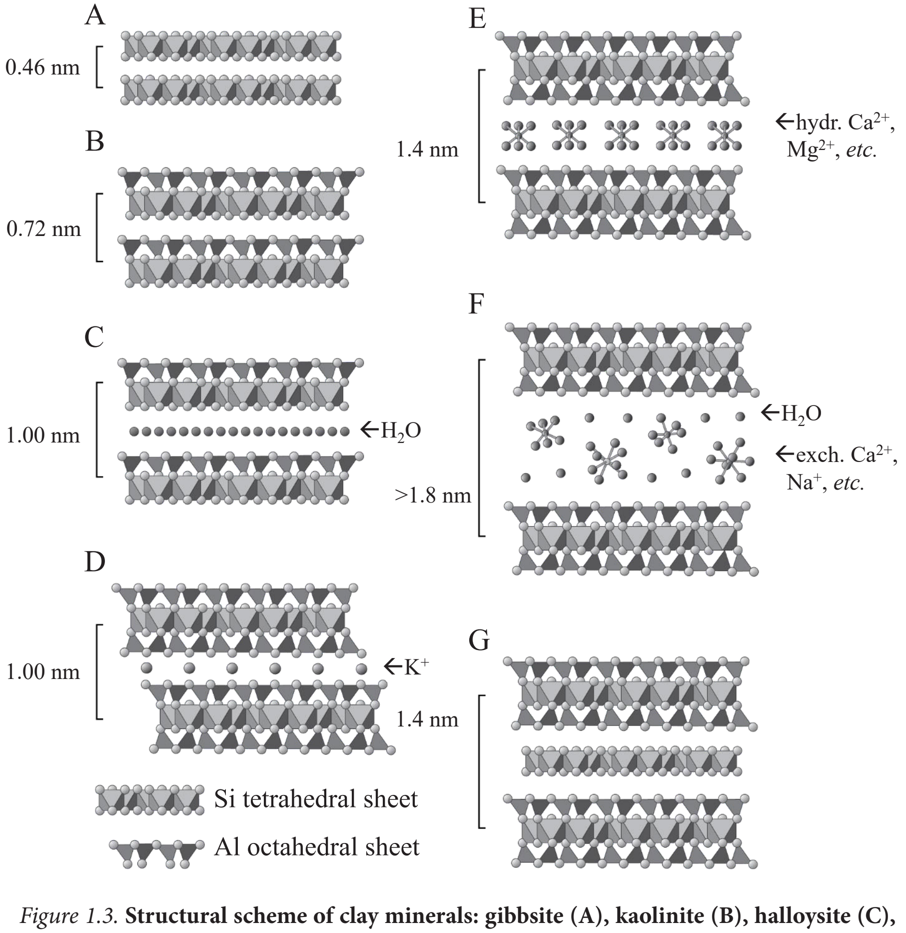


Figure 1.3. **Structural scheme of clay minerals: gibbsite (A), kaolinite (B), halloysite (C), illite (D), vermiculite (E), smectite (F), and chlorite (G)** (adapted from Schulze, 2005).

the octahedral sheet (Schulze, 2005; Brigatti et al., 2013). The layer has little or no permanent charge because of the low amount of substitution. In result, kaolinite has low cation exchange capacity and small surface area (Schulze, 2005; Theng, 2012).

The kaolin group includes minerals kaolinite, dickite, nacrite, and halloysite (7 Å or 10 Å) (Murray, 2007; Christidis, 2010; Theng, 2012). The general molecular formula of kaolinite group minerals is $Al_4Si_4O_{10}(OH)_8$ and the theoretical chemical composition is 46.54% SiO_2, 39.50% Al_2O_3, and 13.96% H_2O (Murray, 2007; Schoonheydt et al., 2018) with minor amounts of Mg, K, Fe, and Ti (Ismadji et al., 2015). Kaolinite is a triclinic mineral with pseudohexagonal crystals that arrange in book-like aggregates (Figure 1.4. A), and with particle size ranging from 0.05 μm to 2 μm (Christidis, 2010; Theng, 2012).

2 : 1 layer silicates: smectite group minerals

A 2 : 1 layer type mineral structure is composed of two silica tetrahedral sheets that encompass one octahedral sheet (contains Al^{3+}, Fe^{3+} or Mg^{2+} cations) (Figure 1.3. D, E, F) (Yariv and Cross, 2002; Stinkule, 2014; Ismadji et al., 2015). One of the smectite clay minerals' characteristics is isomorphous substitution in the octahedral and tetrahedral sheets. In the tetrahedral sheet there is a substitution of trivalent ions (e.g., Al^{+3}) with tetravalent ions (e.g., Si^{4+}), while in the octahedral sheet there is substitution of divalent ions (e.g., Mg^{2+}) with trivalent ions (e.g., Al^{3+}) (Murray, 2007; Stinkule, 2014; Schroeder, 2018). The resulting charge deficiency is balanced by hydrated cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) in the interlayer site (Figure 1.3. F), which are exchangeable, leading to a significant property – high cation exchange capacity (Yariv and Cross, 2002; Christidis, 2010; Schroeder, 2018).

The general molecular formula of smectite group is (Ca, Na, H) (Al, Mg, Fe, Zn)$_2$ (Si, Al)$_4$O$_{10}$(OH)$_2$-xH$_2$O (Ismadji et al., 2015) and the theoretical composition without the interlayer material is 66.7% SiO_2, 28.3% Al_2O_3 and 5% H_2O (Murray, 2007). Smectite mineral particle size is very small, usually <0.5 μm, and their crystal shape varies from subhedral lamellae with irregular outlines (Figure 1.4. B) to euhedral lamellae with rhombic outlines (Christidis, 2010).

The most common smectite minerals are sodium and calcium montmorillonites, whose layer charge deficiency is balanced by the interlayer cations, such as sodium or calcium, and water molecules (Figure 1.3. F) (Murray, 2007). If in the smectite mineral structure the octahedral positions are mainly filled with aluminum, the mineral is beidellite; if filled with magnesium, the mineral is saponite; if by iron, the mineral is nontronite and if octahedral position is filled with lithium, the clay mineral is hectorite (Murray, 2007; Christidis, 2010).

2 : 1 layer silicate: illite

Illite is a member of true mica group and commonly found in soils and sedimentary rocks. Illite's mineral structure is composed of two silica tetrahedral sheets that encompass one alumina octahedral sheet (Figure 1.3. D) (Awad et al., 2019). In the tetrahedral sheet there are replacements of silica (Si^{4+}) by aluminum (Al^{3+}), while in the octahedral sheet may be some replacements of aluminum (Al^{3+}) by magnesium (Mg^{2+}) and iron (Fe^{2+}, Fe^{3+}) ions (Murray, 2007; Theng, 2012; Stinkule, 2014; Ismadji et al., 2015). Isomorphous substitution of aluminium for silicon in the tetrahedral sheet results in a negative charge on the surface of these layers. The negative surface charge is neutralized by potassium (K^+) ions (Velde, 1995; Ismadji et al., 2015; Awad et al., 2019). Due to the size, charge, and coordination number of potassium ions, they fit tightly in the 1.32 Å radius holes in the bases of the silica tetrahedral sheets and as a result are fixed in position and are not exchangeable (Murray, 2007; Stinkule, 2014; Ismadji et al., 2015; Awad et al., 2019). This gives the structure a strong interlocking ionic bond which holds the individual layers together and prevents water and other polar compounds from occupying the interlayer position (Murray, 2007). Part of the water molecules may be present as hydronium (H_3O^+) ions occupying interlayer K^+ deficient positions (Theng, 2012).

The general molecular formula of illite is $(K, H_3O)\ Al_2(Si_3Al)\ O_{10}(H_2O, OH)_2$ (Mueller et al., 2014; Awad et al., 2019). Illite's crystal shape varies from euhedral to subhedral pseudo-hexagonal to fibrous or lath-like crystals (Figure 1.4. E, F) (Christidis, 2010). Glauconite is another true mica mineral with dioctahedral structure, but it contains more iron and less aluminum in its octahedral sheet than illite (Velde, 1995; Mueller et al., 2014). Illite and glauconite commonly are associated

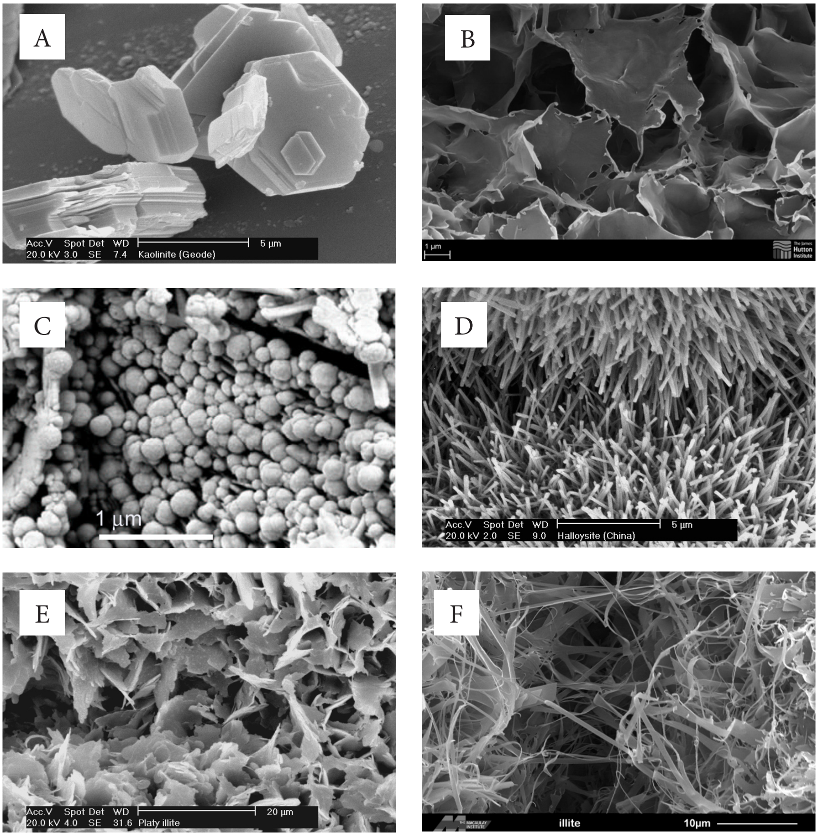


Figure 1.4. **Scanning electron microscope images of some clay minerals with various morphology: (A) pseudohexagonal particles of kaolinite; (B) wavy subhedral smectite particles; (C) spheroidal particles of halloysite; (D) tubular particles of halloysite; (E) flaky illite particles; (F) fibrous illite** (images of the Clay Minerals Society and the Clay Minerals Group of the Mineralogical Society, available at https://www.minersoc.org/images-of-clay.html).

with kaolinites and smectites forming mixed layer group minerals (Table 1.2.) (Velde, 1995; Murray, 2007).

2 : 1 : 1 layer silicates: chlorite group

Chlorite group mineral structure is composed of two silica tetrahedral sheets and one alumina octahedral sheet, thus forming 2:1 layer structure with an excess of negative charge. The negative charge is neutralized by positively charged octahedral or brucite ($Mg(OH)_2$) sheet in the interlayer space (Figure 1.3. G) (Murray, 2007; Mueller et al., 2014; Ismadji et al., 2015). There is a considerable substitution in the octahedral sheet of aluminum (Al^{3+}) by magnesium (Mg^{2+}) and iron (Fe^{2+}, Fe^{3+}), while in the tetrahedral sheet there is a substitution of silica (Si^{4+}) by aluminum (Al^{3+}) (Murray, 2007; Christidis, 2010).

The general molecular formula of chlorite is $(OH)_4(Si,Al)_8(Mg, Fe)_6O_{20}$ and general formula of brucite-like sheet in the interlayer space is $(Mg, Al)_6(OH)_{12}$ (Murray, 2007). The chlorite group includes also other minerals, such as baileychlore, borocookeite, chamosite, clinochlore, cookeite, donbassite, franklinfurnaceite, nimite, orthochamosite, and sudoite. The minerals from the chlorite group are mostly monoclinic (rarely triclinic or orthorhombic) with crystal shape similar to kaolinite's forming pseudohexagonal crystals that can be arranged in aggregates (Christidis, 2010; Ismadji et al., 2015).

1.4. Distribution of clays and clay minerals

On the Earth's surface (the upper 20 km of the Earth's crust) 16% of all rocks are comprised of clay minerals (Schroeder, 2018). The global distribution of clay minerals is mainly related to the climatic regions, for example, mica group minerals, including illite, are abundant in arid and high-latitude regions, while kaolinite in humid tropic regions. Some clay minerals have localized distribution, for example, soil with high content of smectite minerals (vertisol) occurs mainly in East-Central Africa, Eastern Australia, and Central India (Figure 1.5.) (Ito and Wagai, 2017).

In Europe, high (28–98%) topsoil (0–20 cm) clay content is in Central and Southern Italy, France, and Spain, but comparatively low (less than 28%) content is in the Scandinavian countries and in the Baltic States (Ballabio et al., 2016). For example, Vicalvaro in Spain (near Madrid) is the largest deposit in the world of commercial fibrous clay mineral, sepiolite with thickness ranging from 1 m to 5 m (Murray, 2007). The higher content of clay minerals in the Mediterranean region is related to the presence of sedimentary rocks, such as clayey limestone and clay stone (Ballabio et al., 2016).

Clays are distributed in various depths in Latvia and their practical application is related to the economic aspects of mining. The economic importance of clay in the Cambrian, Ordovician, and Silurian deposits is negligible because they are in great depth. The clays of these systems have been studied mainly with regard to the search for oil and natural gas resources. While the clays of the Devonian, Triassic, Jurassic, and Quaternary Systems are of the highest practical feasibility due to suitable depth for the resource acquisition (Sedmalis et al., 2002).

The following subsection provides detailed information about clays of Triassic and Jurassic System as their mineral fraction consists of smectite group clays and have been

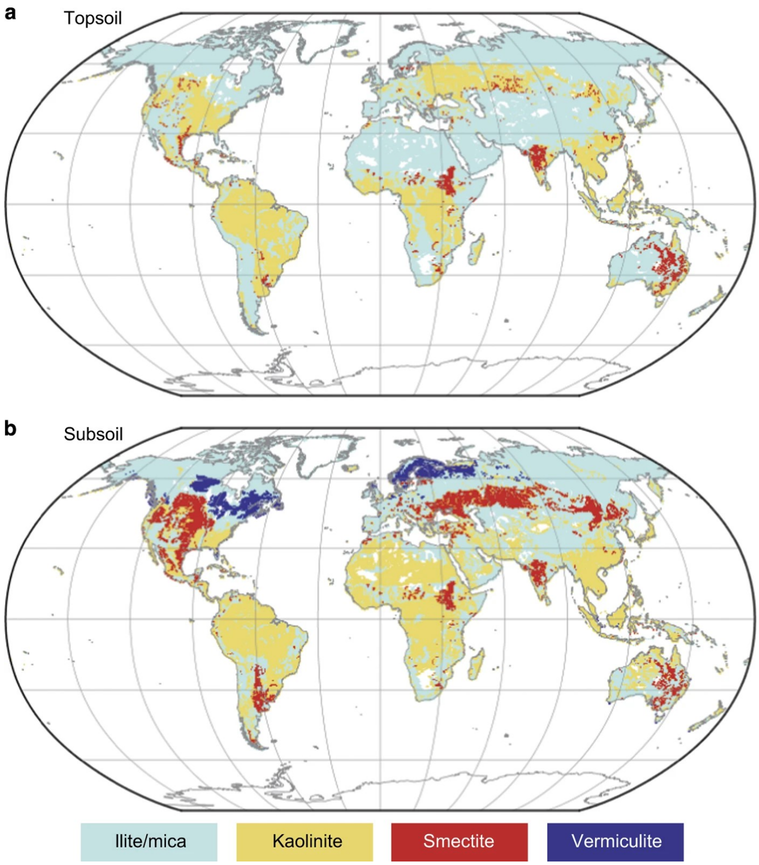


Figure 1.5. **Global distribution of the most abundant clay minerals in topsoil (A) and subsoil (B)** (Ito and Wagai, 2017).

investigated in the modification experiments of this study (Figure 1.6.) (Stinkule, 2014). Smectites are the most suitable minerals for clay modification with chemical modifiers (Bertuoli et al., 2014). In addition, Jurassic clays contain lignite that could increase affinity to organic contaminants (Eiduks et al., 1958; Satkūnas, 2008).

Triassic System clay is only present in the south-western part of Latvia, where the thickness of the layer can reach from 30 m to 74 m. The clay deposits continue in Lithuania with a thickness of 300 m, and up to 400 m in Kaliningrad Oblast (Russia) (Brangulis et al., 1998). Based on the data of lithological composition and paleontological analysis of the found fossils, these Triassic sediments have formed in a freshwater lake (Šliaupa and Chyžienė, 2000).

In the territory of Latvia, the Triassic clayey deposits are mainly exposed in the middle reaches of the Venta on the banks of its tributaries Lose, Zana, Letiza, and Vadakste. The Triassic System deposits here consist of reddish-brown or greenish-gray clay, dolomite marls and sandstones (Segliņš et al., 2013). In Latvia, four potentially significant clay deposits were identified and, according to the assessed resources (16 million m^3), the most significant is the Vadakste deposit (Segliņš, 2010; Stinkule, 2014). However,

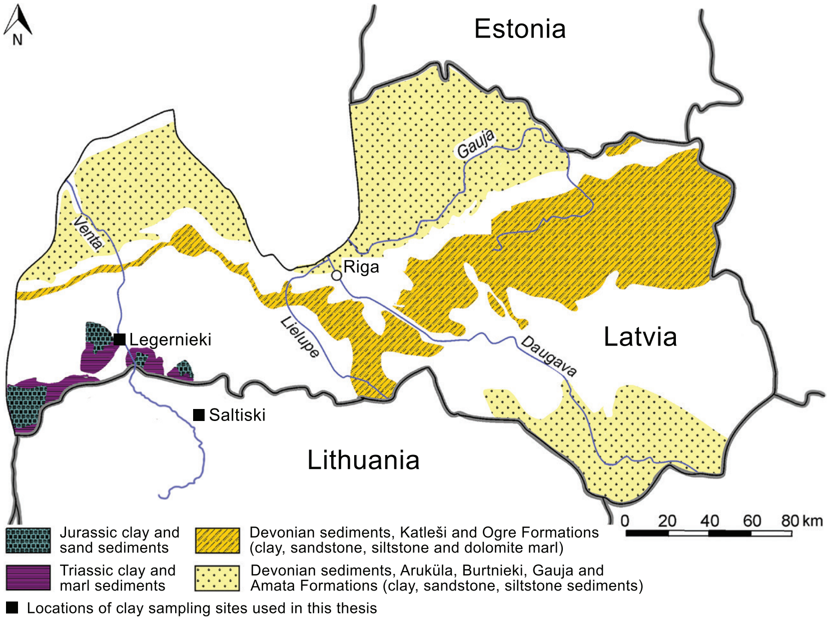


Figure 1.6. **Distribution areas of the pre-Quaternary clayey sediments and clay deposits in Latvia and location of sampling sites for this study** (adapted from Stinkule, 2014).

the economic importance of Triassic clay is significantly greater in north-western Lithuania, in the Akmene district, where the Saltiski clay deposit is located (Figure 1.6.). Clay resources in Saltiski deposit are 20.8 million tonnes and clay mining has been carried out for the cement industry since 1997 (Satkūnas, 2008).

The Triassic System clays of the Baltic region mainly consist of clayey (<0.005 mm) and silt (0.05–0.005) fractions, i.e., 25–45% and 35–45%, respectively (Stinkule, 2014). The clay fraction is dominated by smectite (67–80%), illite (6–25%), a small amount of kaolinite and clinchlore, a chlorite mineral (Kostjukovs and Trubača-Boginska, 2014). Triassic System deposits have a significant amount of terrigenous material admixture – feldspar, quartz, and carbonates (sometimes even up to 50%) (Karasa et al., 2012).

The chemical composition of Triassic clays shows that the clays are rich in iron oxides (4.1%), which are present both in the crystal lattice of minerals and in the form of free oxides. Iron oxides give a typical reddish-brown colour to Triassic clays. Compared to other Latvian clays, the amount of sodium oxide (2.2–2.6%) and potassium oxide (0.3–0.6%) is negligible and therefore suitable for the cement industry (Paškevičius, 1997; Stinkule, 2014). However, in studies by Sarceviča et al. (2011) and Kostjukovs et al. (2011) potassium concentration 3.0% has been found in clays of Vadakste deposit which could be related to a greater admixture of sand and silt fractions containing mica minerals.

The Jurassic System clays also are found only in the southwestern part of Latvia, and their distribution areas are even smaller than of Triassic System – mutually isolated (Eiduks et al., 1958). Due to the action of Pleistocene glaciers, which moved and deformed strata, the Jurassic clay is found in glaciotectonically deformed deposits

(Paškevičius, 1997; Stinkule, 2014). The thickness of the Jurassic deposits in Latvia is up to 25 m, while in the south-western part of Lithuania total thickness reaches 240 m to 260 m (Brangulis et al., 1998).

In the territory of Latvia, there are clastic sediments formed during Callovian Stage of the Middle Jurassic Epoch, which consist of Papile, Papartine, and Skinija formations, as well as deposits of the Ažuolija Formation, Oxfordian Stage, Upper Jurassic (Satkūnas, 2008; Lukševičs, 2018). The Papile Formation deposits contain quartz, clay and lignite. Sediments have formed under continental (coastal) conditions, as evidenced by the shape of the lignite deposits and the dip azimuths of cross-bedded deposits, formed under meandering river conditions. The total thickness of the Papile Formation in Latvia reaches up to 20 m (Brangulis et al., 1998). The sediments of Papartine, Skinija, and Ažuolija formations mainly contain grey sand, clay and calcitic nodules with fossils of marine organisms (such as *Mollusca*, *Foraminifera*, *Echinodermata*). The rich presence of invertebrate fossils indicates that sediments formed during marine transgression (Satkūnas, 2008; Lukševičs, 2018). The thickness of the stratum is less than 3 m (Brangulis et al., 1998). The sediments of the Oxfordian Stage found near Rucava and Sikšņi are made of black sandy siltstones and dark grey fine-grained quartz, their thickness is up to 1.6 m (Brangulis et al., 1998; Satkūnas, 2008).

Outcrops of Jurassic deposits are located in the Venta basin, on the banks and in the bed of the rivers Zana, Letiza, Lose, Vadakste, Skervelis and Dzelda (Brangulis et al., 1998). Two Jurassic clay deposits have been identified in Latvia – Streli, located on the left bank of the Venta next to the estuary of the Lose; Pulvernieki located on the banks of the Letiza (Eiduks and Kalniņš, 1961). The total Jurassic clay reserves at the Pulvernieki and Streli deposits are 25600 m^3 and 13500 m^3, respectively (Stinkule, 2014). Additionally, studies have been carried out in the valley of Zana river and at the Legernieki outcrop, located on the right bank of the Letiza (Pipira et al., 2012) where layers of quartz sand and black clay are exposed (Brangulis et al., 1998).

Visually, the Jurassic clays are black, dark grey, and greenish grey. The presence of iron sulfides and organic substances gives them a distinct black colour (Satkūnas, 2008; Stinkule, 2014). According to the granulometric composition, the coarse fraction >0.063 mm in Jurassic clay sediments consists of quartz (99%) and feldspar in a small amount (Pipira et al., 2012). The content of the clay fraction (<0.005) is less than 40%, and the mineral composition is mainly dominated by kaolinite (>50%), illite (10/%–40%) and smectite (<10%) (Stinkule, 2014).

The Pipira et al. (2012) studies found that the lower part of the grey clay sediment section of the Papile Formation has an increased content of smectite with the addition of chlorite. It is uncharacteristic for the Jurassic System clay in this region, and its presence is related to the adjacent Triassic strata composition. In turn, the highest amount of kaolinite and smectite was found in the admixture of black clays.

1.5. Physical and chemical properties of clay minerals

The structural and composition features of particular clay minerals add to their 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) hydration and 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).

1.5.1. Particle size and shape, and specific surface area

Particle sizes for most of the clay minerals are smaller than 2 μm. Nevertheless, there are some exceptions, for example, kaolin group minerals can form larger crystals, which may reach 20 μm (in the case of dickite), while smectite group minerals tend to form smaller crystals with an average size of 0.5 μm (in the case of bentonite) (Meunier, 2005; Christidis, 2010). The small crystal size of clay minerals results in large specific surface area, which ranges from 10 m^2/g to 800 m^2/g for kaolinite and smectite, respectively. The surface area is available for the exchange of ions and molecules between the solids and the surrounding solution (Christidis, 2010; Schroeder, 2018). Specific surface area is determined by measuring the amount of physically adsorbed nitrogen gas according to the Brunauer, Emmett and Teller- BET method (ISO, 2010).

Isolated crystals of clay species are observed rarely as clay minerals tend to form aggregates, when particles are bonded together by Coulomb forces or by the presence of organic (humin, humic or fulvic acids, etc) or inorganic (Fe–Mn oxides or hydroxides, etc) substances. For example, particles of the smectite group mineral montmorillonite are bound together into a tactoid (Na-saturated state) or quasi-crystal (Ca-saturated state) network. The size of aggregates varies from a few microns to a few tens of microns. The formation of aggregates has an adverse effect on the physical and chemical properties of clay minerals. As a result the specific surface area of aggregates is lower than the specific surface area of isolated crystals of clay minerals (Meunier, 2005; Christidis, 2010).

As commonly clay minerals' shape is like a sheet, their surface area is even greater than for other minerals with the same crystal size, but particle shape is in the form of cube or sphere. The ratio of thickness to length for the clay particles is approximately 20, which makes the surface area of a clay particle nearly three times larger than surface area of a cube with the same volume (Velde, 1995). The size and shape of clay mineral particles and aggregate characteristics can be observed by transmission and scanning electron microscopy (TEM/SEM) (Christidis, 2010).

1.5.2. Ion-exchange capacity

Clay minerals can sorb cations, anions, and polar molecules of inorganic or organic substances (Brovkina et al., 2012). In clay minerals, the active sites may arise from (1) 'broken edge' sites and exposed surface aluminol and silanol groups, (2) isomorphic substitutions, (3) exchangeable cations, (4) hydrophobic silanol surfaces, (5) hydration shell of exchangeable cations, and (6) hydrophobic sites on adsorbed organic molecules (Figure 1.7.) (Zhou and Keeling, 2013).

Anion exchange capacity (AEC) 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 (Meunier, 2005; Christidis, 2010). The smaller the particle size of the clay minerals, the higher is the number of such sites and their

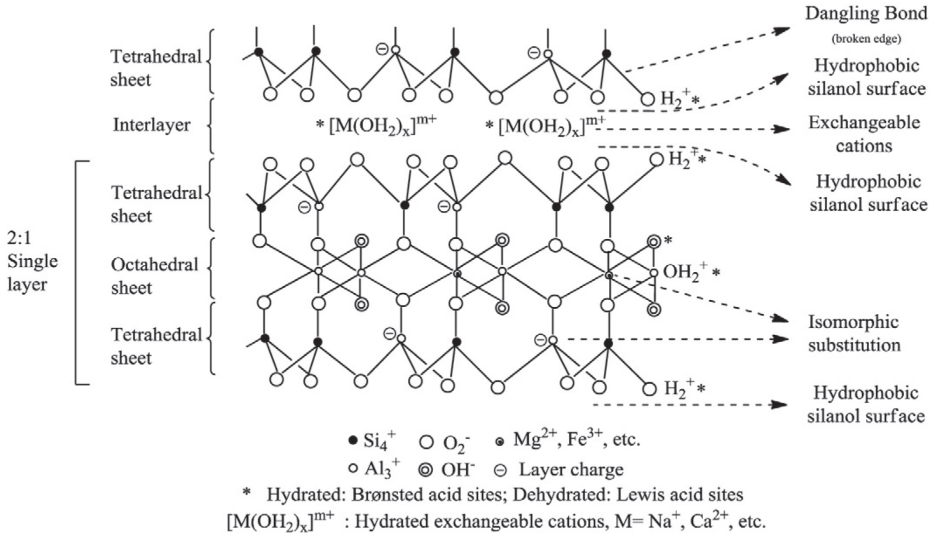


Figure 1.7. **Schematic representation of 2:1-layer clay mineral showing active sites that provide ion exchange and sorption properties** (Zhou and Keeling, 2013).

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 AEC for anionic molecules such as phosphates. Illite and chlorite may also develop significant AEC, while smectite and vermiculite display limited AEC (Christidis, 2010). The charged layers and 'broken edge' sites can be enhanced by chemical reactions, such as acid-activation (Zhou and Keeling, 2013).

Cation exchange capacity (CEC) 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). The order of replaceability of monovalent and bivalent cations are as follows:

$Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ (Carroll, 1956; Meunier, 2005).

This order is defined by the size of the association cation, thus the cation with the smaller diameter displaces the one with the greater diameter. Replaceability varies with electrolyte concentration: the more diluted the solution, the greater the replaceability (Meunier, 2005). Cation exchange capacity is a characteristic property of all clay minerals but particularly notable in smectite group minerals. Commonly found natural Ca-smectites are alki-activited to produce Na-smectites which are more suitable in various industrial applications (Christidis, 2010).

1.5.3. Cation exchange capacity and layer charge

Cation exchange capacity (CEC) provides sorption properties for ionic species and the basis for CEC is associated to charge in clay minerals (Velde, 1995; Ismadji et al., 2015). The charge in the clay minerals exists in two forms: structural and surface charge. The structural charge is permanent and exists due to ion substitutions, while the surface charge is variable and depends on the value of pH (Ismadji et al., 2015). As mentioned previously, for the 1:1 layer type clay minerals, the surface charge contributes a major portion to the total charge, while for 2:1 layer type clay minerals structural charge is dominant (Ismadji et al., 2015). The total cation exchange capacity value is equal to the sum of CEC of variable charges and CEC of permanent charges. The CEC values are expressed in milliequivalents of charge (meq) per 100 g of dry clay mineral (Meunier, 2005) and CEC values of various clay minerals are given in Table 3. CEC is measured at pH 7 to exclude CEC values variation related to pH of the solution and enable comparison of measurements between different clay minerals. Some of the analysis methods are the following: ammonium acetate method (saturation by NH^{+4}); strontium chloride method (saturation by Sr^{2+}); (Meunier, 2005); silver–thiourea method (saturation by Ag^{+}); barium chloride method (saturation Ba^{2+}) (Dohrmann, 2006); and methylene blue method (saturated by $C_{16}H_{18}N_3S^{+}$) (Yukselen and Kaya, 2008).

The point zero charge (pHpzc) is the pH level, where the total net charge is zero and the surface of clay mineral is uncharged or charged with equal densities of positive and negative charges. The pHpzc of clay minerals determines their anion or cation exchange ability. At low pH there is tendency for protons to bind with Si-O groups, which can lead to hydrolysis and leaving the surface with a positive charge. Thus, when solution pH is less than pHpzc, e.g. at <2.5 pH the montmorillonite (Table 1.3.) would have an anion exchange capacity. At high pH there is tendency for hydrolysis to bond with protons on the Si-O groups to make water and leave the surface with a negative charge. Thus, at pH higher than pHpzc, e.g. at >2.5 pH the montmorillonite (Table 1.3.) would have a cation exchange capacity. When pH is equivalent to pHpzc (at isoelectric point), the clay mineral has no change capacity (Ismadji et al., 2015; Schroeder, 2018).

Table 1.3.

Typical ranges of cation exchange capacity and pH of point of zero charge of several clay minerals species (Christidis, 2010; Ismadji et al., 2015; Schroeder, 2018)

Clay mineral	CEC, meq/100g	pH_{pzc}
Vermiculite	130–210	n/a
Hectorite	80–130	n/a
Sodium montmorillonite	80–130	<2.5
Allophane	70	5.5–6.9
Calcium montmorillonite	40–70	<2.5
Palygorskite	30–40	n/a
Sepiolite	30–40	n/a
Illite	10–40	6.8
Chlorite	10–40	4.6
Halloysite	5–10	n/a
Kaolinite	1–15	3.5–4.6

1.6. Modification methods of clay minerals and their applications

The physical and chemical properties of clay minerals (e.g., large specific surface area, swellability, fine particle size, surface charge, etc.) and their availability, low cost, inertness and stability have led to numerous industrial applications (Zhou and Keeling, 2013; Rouquerol et al., 2013). For example, kaolin group minerals are traditionally used as fillers and coating materials in paper, fillers and extenders in paint, plastics, rubber, ink and used in ceramics for the production of pottery, sanitaryware, whiteware, insulators and refractories, while smectite group minerals are commonly used as freshwater drilling muds, foundry bond clays, pelletizers in pulverized iron ore concentrates, 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; Patanjali et al. 2020). 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 minerals (Sarkar et al., 2019; Biswas et al., 2019; Patanjali et al., 2020).

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 (Patanjali et al., 2020). The intended attributes can be achieved through heat, alkali and acid treatments, physical grinding, organic and polymer loading reactions, ion exchange and pillaring reactions, redox reactions, micro- and nanocomposite formation (Figure 1.8.) (Sarkar et al., 2019).

Table 1.4. gives a brief overview of the various modified clay minerals, their preparation, properties and relevant environmental applications. *Organoclays* are prepared by incorporating organic molecules (mainly quaternary ammonium cations) in the interlayer space of expandable clay minerals (mainly smectite group minerals) through an ion exchange reaction (Yariv and Cross, 2002; Sarkar et al., 2019). The obtained organoclay product has induced hydrophobicity and thus enhanced sorption capacity for the removal of hydrophobic organic pollutants, e.g., polychlorinated biphenyls (Fiscal-Ladino et al., 2017), pharmaceuticals (Aftafa et al., 2014; de Oliveira et al., 2018). *Layered double hydroxide* (LDH) are synthetic or natural anionic clay minerals that are modified by the replacement of interlayer anions with desired anions (Biswas et al., 2019). Again, *pillared clays* are created by replacing the exchangeable cations of clay minerals (mainly smectite group minerals) with large inorganic cations (Al, Ga, Ti, Mg, Si etc.) and then stabilized by thermal treatment to dehydrate and dehydroxylate the pillaring species (Rouquerol et al., 2013; Vicente et al., 2013). The resultant materials have increased basal spacing, specific surface area, porosity and thermal stability. Thus, pillared clays are used as sorbents and heterogeneous catalysts for the removal of inorganic and organic pollutants, e.g., heavy

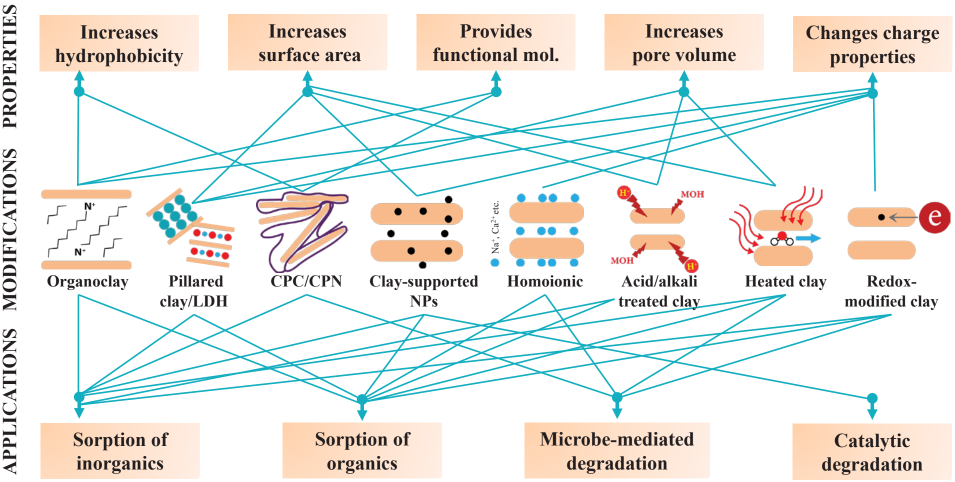


Figure 1.8. **Scheme of potential networks showing modified clay minerals with their properties and environmental applications** (adapted from Biswas et al., 2019).

metals, dyes, pharmaceuticals from wastewater treatment systems (Gil and Vicente, 2020; Najafi et al., 2021).

Clay–polymer composite or clay–polymer nanocomposite (CPC/CPN) are smectite group minerals modified with synthetic (e.g., polyacrylamide, polyvinyl alcohol) or natural (e.g., starch, chitosan) polymers to separate aggregates and/or individual silicate layers of clay minerals (Gao, 2004; Sarkar et al., 2019). The obtained materials can be used in a variety of application sectors, e.g., in medicine as modified drug delivery systems (Li et al., 2017), in agriculture as agents to implement controlled release of fertilizers (El Assimi et al., 2020), in food packaging as a quality improving materials (Mathew et al., 2019) and in water remediation fields as sorbents (Sarkar et al., 2019). *Clay-supported nanoparticles* are clay minerals saturated with other inorganic nanoparticles, such as metal or metal oxide anions (e.g. Fe_3O_4, ZnO) (Biswas et al., 2019). Clay-supported nanoparticles have increased affinity towards various pollutants – organics (e.g., phenols, pesticides), radionuclides (e.g.,^{125}I,^{134}Cs) and heavy metals (e.g., Ni (II), Cr (VI)) (Sarkar et al., 2019; Zhang et al., 2019; Zyoud et al., 2020). Clay minerals that are modified with magnetite have also superparamagnetic properties that ease the separation of the spent sorbent from the environment through an external magnetic field (Sarkar et al., 2019). *Homoionic clay*s are cationic clay minerals (mainly smectite group minerals) saturated with one of mono-, di- or tri-valent metal cations (e.g., Na, K, Mg, Ca, Zn, Al) (Biswas et al., 2019). For example, resultant material can be used in the development of Si nanosheets for lithium-ion battery anodes to improve electrochemical performance parameters (Ryu et al., 2016). Nevertheless, homoionic clays are predominantly prepared to ease ion exchange with quaternary ammonium cations (organoclays), and therefore promote bioremediation of hydrocarbon contaminated soil and water environments (Sarkar et al., 2019; Adauto and Sun-Kou, 2021).

Table 1.4.

Examples of clay modification methods and their application in environmentally friendly technologies

No.	Clay material used	Modification method and modifier	Area of application	Outcome	Reference
1.	Montmorillonite	*Modification with ionic liquids (organoclay):* ▪ hexadecyl-3-methylimidazolium series (HDMIM-Br and HDMIM-OH) ▪ 1-hexadecyl-3-methylimidazolium tetrafluoroborate (HDMIM-BF4) ▪ 1-butyl-3-methylimidazolium series (BMIM-Br, BMIM-OH and BMIM-BF4) ▪ 1-octyl-3-methylimidazolium series (OMIM-Br, OMIM-OH and OMIM-BF4)	Removal of polychlorinated biphenyls (PCBs): PCB 81, PCB 105, PCB 114, PCB 123, PCB 126, PCB 156, PCB 157, PCB 167, PCB 169, PCB 189 from aqueous solutions and wastewater of WWTP Santiago	The highest sorption capacity of PCBs was achieved by montmorillonite modified with HDMIM-Br	Fiscal-Ladino et al., 2017
2.	Sodium montmorillonite	*Modification with ionic liquids (organoclay):* ▪ 1-methyl-3-octyl-imidazolium bromide (C_8mimBr) ▪ 1-methyl-3-undecyl-imidazolium bromide (C_{12}mimBr) ▪ 1-methyl-3-octadecyl-imidazolium bromide (C_{18}mimBr)	Removal of estrogenic hormones: estrone (E1), 17 –estradiol (E2), estriol (E3) and ethynylestradiol (EE2) from aqueous solutions and water samples from river Gediz	The highest sorption capacity of estrogenic hormones was achieved by montmorillonite modified with C_{12}mimBr	Aftafa et al., 2014
3.	Sodium bentonite and montmorillonite	*Modification with ionic liquids (organoclay):* ▪ 3,3′-(hexyl)bis(3-methylimidazolium) bromidechloride ([H(mim)$_2$[Br][Cl]), ▪ 1-hexyl-3-methylimidazolium chloride ([Hmim][Cl]) ▪ 1-octyl-3-methylimida-zolium chloride ([Omim][Cl])	Removal of Cd (II) ion from aqueous solutions	The highest sorption capacities 87.46 and 94.6 mg/g of Cd (II) were achieved by montmorillonite- [H(mim)$_2$] and bentonite-[H(mim)$_2$], respectively.	Naderi et al., 2018
4.	Sodium montmorillonite	*Modification with surfactants (organoclays):* ▪ *Catonic:* benzyldimethyl-tetradecyl ammonium (BDTA) ▪ *Nonionic:* ethylene (20) oleyl ether (Brij-O20)	Removal of antibiotic pharmaceutical products: amoxicillin (AMX), sulfamethoxazole (SMX), trimethoprim (TRI) from aqueous solutions	The highest sorption capacity of AMX, SMX, TRI was 5.68×10^{-3} mol/g, 9.73×10^{-4}mol/g, 4.13×10^{-4} mol/g, respectively, achieved by montmorillonite- BDTA	de Oliveira et al., 2018

No.	Clay material used	Modification method and modifier	Area of application	Outcome	Reference
5.	Chlorite, kaolinite, montmorillonite and illite	*Modification with surfactants (organoclays):* ▪ *Nonionic:* polyoxyethylene sorbitan monolaurate (Tween20) and octyl phenoxy poly ethoxy (Triton X-100) ▪ *Anionic:* dodecyl methylnaphthalene sulfonates (Dodec-MNS) and nonylphenol ethoxylates (10) ammonium sulfate (NPS-10)	Removal of petroleum hydrocarbons from contaminated clay samples with crude oil and petroleum-contaminated soil	The highest removal efficiency of petroleum hydrocarbons 68% was achieved by montmorillonite-Dodec-MNS	Li et al., 2016
6.	Natural red palygorskite clay	*Acid treated clay*: Oxalic acid	The material in sodium alginate film (mainly used in biomedicine)	Acid treatment removes hematite from palygorskite and improve the mechanical properties of polymer film	Lu et.al., 2020
7.	Bentonite	*Acid treated clay*: Phosphoric acid, Acetic acid, Citric acid, Oxalic acid	Removal of Mordant Red 73 from textile wastewater (Al-Rehmat Textiles. Pvt. Ltd)	The highest sorption capacity of Mordant Red 73 dye was achieved by bentonite treated with phosphoric acid	Javed et al., 2018
8.	Natural kerolite-stevensite mixed layer clay	*Acid treated clay*: Nitric acid (HNO_3) *Additionally, functionalized with amine species by 3-aminopropyltriethoxysilane (APTES) and polyethylenimine (PEI)	Capture of CO_2	The maximum value of CO_2 capture was 1.98 mmol/g at 65 °C and 760 mm Hg using acid treated (and functionalized with PEI) kerolite-stevensite clay	Franco et al., 2020
9.	Calcium montmorillonite, kaolinite and halloysite	*Thermally treated clays*: Temperature (120 °C and 600 °C)	Sorption of volatile organic compound – benzene	The highest sorption capacity 141.2 mg/g of benzene was achieved by Ca-montmorillonite heated at 120 °C	Deng et al., 2017
10.	Montmorillonite	*Thermally treated clays*: Temperature (200–800 °C)	Removal of Uranium(VI) from aqueous solutions	The highest sorption capacity of U(VI) was achieved by montmorillonite treated at 600 °C	Zuo et al., 2017

No.	Clay material used	Modification method and modifier	Area of application	Outcome	Reference
11.	Montmorillonite	*Homoionic clay and thermally treated* NaCl + Mg Temperature (650 °C and 900 °C)	Si nanosheets for lithium-ion battery anodes	Obtained two-dimensional Si nanosheets with excellent electrochemical performance, including, high specific capacity (865 mAh/g 0.5 C rate), cycling stability (capacity retention of 92.3% after 500 cycles), suppressed volume expansion (42% after 200 cycles), etc.	Ryu et al., 2016
12.	Halloysite	*Clay–polymer composite*: hydroxypropyl methylcellulose acetate succinate (HPMCAS)	Oral drug delivery system for atorvastatin and celecoxib in colon cancer treatment	Controlled release of atorvastatin and celecoxib depending on the pH of the gastrointestinal environment	Li et al., 2017
13.	Sodium montmorillonite	*Clay–polymer composite*: Chitosan	Slow and controlled release of hydro-soluble diammonium phosphates (DAP) fertilizer	Coating of fertilizers with clay-polymer materials slowed the dissolution rate of phosphorus in water and soil medium	El Assimi et al., 2020
14.	Montmorillonite K10	*Clay–polymer composite*: Polyvinyl alcohol (PVA) *Additionally, ginger rhizome extract, $AgNO_3$	The nanocomposite clay blend film in food packaging materials	Montmorillonite improved mechanical, light barrier and water-resistant properties of food packaging material	Mathew et al., 2019
15.	Natural clay composed of kaolinite and montmorillonite	*Clay-supported nanoparticles*: ZnO nanoparticles	Photodegradation of aqueous 2-chlorophenol (2-CP) in aqueous solutions	4 times higher sorption and photodegradation efficiency in 2-CP degradation was achieved by Clay-ZnO composite compared to ZnO only	Zyoud et al., 2020
16.	Attapulgite	*Clay-supported nanoparticles*: zero-valent iron (nZVI)	Removal of the model heavy metal contaminant Cr(VI) from aqueous solutions	The highest removal efficiency 90% of Cr(VI) was achieved by attapulgite-nZVI	Zhang et al., 2019
17.	Bentonite	*Clay-supported nanoparticles:* $AgNO_3$ and ZnO nanoparticles	Antibacterial material against bacteria growth (*Escherichia coli* and *Enterococcus faecalis*) in aqueous solutions	Bentonite – Ag/ZnO composite is an effective bactericide that can deactivate *Escherichia coli* and *Enterococcus faecalis* in aqueous solutions	Motshekga et al., 2013

Acid or alkali-treated clay – clay minerals that are treated or washed with organic (e.g., acetic acid, oxalic acid) or mineral acids (e.g., sulfuric acid, hydrochloric acid) or alkali (e.g., potassium hydroxide, sodium hydroxide) at intended acid or alkali concentration. Acid treatment partially dissolves the clay mineral crystalline structure by leaching part of cations (e.g., Mg^{2+}, Al^{3+}, Fe^{2+}) from the octahedral sheet. The resultant material has increased porosity, specific surface area and surface acidity (Sarkar et al., 2019). Thus, acid treated clays can be used to remove environmental pollutants, such as heavy metals (Sarkar et al., 2019), organics (Javed et al., 2018), and exhaust gases (e.g. CO_2) (Franco et al., 2020). *Heated clays or thermally activated* clay minerals are exposed to mild to moderate levels of thermal treatment to manipulate hydration states. The obtained material has changed electronegativity, pore size distribution, specific surface area and enhanced sorption of organics (Deng et al., 2017), radionuclides (Zuo et al., 2017) and heavy metals (Sarkar et al., 2019). *Redox-modified clay* is produced by the manipulation of oxidation and reduction states of iron-rich clay mineral anions (Biswas et al., 2019). The redox state of iron in clay minerals changes the physicochemical properties of clay minerals including swelling and cation exchange capacity. For example, Fe^{2+} in clay minerals may increase the removal of heavy metals, organics and radionuclides altering their mobility, bioavailability, and toxicity (Anastácio et al., 2008; Gorski et al., 2012). While Fe^{3+} serves as a terminal electron acceptor for iron reducing bacteria, providing a mechanism by which Fe^{2+} can be regenerated (Gorski et al., 2012).

Modification of clay minerals can be used to achieve defined properties to target a specific type of contaminants in water, soil, and air systems. The intended attributes favourable for attracting specific environmental contaminants can be achieved through, thermal, acid or alkali treatments, oxidation-reduction reactions, ion exchange and pillaring reactions, organic and polymer loading reactions, etc. However, the main limitations for using modified clay minerals, e.g., in wastewater treatment systems, are related to the problem of removal and regeneration of the used sorbent particles. The fine particle size of clay minerals increases the required time to settle, and they are not suitable for separation by sedimentation (Salinas et al., 2018). As mentioned before, one of the solutions is the impregnation of clay sorbents by iron oxide nanoparticles to obtain magnetic clays – sorbents that can be easily removed from wastewater by magnetic separation (Akkari et al., 2017). The used organoclay sorbents can be regenerated after the pollutant intake and repeatedly employed for water purification by the following methods: biological degradation, photo-assisted oxidation, chemical extraction/desorption, supercritical extraction (Zhu et al., 2009), electrochemical control (Li et al., 2018), thermal desorption (Mikeska et al., 2018). Nevertheless, research on the application of modified clay materials mostly includes batch and laboratory-scale studies with the exception of industrial utilization of clay sorbents in the removal of oil spills (Awad et al., 2020). Therefore, pilot and full-scale investigations in the future are necessary to assess the performance of modified clay minerals not only in environmental remediation but also in medicine, agriculture, food packaging, and other emerging fields.

2. MATERIALS AND METHODS

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

The following clay samples of 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 referred to as T clay (Figure 1.6. and 2.1.);
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 referred to as J clay (Figure 1.6. and 2.1.);
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.

Clays of natural origin were collected from outcrops and air-dried, crushed in an agate mortar and sieved through a 63 μm sieve. T clay before modification was purified from different matrix materials, such as carbonates, organic substances and quartz.

Figure 2.1. **(A) Triassic clay at Saltiski deposit (Lithuania), (B) Jurassic clay outcrops at Legernieki deposit (Latvia) and (C) fossil of *Frondicularia concinna* in Jurassic clay outcrop** (Photo credit: J. Jeskins).

The purification of the raw clay material was performed according to the method described in Karasa et al. (2012). The clay powder was suspended in the water-sodium pyrophosphate solution (clay-water-salt ratio – 1 : 20 : 0.075). The suspension was mixed and left for 24 h. Then the solution was decanted and soluble coagulant, KOHIDRAC, was added to separate the clay part from the suspension. After the treatment process the purified clay sample was filtrated, washed and air dried.

According to the product's specification, the Mt clay is white to faint grey powder with pH 2.5–3.5, a specific weight 300–370 kg/m^3 and a surface area 220–270 m^2/g. According to the certificate of analysis from Alfa Aesar, the Bt clay has the appearance of cream to brown or grey powder, exhibited a mass loss upon drying from 10% to 15 wt.% and swelling volume from 20 mL to 40 mL (2 g in 100 mL of water). Detailed description of T, J, Mt and Bt clay is included in the Chapter 3.1.1.

All used chemicals were of analytical grade and used without further purification. All solutions were prepared using high purity deionized water (10–15 MΩ cm) obtained with a Millipore Elix 3 (Massachusetts, USA) purification system.

2.2. Clay mineral modification methods

Clay samples were treated using inorganic and organic modifiers. Iron oxy-hydroxide and hydroxyapatite 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 (Table 2.1.).

2.2.1. Clay modification with iron oxy-hydroxide

The modification method was based on the impregnation of the clay material with iron oxy-hydroxide (FeOOH) as described in the Paper III – Ozola et al. (2019b). 250 mL of 0.25 M $FeCl_3 \cdot 6H_2O$ were mixed with 250 mL 3M NaOH and left to rest for at least 3 h. The formed precipitates were decanted and washed. Then, 100 g of clay sample was mixed into the precipitate and washed with 500 mL of deionized water. The filtered and washed mass was air-dried for 24 hours at room temperature, followed by drying in a Gallenkamp Plus II Oven (London, UK) for 4 hours at 60 °C.

2.2.2. Clay modification with hydroxyapatite

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) was prepared by the precipitation method under continuous mechanical stirring as described in the Paper VII – Ozola et al. (2017). 20 g of clay sample was mixed with 100 mL 0.5 M $CaCl_2$. Then 59 mL of 2 M KH_2PO_4 was slowly added to obtain 1.667 equimolar proportions of Ca/P. The pH for reactions was adjusted with 0.5 M NH_4OH to maintain it in the range of 9 and 9.5 pH, the reaction temperature was kept at 50 °C. After synthesis mixture was left overnight; then decanted and washed with deionized water until a neutral environment was achieved. Ethanol for the final removal of unnecessary salts was used and the substance was dried in Gallenkamp Plus II (London, UK) oven for 24 h at 40 ^{o}C.

2.2.3. Clay modification with surfactants

Modification with surfactants was carried out accordingly as described in the Paper II – Ozola et al. (2019a). The method is based on the exchange of inorganic ions in

Table 2.1.

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)	Ci = 5–400 mg/L; v = 40 mL; m = 0.5 g; t = 24 h; pH = 2–9; T = 24 °C	XRD, FTIR, SEM, SSA by BET, TGA, CEC, Content of Fe_2O_3	Paper III
	silver(I), aluminum(III)	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		n/a
Mt/T/J clay–Hap	lanthanum(III), neodymium(III), cerium(III)	Ci = 5–600 mg/L; v = 100 mL; m = 0.1 g; t = 24 h; pH = 6; T = 24 °C	XRD, FTIR, SEM, SSA by BET, TGA	Paper VII
	silver(I), aluminum(III)	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		n/a
Mt/T/J clay – DDAO NMO BTMAC DTAC	*p*-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_4mimCl C_8mimCl C_{12}mimCl CmmimDMP C_4mmimDMP C_8mmimDMP 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	anthocyanins rich extract from berry residues	Patent pending	Not included in this thesis	Patent (pending)

clay minerals with cationic surfactants (dodecyltrimethylammonium chloride (DTAC); benzyltrimethylammonium chloride (BTMAC)) or nonionic (dimethyldodecylamine N-oxide (DDAO); 4-methylmorpholine N-oxide (NMO)) molecules. The clay sample was first converted into sodium ions (Na^+) saturated form by stirring 100 g of clay with 1 L of 0.5 M NaCl solution for 24 h at 60 °C. Subsequently, the Na^+-saturated clay sample was washed and dried in Gallenkamp Plus II (London, UK) oven for 24 h at 60 °C. Then 10 g of Na^+-saturated clay sample was dispersed in 400 mL of deionized water using a Jenway 1000 hotplate/stirrer (Stone, Staffordshire, UK) (for 30 min). The selected amount of particular surfactant was dispersed in 100 mL of deionized water and stirred for 30 min. The dissolved surfactant was added slowly into the clay suspension and mixtures were stirred for 24 h at 60 °C. 0.1 M $AgNO_3$ was added to the suspension and it was washed several times with deionized water until no chloride ions were detected, filtered, dried at room temperature, and dried for 24 h at 60 °C. The chemical structures of used surfactants are depicted in Figure 2.2.

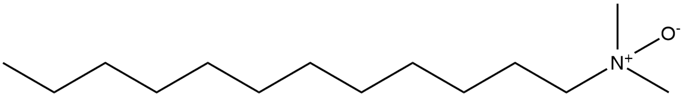
Corresponding weight of the surfactant was calculated using the following equation:

$$m_s = m_c \cdot CEC \cdot 10^{-3} \cdot Q_{CEC} \cdot M \tag{1}$$

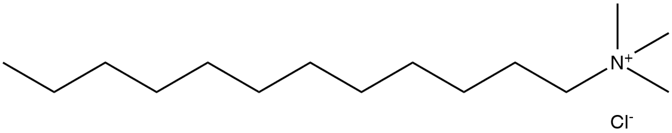
where m_s is mass of the surfactant (g), m_c is mass of the used clay sample (g), CEC is cation exchange capacity of the clay samples used (mmol/g), Q_{CEC} is the necessary amount of added proportion of surfactant/CEC, and M is molecular weight of the surfactant (g/mol). Proportions of added surfactant/cation exchange capacity of clay sample ranged from ½ to 3.

2.2.4. Clay modification with ionic liquids

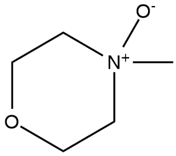
Modification with ionic liquids was carried out according to the method described in the Paper I – Ozola-Davidane et al. (2021). Modification was done in a similar way as the above-mentioned method by exchanging natural metal cations in the interlayer space of smectite type clay with cations contained in ionic liquids. Imidazolium-based ionic liquids with different alkyl chain lengths were used in the modification: 1-butyl-3-methylimidazolium chloride (Bent_C_4mimCl), 1-octyl-3-methylimidazolium chloride (Bent_C_8mimCl) and 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl). Additionally, imidazolium-based ionic liquids with different alkyl chain lengths and dimethyl phosphate anion were used in the modification: 1,3-dimethylimidazolium dimethyl phosphate (C_1mmimDMP); 1-butyl-3-methylimidazolium dimethyl (C_4mmimDMP); 1-octyl-3-methylimidazolium dimethyl phosphate (C_8mmimDMP); 1-dodecyl-3-methylimidazolium dimethyl phosphate (C_{12}mmimDMP). The chemical structures of used ionic liquids are depicted in Figure 2.3. and 2.4.



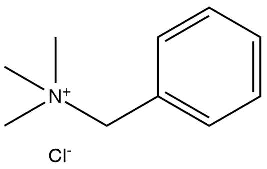
dimethyldodecylamine N-oxide



dodecyltrimethylammonium chloride

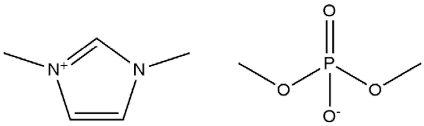


4-methylmorpholine N-oxide

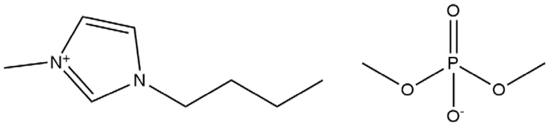


benzyltrimethylammonium chloride

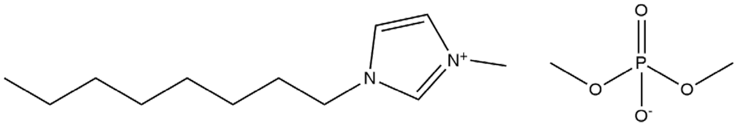
Figure 2.2. **Chemical structures of the surfactants used for clay modification.**



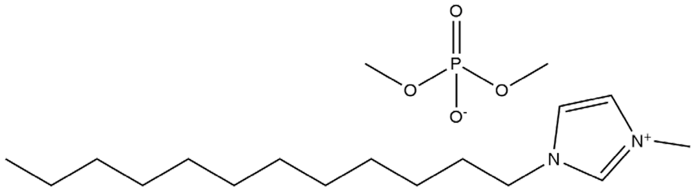
1,3-dimethylimidazolium dimethyl phosphate



1-butyl-3-methylimidazolium dimethyl phosphate

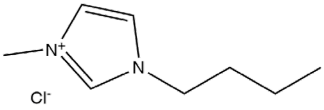


1-octyl-3-methylimidazolium dimethyl phosphate

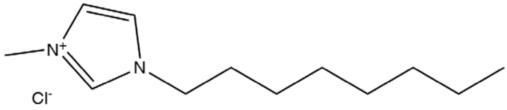


1-dodecyl-3-methylimidazolium dimethyl phosphate

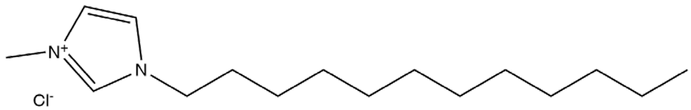
Figure 2.3. **Chemical structures of ionic liquids with dimethyl phosphate anion used for clay modification.**



1-butyl-3-methylimidazolium chloride



1-octyl-3-methylimidazolium chloride



1-dodecyl-3-methylimidazolium chloride

Figure 2.4. **Chemical structures of ionic liquids with chloride anion used for clay modification.**

Ionic liquids were prepared by Sindija Zeltkalne from the University of Latvia, Faculty of Chemistry according to a published method (Brica et al., 2017). The ionic liquids with chloride anion were obtained by alkylation of 1-methylimidazole with corresponding alkyl chlorides in an ethyl acetate solution at 80 °C for 72 hours. The ionic liquids with dimethyl phosphate anion in their turn were obtained by alkylation of 1-butyl-3-methylimidazolium chloride with trimethyl phosphate at 110 °C for 24 hours.

The corresponding amount of ionic liquid was dissolved in 100 mL deionized water. The proportion between the added ionic liquid and cation exchange capacity of the clay sample was 1. Then 5 g of clay were added to the ionic liquid solution and the mixture was stirred for 10 min using magnetic stirrer. Afterwards the ionic liquid and clay solution was put in a shaker for 24 h at room temperature. Finally, the mixture was centrifuged at 3000 rpm for 15 min and washed several times with deionized water by adding 0.1 M $AgNO_3$ until no chloride ions were detected, filtered, dried at room temperature, and dried 24 h at 60 °C.

2.2.5. Clay modification with anthocyanins

First step for preparing clay-anthocyanin composites was the extraction of anthocyanins from berries with ultrasound-assisted extraction method as described by Klavins et al. (2017).

Fresh berries were put into a domestic hydraulic juice extractor (Biowin, Poland) to obtain drained juice and berry press residues (seeds, skins). Then berry residues were dried in Gallenkamp Plus II (London, UK) oven for 24 h at 40 °C. Finally, dried berries were homogenized to a fine powder using IKA M20 analytical mill.

Then the berry press residues (50 g) were weighed, and 500 mL of 70% ethanol was added. Next the sample was put in 100 W ultrasound (Cole-Parmer) for 40 min. The temperature of ultrasound bath was monitored so that it would not exceed 30 °C, thus the water was changed every 20 minutes. After the treatment with ultrasound, the samples were filtered through filter paper to remove berry particles and insoluble matter.

Then the extract was evaporated in the rotary evaporator (Heidolph RotaVap) under reduced pressure at 40 °C until 200 mL of solution were obtained. 50 mL of the concentrated extract were placed in a glass column filled with Amberlite XAD7-HP sorbent (Sigma Aldrich) to remove other unnecessary substances (Denev et al., 2010). After sorption sorbent was washed several times with deionized water. Desorption of polyphenols was done using 250 mL 96% ethanol with added 5% formic acid (v/v %). The collected solution was dried in a rotary evaporator until 50 mL were obtained. Then the extract was freeze-dried for 2 days in the Labconco FreeZone benchtop freeze dryer at –45 °C. The anthocyanin extract obtained from berries was stored in a dark place at 4 °C.

The modification of the studied clay was done by treatment of the specific anthocyanins in optimal environmental conditions as described in detail in the patent (pending).

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 detailed described 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 2.1.). 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. 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:

$$q_e = \frac{(C_i - C_e)}{m}\, v \qquad (2)$$

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). Method is based on anthocyanin molecules' ability to change colour at different pH levels. The difference in absorbance is proportional to the anthocyanin content.

Two buffer solutions with different pH were prepared: 0.025 M potassium chloride solution at pH 1.0 and 0.4 M sodium acetate solution at pH 4.5; pH was adjusted with concentrated HCl. Two dilutions of the same sample were prepared using both buffers, so that the sample/buffer ratio did not exceed 1 : 5. The diluted samples were left in the dark for 20–40 minutes and measured within 20–50 minutes. The absorbance of each dilution was measured at 520 nm and 700 nm against a deionized water blank using Shimadzu UV-1800 UV-VIS spectrophotometer.

The total anthocyanin content, expressed as cyanidin-3-glucoside equivalents (cyd-3-glu), was calculated using the following equation:

$$\textit{Anthocyanin pigment content (cyd-3-glu eq., mg/L)} = \frac{A \times MW \times DF \times 1000}{\varepsilon \times L} \qquad (3)$$

where A is (A 520 nm – A 700 nm) $_{\mathrm{pH}\ 1.0}$ – (A 520 nm – A 700 nm) $_{\mathrm{pH}\ 4.5}$, MW is molecular weight of anthocyanins (cyd-3-glu) (449.2 g/mol), DF is dilution factor, L is the path length (1 cm) and ε is molar extinction coefficient for cyd-3-glu (26 900 L/cm mol).

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

2.4.1. Specific surface area

The specific surface area and pore structure parameters were measured using BET-N_2 absorption method (the Brunauer-Emmett-Teller isotherm) on the Micromeritics Gemini 2360 surface area and with the porosity analyser (Norcross, Georgia, USA) using the gas sorption technique. In the case of clay-ionic liquids and clay-Hap composite materials surface area measurements were performed on the Quantachrome Quadrasorb S1 surface area and with the pore size analyser using the gas sorption technique. The pore size was obtained using the built-in Quantachrome Quadrasorb S1 Density Functional Theory (BJH) model method. Before measurements samples were pre-heated at 80 °C under N_2 overnight.

The specific surface area measurements were taken in the testing laboratories of J. S. Hamilton Poland LTD and in Riga Technical University, Institute of General Chemical Engineering by Valentina Stepanova.

2.4.2. X-ray diffraction

The X-ray diffraction (XRD) analysis was performed on the Bruker D8 Advance diffractometer (Billerica, Massachusetts, USA) using CuKa radiation in the 2q range from 2° to 55° at scanning rate 0.02°/s. X-ray measurements were taken in the University of Latvia, Faculty of Chemistry, Clay research laboratory under the guidance of Juris Kostjukovs, Anna Trubača-Boginska and in the University of Tartu, Faculty of Science and Technology under the guidance by Ilze Vircava.

XRD was used to describe the mineral composition of clay samples and interlayer changes of smectite minerals after modification. The height of interlayer space was estimated from basal spacing (d_{001}) and the thickness of the sheet of phyllosilicate (9.6 Å) using the following equation (Bertuoli et al., 2014):

$$\text{Interlayer space height (Å)} = \text{distance } d_{001} - 9{,}6 \text{ Å} \qquad (4)$$

2.4.3. Fourier-transform infrared spectroscopy

The Fourier-transform infrared spectroscopy (FTIR) was used to determinate new functional groups in modified clay samples. FTIR spectra were recorded using the Shimadzu IR-Tracer 100 spectrophotometer (Kyoto, Japan) in wavenumber range of 400–4000 cm^{-1}, using 20 scans per spectrum with resolution of 2 cm^{-1}.

2.4.4. Scanning electron microscopy

Scanning electron microscopy (SEM) data was obtained by the scanning electron microscope FE-SEM Hitachi S4800 (Tokyo, Japan). Samples were measured in the secondary electron regime, with the SEM operating voltage of 1–5 kV. In the case of clay-FeOOH SEM data was obtained by the scanning electron microscope Tescan

Mira/LMU (Brno–Kohoutovice, Czech Republic) using backscattered electron regime, with operating voltage of 15 kv. SEM was used to study the morphological changes after clay modification. SEM pictures were taken in the University of Latvia, Institute of Chemical Physics under the guidance of Daniel Jevdokimov and in Riga Technical University, Institute of General Chemical Engineering.

2.4.5. Determination of iron (III) oxide content

Iron (III) oxide content was determined of clay-FeOOH composites, and the method is described in the Paper III – Ozola et al. (2019b). To 1 g of the dry sample (previously dried at 105 °C) 3 mL of 35% HCl and 5 mL of 65% HNO_3 were added and shaken for 24 h. Then the sample was filtrated and heated for 2 h at 120 °C. In corresponding filtrates iron (III) content was analysed using an atomic absorption spectrometer with flame atomization (FAAS) (Perkin-Elmer Analyst 200 atomic absorption spectrometer). The content of iron (III) oxide was calculated according to the following equation:

$$w_{Fe_2O_3} = \gamma Fe \cdot \frac{M_{Fe}}{M_{Fe_2O_3}} \cdot \frac{v}{m} \tag{5}$$

where w_{Fe2O3} is content of iron (III) oxide, γ_{Fe} is the concentration of iron in the sample (mg/g), M_{Fe} and M_{Fe2O3} is molecular weight of Fe and Fe_2O_3 (g/mol), v is volume of the sample (L), and m is mass of sorbent (g).

2.4.6. Thermogravimetric analysis

Approximately 5 mg as sample size was heated in crucible for thermogravimetric analysis (TGA) using TA Instruments – Waters LLC SDT Q600. For pyrolysis process nitrogen gas with flow rate 100 ml/min was used to ensure inert atmosphere. Samples were heated within constant heating rate 20 °C/min. At 105 °C temperature was held isothermal for 5 min, to detect amount of moisture. Afterwards heating continued to 900 °C, when the temperature was held isothermal for 2 minutes. Then nitrogen atmosphere was changed to oxygen with the same gas flow rate and the temperature was held isothermal again for 5 minutes, to detect amounts of fixed carbon and residues. For each experiment data of weight loss (w%), derivative weight loss was recorded (w%/°C) every second. The thermogravimetric analysis was done in the University of Latvia, Faculty of Geography and Earth Sciences by Viesturs Ozols.

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 (sampled in Latvia, Lithuania) as well as industrially produced mineralogically pure samples were used (see the Chapter 2.1.). The selected samples were chosen considering prospects to develop new applications of clay resources being relevant for Latvia as well as to test the elaborated design concepts on mineralogically well characterised clay samples. In order to develop new clay material applications, modification of the selected clays was aimed at increasing their sorption capacity in respect to the selected substances (having the capacity of being useful for developing new applications in environmental technologies and bioeconomy). The concept of clay composite design is based on two principles (Figure 3.1.):

1. Clay covering with another material providing new sorption capacities. 2 groups of substances were selected as materials for the development of this type of clay-based composites: 1) iron oxy-hydroxides and 2) hydroxyapatite. Sorption capacities of the selected materials are widely studied (Ansone-Bērtiņa, 2015; Burlakovs, 2015; Krauklis et al., 2017; Ozola et al. 2017; Ozola et al., 2019a) and the combination of the sorption profile of original clays and the clay 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 involving basic changes in the clay structure, considering the intercalation of the modifier into the clay mineral interlayer space. In this respect clay modification with a new (so far not used for clay modification) group of surfactants has been proposed. Another approach included clay modification with ionic liquids. As the result, newly developed materials become hydrophobic with increased sorption capacity for the sorption of organic substances.

The characteristic parameters of clay samples used in this study are summarized in Table 3.1. According to the XRD data, the major mineral phases in Mt clays are montmorillonite (w.t. 65.4%), muscovite (w.t. 12.8%), and quartz (w.t. 8.6%), also kaolinite and feldspars (w.t. <5%) as minor phases as well as traces of anatase and gibbsite were identified (Figure 3.3.). The first peak of basal $d_{(001)}$ reflection of Mt clay is at 13.40 Å. According to Moore and Hower (1986), basal spacing of montmorillonite with 0 water sheets is ~ 9,6 Å, but with 1, 2 or 3 water layers gives a reflection at ~12.4, ~15.2, and ~18Å respectively. The *c*-dimension value of unmodified Mt clay corresponds to a montmorillonite structure where an interlayer zone saturates one adsorbed water layer.

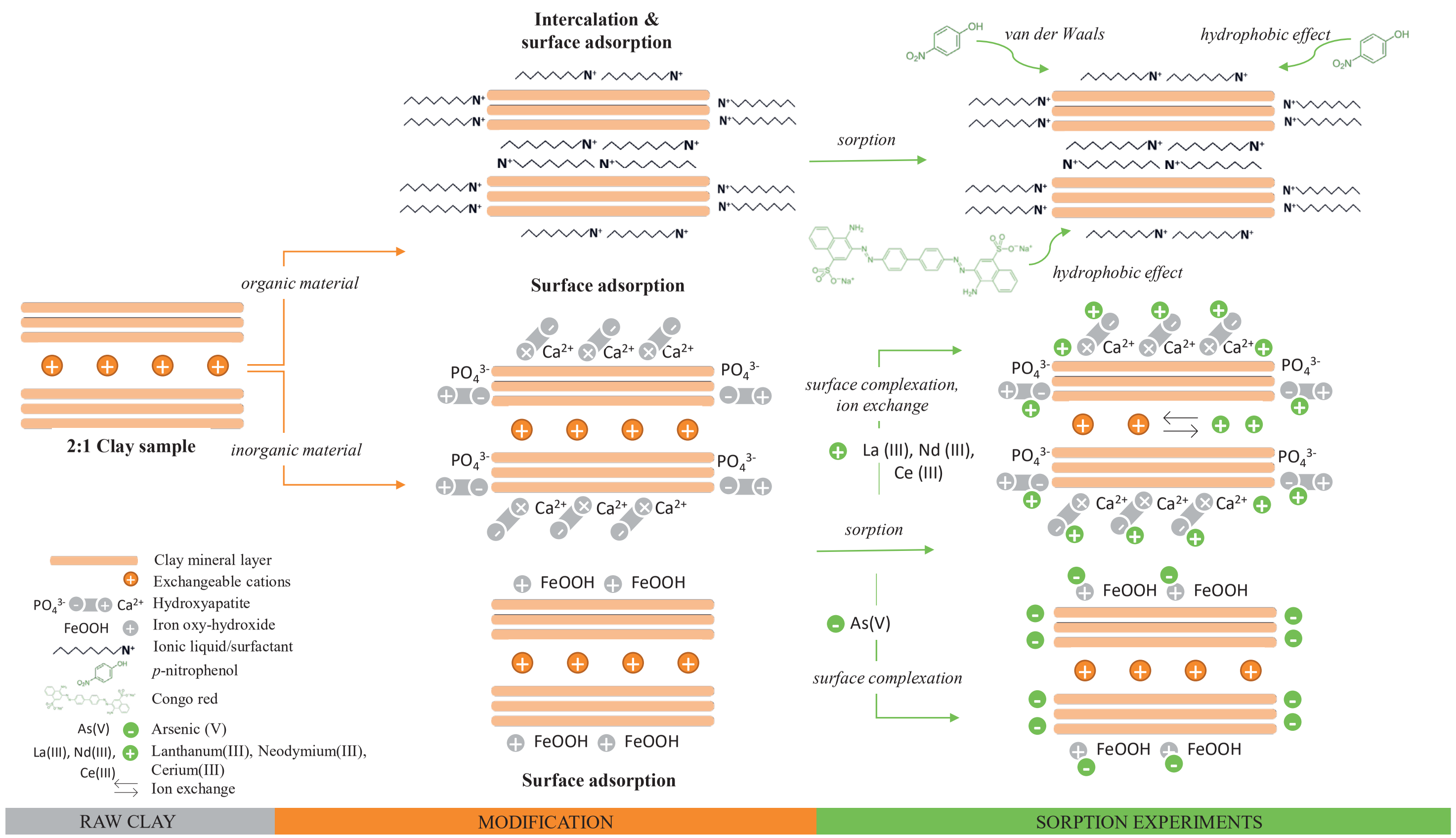


Figure 3.1. **Schematic representation of modification methods used in this study and possible sorption mechanisms of model contaminants onto obtained sorbents.**

Table 3.1.

Characteristics of the raw clay samples selected for 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 the methylene blue test

The main phase of the Bt clay is sodium montmorillonite with impurities, such as gypsum, quartz, plagioclase, dolomite, pyrite, and biotite. The ionic formula of the montmorillonite is $(Na_{0.83}\,K_{0.06}Ca_{0.17})(Mg_{0.71}Fe^{2+}_{0.04}Fe^{3+}_{0.74}Al_{2.44}Ti_{0.07})(Al_{0.56}Si_{7.44})O_{20}(OH)_4$. Bt clay consists of the following elements: SiO_2 65.58%, Al_2O_3 18.72%, Fe_2O 36.55%, MgO 1.74%, Na_2O 0.78%, CaO 0.53%, K_2O 0.25% (Choo and Bai, 2015). Basal $d_{(001)}$ reflection of the Bt clay is 12.63 Å and it corresponds to the structure where interlayer zone saturates one adsorbed water molecule layer.

The natural T clay contains almost half of the clay phases (smectite 12 w.t.%, illite-smectite 14 w.t.%, illite 9 w.t.%, chlorite 6 w.t.%, kaolinite 3 w.t.%), another main half of the mixture is presented with non-clay phases as quartz 19 w.t.%, calcite 20 w.t.%, dolomite, and hematite ~ 5 w.t.%, also with mica and feldspars (Figure 3.3.).

The natural J clay mainly contains non-clay phases, such as quartz and muscovite (w.t. 80%), and a small part of dolomite and calcite. The clayey fraction is composed of proportionally equal amounts of Ca and Na smectites, illite, clinochlore, and kaolinite (w.t. 20%) (Figure 3.3.). The J clay also contains an admixture of ancient organic matter (w.t. 2%) (Burlakovs et al., 2015) and fossils of marine fossil *Frondicularia concinna* from the Lower Cretaceous (Figure 2.1.).

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

Clay modification with iron oxy-hydroxide (FeOOH) was conducted as described in the Paper III – Ozola et al. (2019b) (see also the Chapter 2.2.1.). 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). As a result, the obtained composite materials were a combination of two or more components having unique properties that were not achievable with individual components (Vasiliev and Morozov, 2018; Amir et al., 2019).

Properties of composites were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), specific surface area (SSA), Fourier-transform infrared spectroscopy (FTIR), thermogravimetry (TG) methods. The SEM images showed the surface morphology of clay – FeOOH composite materials have changed compared to the raw clay samples. For all composite materials, the characteristic smectite type mineral crystal shape of a wavy subhedral was no longer visible because the surface has been saturated with iron compounds (Figure 3.2. E, G and H).

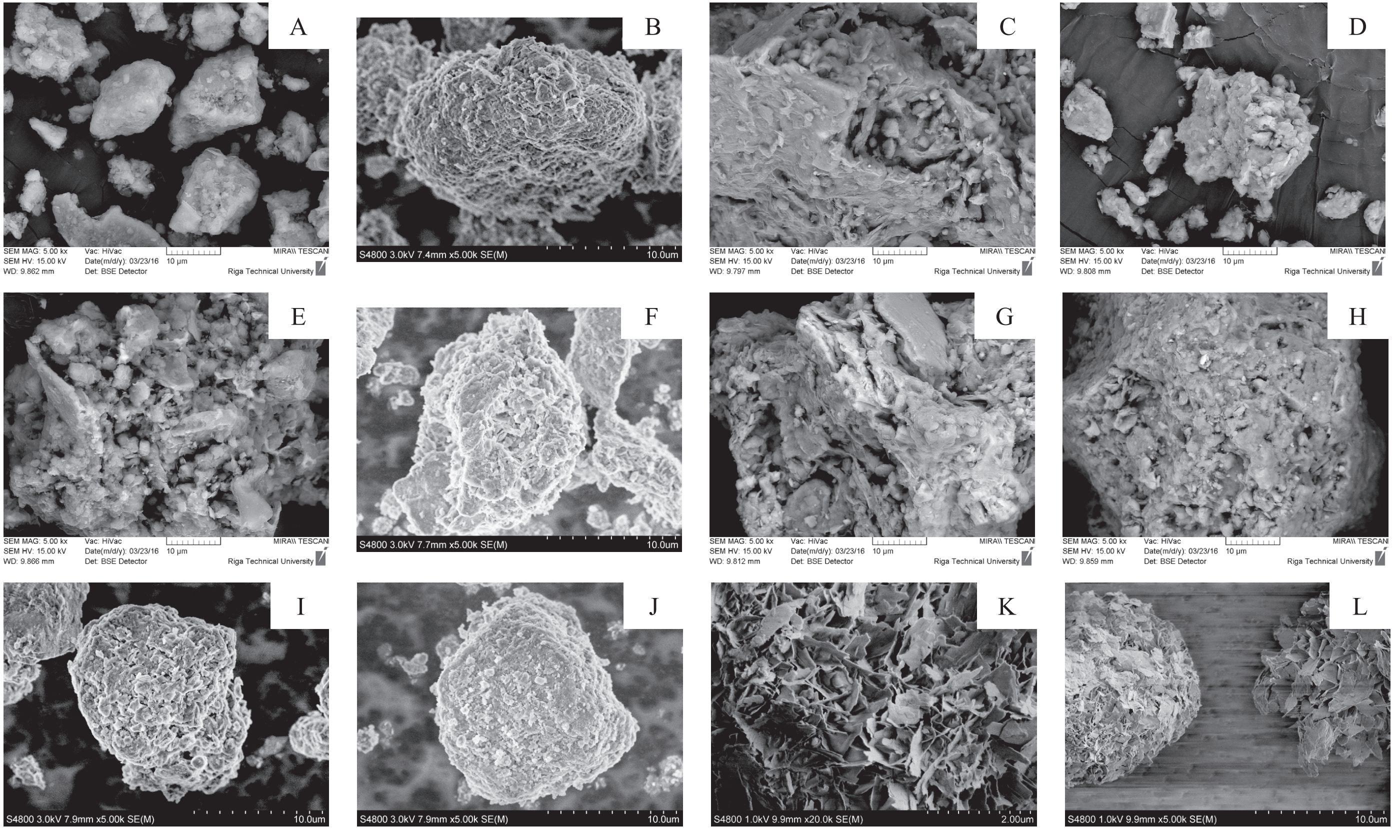


Figure 3.2. **SEM images (5k magnification) of raw clay samples ((A) Mt clay; (C) J clay; (D) T clay); Mt, T and J clay modified with iron oxy-hydroxide ((E) Mt-FeOOH; (G) J-FeOOH; (H) T-FeOOH); Mt clay modified with surfactants ((B) Mt_NMO_2; (F) Mt_BTMAC_2; (I) Mt_DDAO_2; (J) Mt_DTAC_2); T clay modified with hydroxyapatite ((K, L) T_Hap).**

XRD patterns show a significant decrease in intensity and smoothing of the first basal peak of smectite (region of 15–15.5 Å) in the clay samples modified with FeOOH (Figure 3.3). Also, the Roentgen-line light shifting in modified clay specimens between 10 Å and 15 Å indicate modifier influence on smectite phases in all samples. In addition, it was found that diffractograms do not indicate new phases in modified materials compared to the raw clays. This is consistent with the 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).

Functional groups and structural changes of clay minerals after modification were determined by Fourier-transform infrared spectroscopy (FTIR). There was no new absorbance peaks for Mt-FeOOH composite. However, the FTIR spectra of the modified T and J clay indicated the occurrence of new absorbance peaks with wavenumber at ~1400 cm^{-1} (Figure 3.4.) which is the indication of the presence of Fe–O functional group for maghemite (γ-Fe_2O_3) (Khorshidi and Azadmehr, 2017). XRD data also supports FTIR results, where the presence of iron oxide (hematite, α- Fe_2O_3) was found in the clay samples.

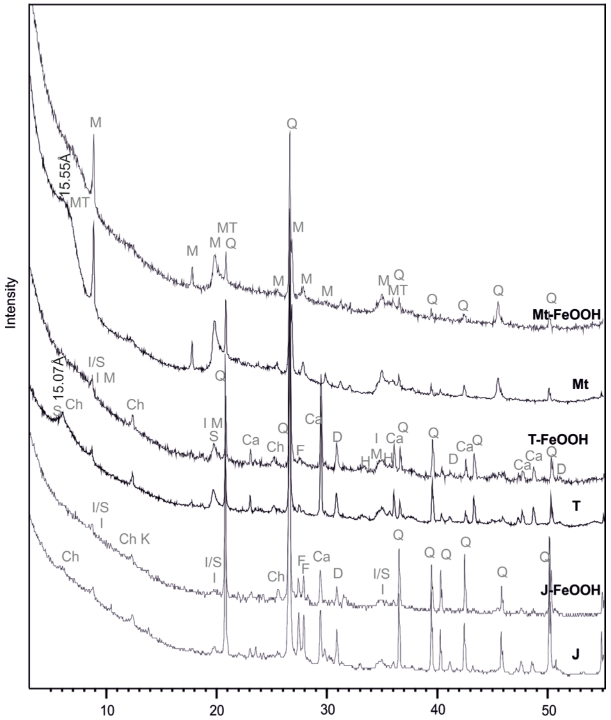


Figure 3.3. **XRD diffractograms of raw clay samples (Mt,T and J) and clay modified with iron oxy-hydroxide (Mt-FeOOH, T-FeOOH, J-FeOOH). Mineral denotations: M – muscovite, MT – montmorillonite, Q – quartz, S – smectite, I – illite, F – feldspar, Ca – calcite, Ch – chlorite, D – dolomite, K – kaolinite, H – hematite.**

Thermogravimetric analysis of the raw clay samples and the samples modified with FeOOH showed loss of adsorbed water molecules around 120 °C (Šaponjić et al., 2017; Schroeder 2018) and weight loss around 700 °C due to decomposition of the structural hydroxyl groups in the aluminosilicates (Figure 3.4. A–F) (He et al., 2010; Takahashi et al., 2013; Schroeder, 2018). Dehydroxylation of hydrated iron oxides present in the clay-FeOOH composites occurred at 160 °C as indicated by an exothermic peak in the DTG curves (Figure 3.4. A–F) (Oliveira et al., 2003; Yuan et al., 2008; Vianna et al., 2010; Parvinzadeh and Eslami, 2011). The weight loss observed for the modified materials at the temperature around 500 °C and 800 °C should be attributed to partial transformation of maghemite (γ-Fe_2O_3) phase to hematite (α-Fe_2O_3) present in the composites, as reported by Fan et al. (2013) and 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.

The CEC and SSA values significantly increased after the modification of clay materials. The highest CEC was established for T-FeOOH (1.0076 mmol/g), followed by Mt-FeOOH (0.9752 mmol/g) and J-FeOOH (0.8379 mmol/g). The highest SSA determined by BET, in turn, was observed for Mt-FeOOH (245.63 m^2/g), followed by T-FeOOH (91.75 m^2/g) and J-FeOOH (63.79 m^2/g). These parameters indirectly indicate that the sorption capacity of clay-FeOOH composites will be higher than for the unmodified clay samples.

The amount of iron oxide in composite materials showed that the elaborated method of modification was effective as the content of Fe_2O_3 significantly increased after modification. For example, the Mt clay contained 1.4 mg/g of Fe_2O_3 but after modification Fe_2O_3 content reached 31.50 mg/g, while for T-FeOOH and J-FeOOH samples iron oxide content was 39.75 mg/g and 43.22 mg/g, respectively.

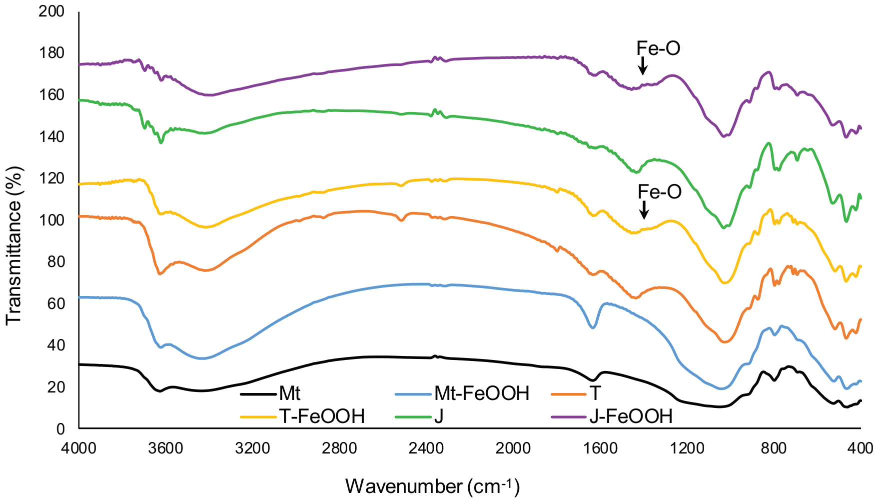


Figure 3.4. **FTIR spectra comparison of raw clay (Mt, T and J) and modified with iron oxyhydroxide (Mt-FeOOH; T-FeOOH and J-FeOOH).**

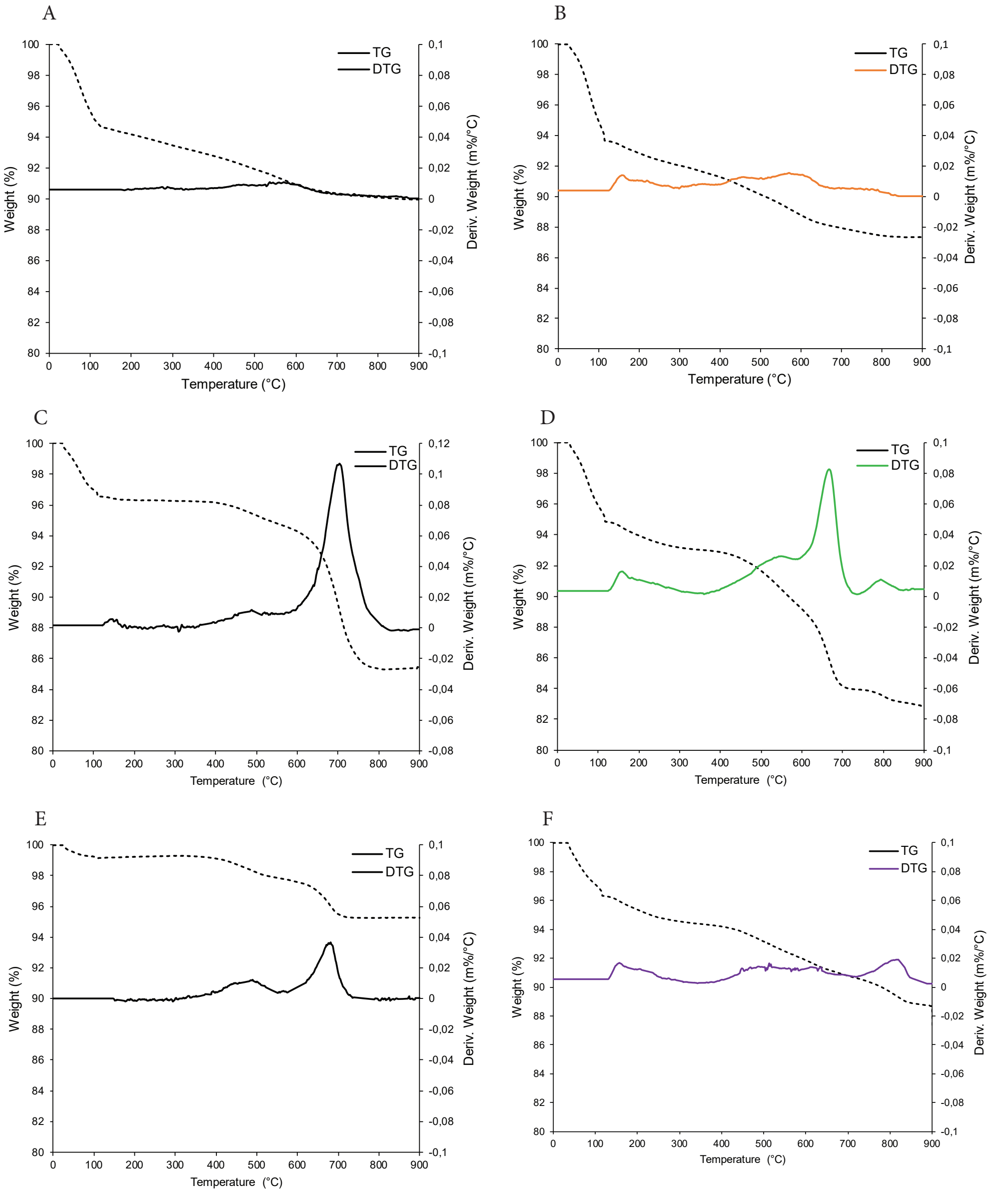


Figure 3.5. **TG and DTG curves of raw clay ((A) Mt clay (C) T clay (E) J clay) and clay modified with iron oxy-hydroxide ((B) Mt-FeOOH, (D) T-FeOOH, (F) J-FeOOH).**

Considering, that metalloids have a high affinity to interact with iron compounds, it can be predicted that the sorbents with the highest content of iron oxide will also have the highest sorption capacity. In this case, modified Triassic and Jurassic natural clays from Lithuania and Latvia have relevant properties ensuring possibly higher sorption capacities and thus could improve the removal of As(V).

3.1.3. Characterization of clay – hydroxyapatite composite materials

Clay modification with synthetic hydroxyapatite (Hap) was performed as described in the Paper VII – Ozola et al. (2017) (see also the Chapter 2.2.2.). The modification method was based on the Mt, T and J clay material saturation with mixture of $CaCl_2$ and KH_2PO_4 at pH of 9 ±0.5 to gain 1.6 equimolar proportion of Ca/P. Consequently, the composite material has increased sorption sites for positively charged elements, such as rare earth elements (REE), lanthanum (III), neodymium (III), and cerium (III).

Properties of clay-Hap composites were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), specific surface area (SSA) by BET method, Fourier-transform infrared spectroscopy (FTIR), and thermogravimetry (TG) methods. SEM images showed that after modification with Hap the morphology of the clay surfaces has changed. Clay mineral surface was completely covered with calcium hydroxyapatite precipitated crystals and particles were bound into larger agglomerations. For example, after modification of the T clay (Figure 3.2. D) with Hap (Figure 3.2. K, L) predominantly plate-like crystals with some acicular crystals of hydroxyapatite have appeared. Similar morphological changes were also reported by Chen et al. (2011), Mobasherpour et al. (2012), and Gallinetti et al. (2014).

After modification with Hap specific surface area of composite materials has slightly decreased, for example, in case of Mt-Hap from 252.03 m^2/g to 121.53 m^2/g. BET specific surface of T-Hap and J-Hap was 53.37 m^2/g and 24.04 m^2/g, respectively.

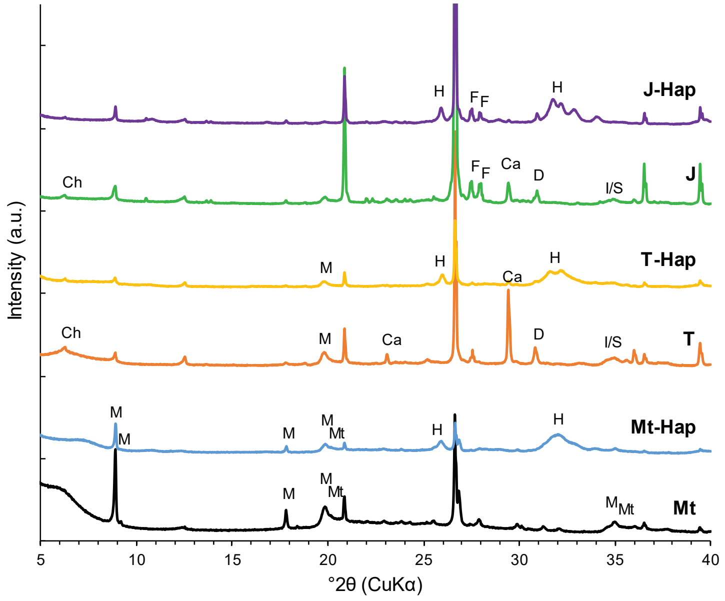


Figure 3.6. **XRD diffractograms of the raw clay samples (Mt, T and J) and clay samples modified with iron hydroxyapatite (Mt-Hap, T-Hap, J-Hap). Mineral denotations: M – muscovite, MT – montmorillonite, S – smectite, I – illite, F – feldspar, Ca – calcite, Ch – chlorite, D – dolomite, H – hydroxyapatite.**

The decrease of a surface area of composite materials is attributed to the attached hydroxyapatite particles on clay nanosheets and the resulting morphological changes (Zhu et al., 2008; Ibrahim et al., 2015; El-Nagar et al., 2020).

XRD data showed that the mineral composition is completely changed in clay modification processes with hydroxyapatite. The characteristic peaks of chlorite, calcite, illite/smectite, feldspar and other mineral phases noticeably decreased in their intensity or disappeared entirely. The clay mineral phase d-space expansion was not identified, but new peaks with high intensities of hydroxyapatite remnants appeared in diffraction pattern at ~26° and ~32° 2θ scale (Figure 3.6.).

Diffraction reflection characteristic to hydroxyapatite and monetite was also found in previous research (Ozola et al., 2017) modifying Quaternary Lielauce clay with Hap in 1.5 Ca/P equimolar proportion.

FTIR spectra demonstrate that the newly developed composite material has new functional groups (Figure 3.6.). The new absorption bands of clay-hydroxyapatite composites were exhibited at 1412 cm^{-1} and 1450 cm^{-1}, which is assigned to the carbonate ion presence CO_3^{2-} (Chen et al., 2011; Shaltout et al. 2011; Hokkanen et al., 2018) and absorption band at 600 cm^{-1} was indicative of to the phosphate ions PO_4^{3-} (Shaltout et al., 2011; Sofronia et al., 2014).

The results of the differential and gravimetric thermal analysis (DTA/TGA) of clay samples modified with Hap are presented in Figure 3.7. Mt-Hap, T-Hap and J-Hap samples with thermal loss of 8.43%, 7.32% and 6.54%, respectively, show three decomposition regions. The first region occurs at 120 °C with a weight loss of 2.09% (J-Hap), 3.84% (T-Hap), 4.02% (Mt-Hap) and it is mainly attributed to the physical removal of adsorbed water. Liberation of the chemically bonded water was indicated by exothermic peak in the DTG curves at 160 °C (T-Hap and J-Hap) and between 130 °C and 320 °C (Mt-Hap). The third decomposition region occurs at 610 °C with a weight loss of 1.72% (J-Hap), 2.68% (Mt-Hap), 2.89% (T-Hap) and it is related to the carbon dioxide released from carbonated apatite. In the case of T-Hap sample it was found

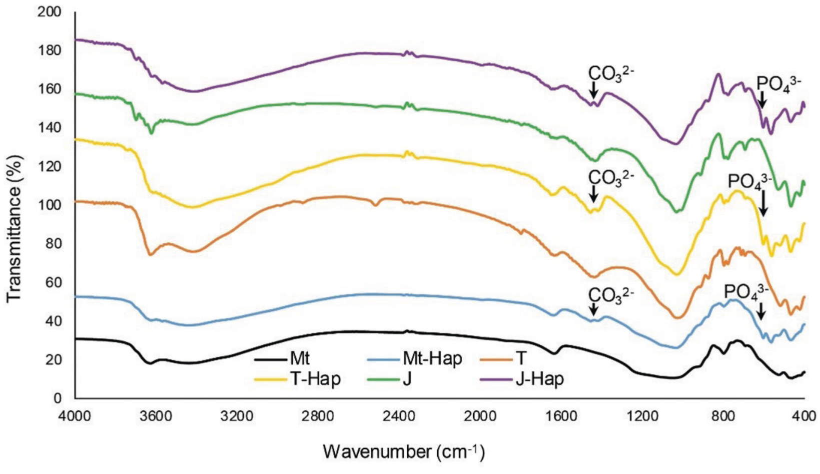


Figure 3.7. **FTIR spectra comparison of the raw clay (Mt, T and J) and the clay modified with hydroxyapatite (Mt-Hap; T-Hap and J-Hap).**

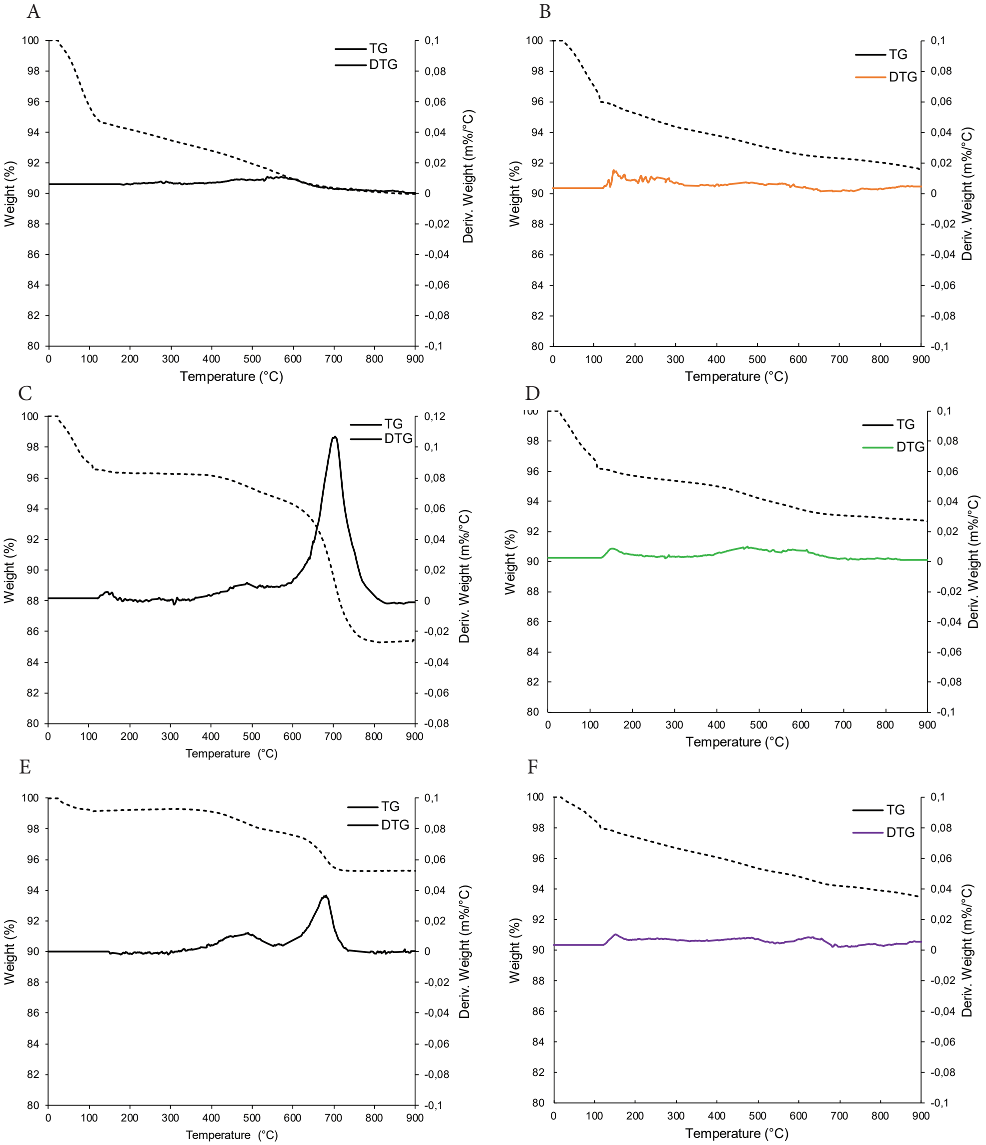


Figure 3.8. **TG and DTG curves of the raw clay ((A) Mt clay (C) T clay (E) J clay) and the clay modified with iron hydroxyapatite (B) Mt-Hap, (D) T-Hap and (F) J-Hap.**

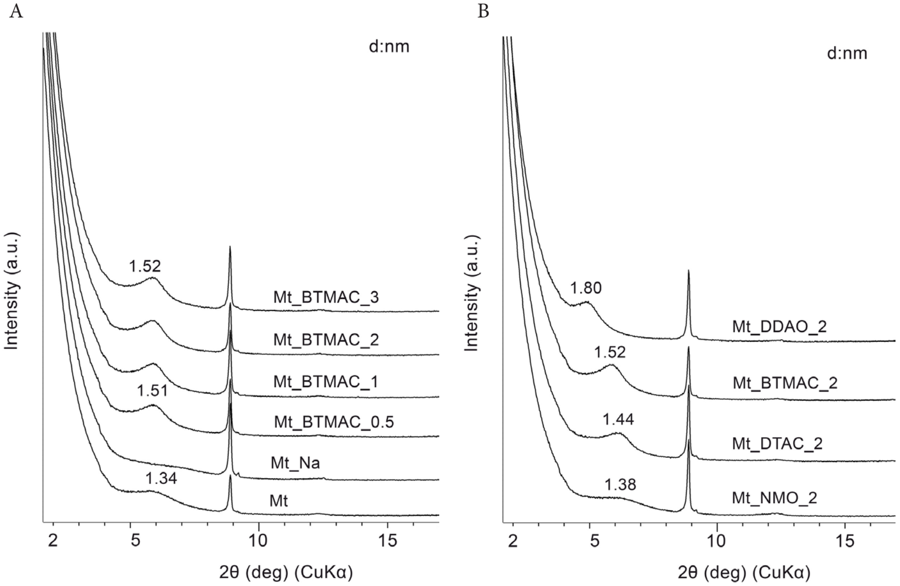
that the modification with Hap has increased its thermal stability compared to the raw T clay. Thus, the presence of hydroxyapatite provides additional thermal barrier, and hence delays the weight loss more than two times.

The thermal behavior of synthesized Hap corresponds to similar findings reported in the literature Peters et al. (2000), Katti et al. (2008), Shaltout et al. (2011), Gunduz et al. (2014) and Sofronia et al. (2014). In general, the FTIR results are in accordance with the data obtained by 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 the Paper II – Ozola et al. (2019a) (see also the Chapter 2.2.3.). The method was based on the sodium ion exchange with surfactant ion within the interlayer space of smectite type mineral (Mt clay). Thus, the clay surface becomes hydrophobic and improves the sorption ability of organic pollutants, such as *p*-nitrophenol (PNP) (de Paiva et al., 2008; He et al., 2014; Zhang et al., 2015; Guégan, 2019). As a result, organo-clay materials were obtained and properties of composites were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), specific surface area (SSA), Fourier-transform infrared spectroscopy (FTIR), thermogravimetry (TG) methods.

The X-ray diffraction patterns for clay sorbents modified in various proportions of BTMAC/CEC (Mt clay) revealed that the d_{001} peak for the Na-exchanged montmorillonite at 1.34 nm shifted to greater values as a result of the exchange of Na^+ ions with the surfactant cations (Figure 3.9.). Compared to the raw Mt clay, the interlayer space



Sample	$d_{(001)}$ (nm)	Interlayer space (nm)	Interlayer space expansion (nm)
Mt	1.34	0.38	–
Mt_NMO_2	1.38	0.42	0.04
Mt_DTAC_2	1.44	0.48	0.10
Mt_BTMAC_2	1.52	0.56	0.18
Mt_DDAO_2	1.80	0.84	0.46

*Calculated by Eq. (3).

Figure 3.9. **XRD diffractograms and interlayer spacing of modified Mt clay with nonionic (DDAO, NMO) and cationic surfactants (BTMAC, DTAC): (A) at various surfactant/CEC ratios and (B) at surfactant/CEC ratio 2.**

distance increased by 0.17, 0.17, 0.18, and 0.18 nm after modification with surfactant/CEC ratios of 0.5, 1.0, 2.0, and 3.0, respectively.

Cation exchange by the DTAC, DDAO and NMO yielded a maximum increase in the interlayer distance also with a surfactant/CEC ratio of 2.0, and it did not change significantly when the surfactant concentration was increased. The largest increase in interlayer spacing occurred with surfactant DDAO (0.46 nm), whereas a smaller change was observed with NMO (0.04 nm) (Figure 3.9.). These changes can be explained by the length of the surfactant alkyl chain (n_c, number of carbon atoms) (He et al., 2014). In the case of NMO, the value of n_c is 5, which is short compared to DDAO where n_c is almost three times longer at 14. In these organo-clay samples, the alkyl chains of NMO, DTAC, and BTMAC formed only one parallel layer in the interlayer, as the basal 001 reflection was ≤1.5 nm, while in the case of DDAO, the alkyl chains were ordered in two parallel layers between the montmorillonite plates, indicated by the basal 001 reflection at 1.80 nm (Figure 3.9.) (Yariv and Cross, 2002; Zhu et al., 2007; Zhang et al., 2015).

The specific surface area of organoclays changed depending on the proportion of added surfactant/CEC ratio. The specific surface area of Mt clay saturated with sodium ions (Mt_Na) decreased from 262.16 m^2/g to 224.46 m^2/g after treatment with 3.0 BTMAC/CEC ratio. Overall, the SSA diminishes in the following order: Mt_Na > Mt_BTMAC_0,5 > Mt_BTMAC_1 > Mt_BTMAC_2 > Mt_BTMAC_3 (Ozola et al., 2019a). The correlation of SSA measurements to surfactant loading was also found in the literature (Zhou et al., 2008; Wu et al., 2012; Park et al., 2013; Parolo et al., 2014; Zhang et al., 2015). Decrease of the SSA after modification occurs 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. This process results in a reduction of pore size and molecular nitrogen adsorption, thus decreasing reported values via BET of the SSA with an increasing degree of modification (Parolo et al., 2014; Zhang et al., 2015). As for the clays treated with surfactants, the interlayer space has significantly increased; therefore, it could be assumed that the SSA is not determining factor for the improvement of sorption capacity (Park et al., 2013; Zhang et al., 2015).

SEM images showed that after modification with surfactants the characteristic morphology of the smectite type mineral remains intact. The wavy subhedral crystal shape of the Mt clay was observed in both cases, when modified with nonionic surfactants (Mt_NMO_2 and Mt_DDAO_2) and cationic surfactants (Mt_BTMAC_2 and Mt_DTAC_2) (Figure 3.2. B, F, I and J). However, particles of composite materials Mt_NMO_2, Mt_DTAC_2, and Mt_DDAO_2 (Ozola et al., 2019a) were forming larger agglomerations.

The infrared spectroscopy revealed characteristic functional groups of the Mt clay which appeared at 3621 cm^{-1} and 3428 cm^{-1} and were assigned to OH-stretching vibrations of the structural hydroxyl groups and OH-stretching of water absorbed within the interlayer space of the clay (Zhang et al., 2015). The bands at 1040 cm^{-1} and 920 cm^{-1} indicate the Si–O stretching and Al-Al–O deformation (Zhou et al., 2011). The bands of quartz at 798 cm^{-1}, 515 cm^{-1}, and 460 cm^{-1} are typical bending vibrations of O–Si–O (Figure 3.10.) (Alkaram et al., 2009).

After modification of the Mt clay with DDAO, BTMAC, DTAC surfactants, a pair of strong bands at 2930 cm^{-1} and 2854 cm^{-1} was observed, which is assigned to the asymmetric and symmetric C–H stretching vibrations of the methylene groups (CH_2), and

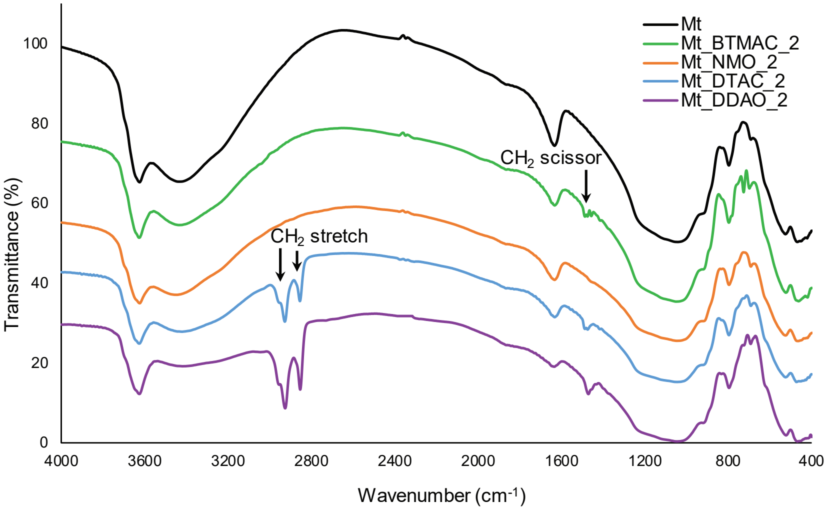


Figure 3.10. **FTIR spectra of Mt clay and modified with nonionic (DDAO, NMO) and cationic surfactants (BTMAC, DTAC) at surfactant/CEC ratio 2.**

their scissoring vibrations were detected at 1466 cm^{-1}. While after modification of the Mt clay with NMO new functional groups have not been found (Figure 3.10.).

The characteristic absorption bands of the Mt clay modified with surfactants were highly consistent with the results of organo-clay studies reported in the literature (Alkaram et al., 2009; Zhou et al., 2011; Wu et al., 2012; Zhang et al., 2015) and similar to FTIR spectra of bentonite modified with ionic liquids (see the Chapter 3.1.5. and the Figure 3.12.)

Differential and thermal gravimetric analysis of the raw and modified montmorillonite with cationic and nonionic surfactants are depicted in Figure 3.11. Overall, three decomposition regions were observed for all samples. The first decomposition region at 117 °C was attributed to the dehydration of physically adsorbed water molecules. Compared to the raw Mt clay saturated with sodium ions after modification with surfactants, the total water mass loss decreased from 6.77% for the Mt clay to 3.56% for the Mt_BTAC_2, 3.27% for the Mt_DTAC_2, 5.63% for the Mt_NMO_2 and 1.63% for the Mt_DDAO_2. These results demonstrate that the surface affinity of bentonite transformed from hydrophilic to hydrophobic after modification with cationic or nonionic surfactants (Ma et al., 2015; Taleb et al., 2018). Removal of the water molecules around metal cations (Na^+ and Ca^{2+}) on exchangeable sites in interlayer space of montmorillonite were indicated by exothermic peak in the DTG curves at 178 °C (Mt clay, Mt-BTMAC and Mt-NMO), while in the case of Mt-DDAO at 164 °C and at 215 °C. The second dehydration peak was not observed only for the Mt clay modified with DTAC. The third decomposition region at the range of 576 °C to 743 °C corresponds to the dehydroxylation of structural hydroxyl units of the clay and probable formation of an amorphous meta-montmorillonite phase (He et al., 2005; Xi et al., 2010; Ma et al., 2015; Andrunik and Bajda, 2019). The third dehydroxylation peak was not observed only for the Mt-DDAO sample.

The combustion and loss of the cationic surfactants (BTMAC and DTAC) from the surface and the interlayer space of the Mt clay was observed around 340 °C

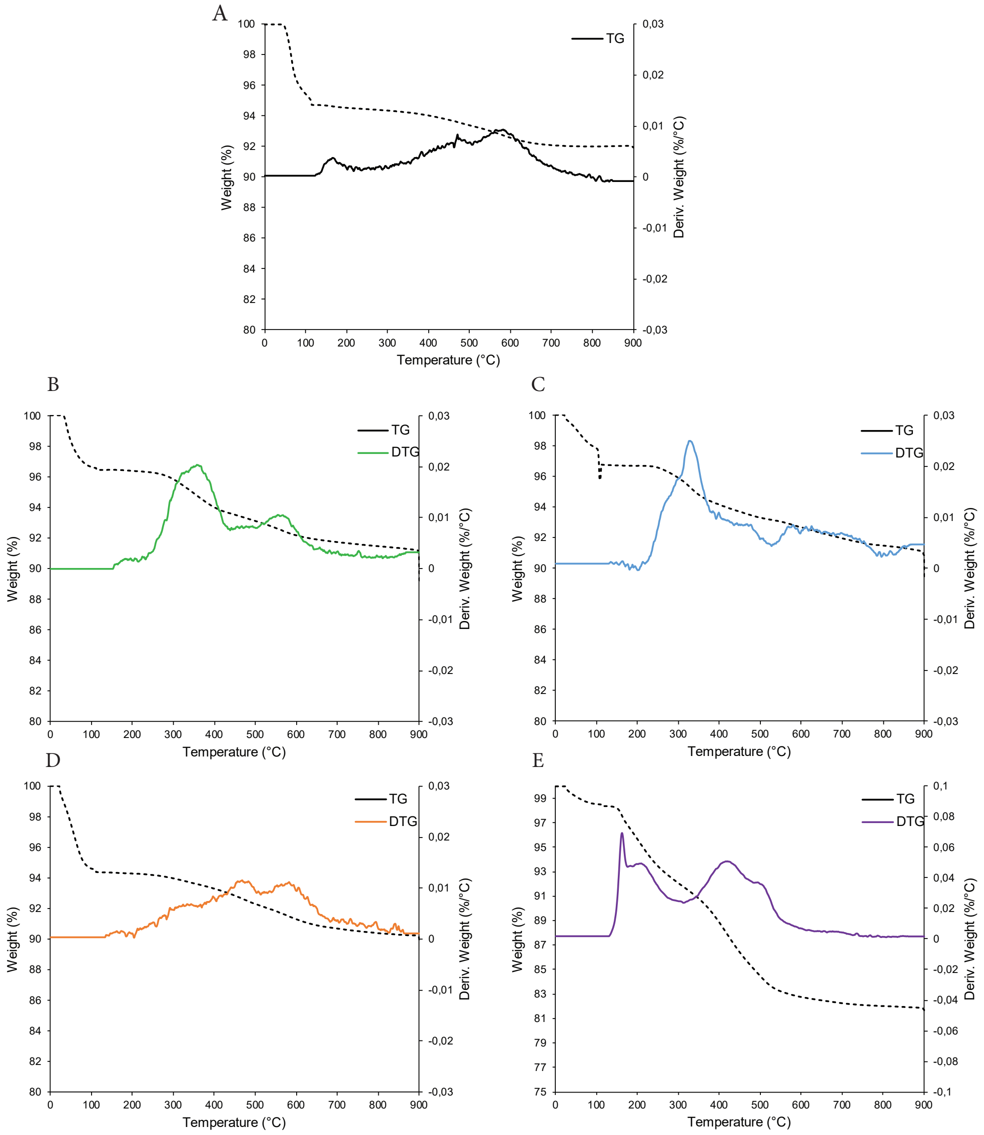


Figure 3.11. **TG and DTG curves of (A) raw Mt clay and modified with cationic (B) BTMAC, (C) DTAC and nonionic surfactants (D) NMO (E) DDAO at surfactant/CEC ratio 2.**

(Figure 3.11. A, B), while in the case of Mt_DDAO_2 the combustion of nonionic surfactant was observed in two steps at 420 °C and at 501 °C (Figure 3.1.1 E). Decomposition of the NMO surfactant was detected by slightly visible exothermic peak at 473 °C (Figure 3.11. D). The decomposition of DDAO after 400 °C indicates that the nonionic surfactant molecules are strongly bonded in the interlayer space of Mt clay (Ma et al., 2015). The total weight loss of Mt_BTMAC_2, Mt_DTAC_2, Mt_NMO_2, Mt_DDAO_2, which is attributed to the decomposition of surfactant molecules, was 3.02%, 3.04%, 2.27%, 9.28%, respectively. The characteristic exothermic effects in the temperature range of 200 °C to 500 °C related to the combustion and loss of surfactant molecules from the montmorillonite also were reported in the literature (Zhou et al., 2007; Xi et al., 2010; Ma et al., 2015; 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 in the Paper I – Ozola-Davidane et al. (2021) (see also the Chapter 2.2.4). The method was based on the intercalation of imidazolium-based ionic liquids with different lengths of the alkyl chains in the interlayer space of sodium bentonite via an ion exchange reaction. Likewise, in the clay-surfactant modification the obtained material becomes hydrophobic and improves the sorption ability of organic contaminants, such as anionic azo dye Congo red (CR) from aqueous solutions. Properties of the composite materials were characterized using X-ray diffraction (XRD), specific surface area (SSA), Fourier-transform infrared spectroscopy (FTIR), thermogravimetry (TG) methods.

As similar results were obtained using the same ionic liquids with both an anion of phosphate and chloride, clay minerals modified with ionic liquids with chlorite anion will be further discussed in this chapter. The general trends are similar to the case of chloride ion as an anion, but some differences can be explained by differences in the size of phosphate and different polarity (Ozola-Davidāne et al., 2022).

FTIR spectra revealed several characteristic functional groups of the bentonite clay. The absorbance peaks at 3622 cm^{-1} and at 3429 cm^{-1} are assigned to OH stretching vibrations, which may rise from the isomorphic substitution in the tetra and octahedral layers in bentonite (Alkaram et al., 2009; Zhang et al., 2015). The band at 1038 cm^{-1} indicated asymmetric stretching vibration of Si-O-Si. Also, the presence of quartz was indicated by bonds at 716 cm^{-1}, 781 cm^{-1}, 848 cm^{-1} and the bands ranging from 428 cm^{-1} to 513 cm^{-1}, which are attributed to O-Si-O bending vibrations (Figure 3.12.) (Stuart, 2004; Alkaram et al., 2009; Schroeder, 2018).

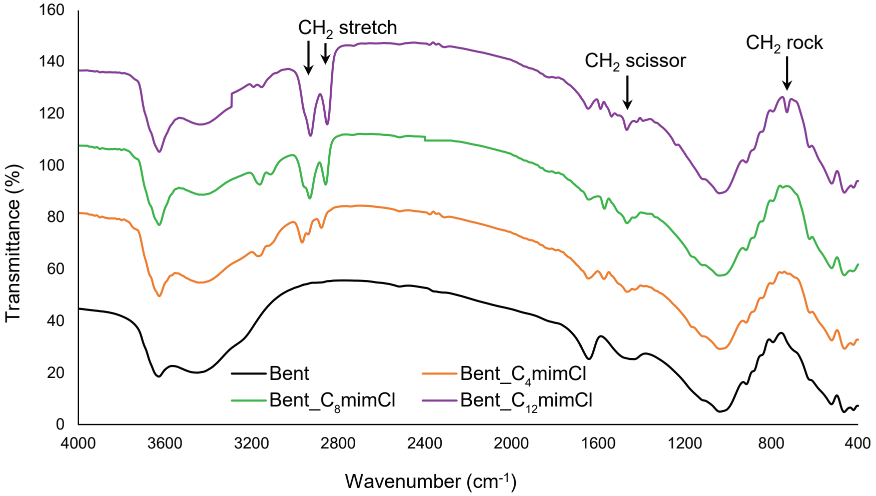
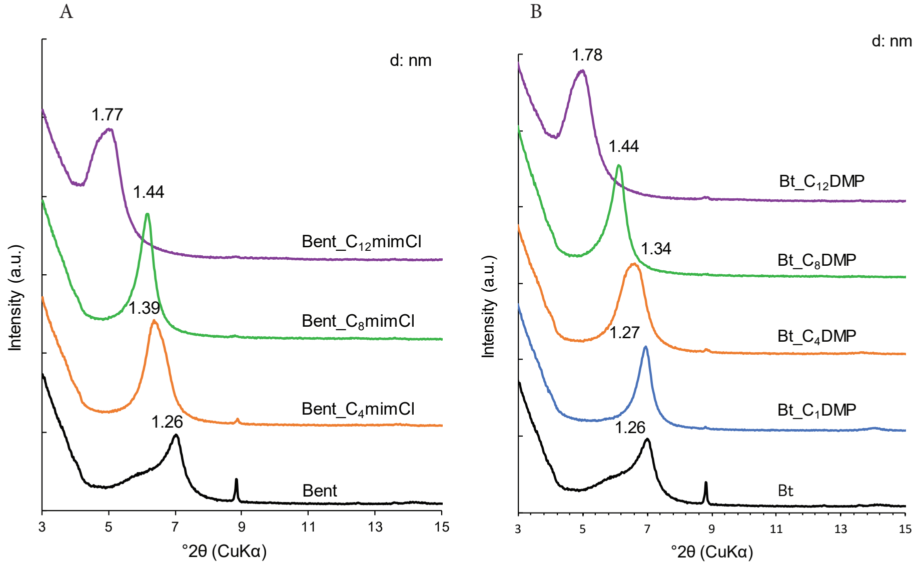


Figure 3.12. **FTIR spectra of the raw Bent clay and modified with imidazolium-based ionic liquids with different lengths of alkyl chains.**

After modification of bentonite with imidazolium-based ionic liquids with different lengths of alkyl chains, several new bands were observed. The absorbance peaks at 2927 cm^{-1} and 2847 cm^{-1} correspond to the asymmetric and symmetric C–H stretching vibrations of the methylene groups (CH_2). The bands at 1462 cm^{-1} and 721 cm^{-1} indicate scissoring and rocking vibrations of methylene groups (Figure 3.12.) (Stuart, 2004). The presence of these bonds 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 (Ha and Xanthos, 2011; Sprynskyy et al., 2015; Sun et al., 2017).

The X-ray diffraction pattern revealed that after bentonite modification with ionic liquids with different lengths of alkyl chains the d_{001} peak shifted to lower angular values. The interlayer spacing was related to the length of alkyl chain of the imidazolium cation – longer alkyl chain corresponds to larger interlayer space expansion.



Sample	$d_{(001)}$ (nm)	Interlayer space (nm)	Interlayer space expansion (nm)*
Bent	1.26	0.30	-
Bent_C_4mimCl	1.39	0.43	0.13
Bent_C_8mimCl	1.44	0.48	0.18
Bent_C_{12}mimCl	1.77	0.81	0.51
Bent_C_1mmimDMP	1.27	0.31	0.01
Bent_C_4mmimDMP	1.33	0.38	0.08
Bent_C_8mmimDMP	1.44	0.48	0.18
Bent_C_{12}mmimDMP	1.77	0.82	0.51

*Calculated by Eq. (3).

Figure 3.13. **XRD diffractograms and interlayer spacing of the modified Bent clay with imidazolium-based ionic liquids with different lengths of alkyl chains and anions.**

For the Bent_C_4mimCl, Bent_C_8mimCl and Bent_C_{12}mimCl samples interlayer space expansions were 0.13 nm, 0.18 nm and 0.51 nm, respectively (Figure 3.13.). Similar results were achieved also by modifying the Bent clay with ionic liquids with an anion of phosphate (Figure 3.13.).

Also other studies show equal results (Reinert et al., 2012; Takahashi et al., 2013; Nasser et al., 2016; Sun et al., 2017) confirming that the shift of basal d spacing, d_{001}, to lower values indicate successful intercalation of ionic liquid cations into the interlayer space of the bentonite.

The specific surface area and pore volume values of the clay-ionic liquid composites decreased with an increasing length of the alkyl chain of the ionic liquid used. SSA of the Bent clay gradually diminished from 45.21 m^2/g to 29.83 m^2/g, 18.80 m^2/g, 6.89 m^2/g after modification with C_4mimCl, C_8mimCl, C_{12}mimCl, respectively. The pore volume of the Bent clay decreased from 0.092 m^3/g to 0.066 m^3/g, 0.045 m^3/g, 0.029 m^3/g after modification with C_4mimCl, C_8mimCl, C_{12}mimCl, respectively. However, the average pore diameter of modified bentonite gradually enlarged by 0.84 nm, 1.55 nm, and 11.72 nm for Bent_C_4mimCl, Bent_C_8mimCl, and Bent_C_{12}mimCl respectively, compared to the unmodified bentonite. The pore diameter results correspond to the XRD investigation and interlayer space expansion.

The textural properties of the unmodified bentonite and the obtained bentonite-ionic liquid composites show that ionic liquid cations not only have entered

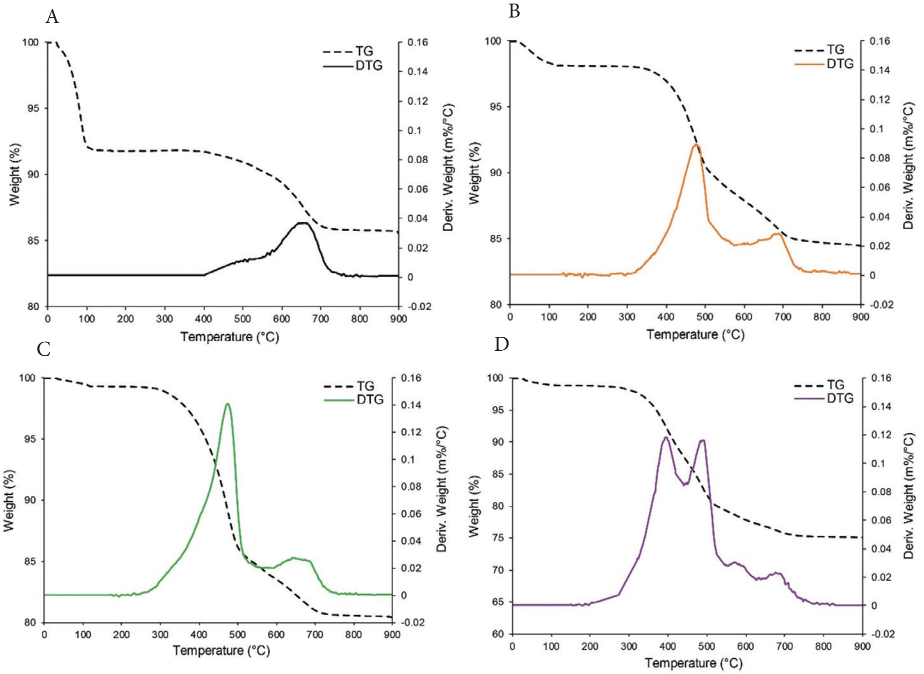


Figure 3.14. **TG and DTG curves of the raw Bent clay (a) and the clay modified with ionic liquids: 1-butyl-3-methylimidazolium chloride (Bent_C_4mimCl) (b); 1-octyl-3-methylimidazolium chloride (Bent_C_8mimCl) (c) and 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl) (d).**

the bentonite interlayer space but also have adsorbed in the exterior surface, occupying pores among the clay particles. This process results in a reduction of the specific surface area and pore volume (Srivastava et al., 2009; Zhou et al., 2011; Park et al., 2013; Zhang et al., 2015). From these results, it can be assumed that the SSA and pore size are not determining factors for the improvement of the sorption capacity of organic pollutants.

Differential and thermal gravimetric analysis of the raw and modified montmorillonite with cationic and nonionic surfactants is depicted in Figure 3.14.

Thermal gravimetric analysis curves of the raw Bent clay revealed mass loss (8.19%) from room temperature up to 100 °C due to the release of physically adsorbed water molecules. In this temperature range, a small mass loss of a maximum of 2% was observed for the bentonite-ionic liquid composites, indicating that the modification with ionic liquids has gained hydrophobic properties for the clay-ionic liquid composites. The decomposition region around 700 °C corresponds to the dehydroxylation of the structural hydroxyl groups in the aluminosilicate (Schroeder, 2018; Takahashi et al., 2013; He et al., 2010).

The combustion and loss of the ionic liquids from the surface and the interlayer space of clay-ionic liquid composites was observed around 480 °C for Bent_C_4mimCl and Bent_C_8mimCl samples, while in the case of Bent_C_{12}mimCl the decomposition was observed in multiple steps in the range of 395 °C and 580 °C (Figure 3.14.). The exothermic effects between 395 °C and 580 °C in the DTG curves correspond to evaporation and decomposition of the intercalated ionic liquid species between the Bent clay mineral layers (He et al., 2006; Livi et al., 2010; Dedzo and Detellier, 2014; Litefti et al., 2019). Mass loss of Bent_C_4mimCl, Bent_C_8mimCl, and Bent_C_{12}mimCl, which is attributed to the decomposition of organic molecules, was 8.30%, 13.59%, and 18.61%; and total mass loss was 15.51%, 19.59%, and 24.88%, respectively.

3.2. Sorption studies of inorganic and organic ions onto composite materials

3.2.1. Sorption studies of arsenic (V)

Negatively charged arsenic(V) ions were chosen as a model inorganic pollutant to investigate the removal efficiency from aqueous solution with raw Mt, T, and J clays and clays modified with iron oxy-hydroxide (FeOOH). Arsenic is carcinogenic (EPA, 2001) substance and it is included in the Priority List of Hazardous Substances (ATSDR, 2014). The environmental pollution with arsenic compounds can be considered as a major environmental problem, especially in the Americas, Europe, Australia, and Africa but mostly in South and South-Eastern Asia (Fendorf et al., 2010). In these areas concentration of arsenic in the drinking water exceeds the maximum permissible levels and in distinct geological regions termed as the 'largest mass poisoning of a population in history' (Smith et al., 2000; Zhang and Itoh, 2005; Dupont et al., 2007; Nemade et al., 2009; Negrea et al., 2011). Use of sorbents for arsenic removal can be considered as a prospective solution especially with regard to the sorbents based on natural materials (Goldberg, 2002; Mohapatra et al., 2007; Ansone-Bērtiņa, 2015)

Sorption experiments were conducted as described in the Paper III – Ozola et al., (2019b) (see also the Chapter 2.3.). As(V) sorption capacity was investigated under various environmental conditions: the concentration of the sorbate, type of sorbent and pH of the solution. Physical Langmuir (Langmuir, 1918) and empirical Freundlich (Freundlich, 1906) isotherm models were used to describe the sorption mechanism between the sorbate and the sorbent. The analytical equations were as follows:

$$\text{Langmuir: } q_e = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{6}$$

$$\text{Freundlich: } q_e = \mathrm{K_F} \cdot \mathrm{C_e}^{1/n} \tag{7}$$

where $q_{\max}$ (mg/g) is the theoretical monolayer capacity of the Langmuir equation, K_L (L/mg) is the Langmuir equilibrium constant, and C_e (mg/L) is the equilibrium solution concentration (Eq. 2). K_F (L/mg) and n are Freundlich constants defining relative capacity and sorption intensity, respectively (Eq. 7).

Effect of the initial concentration of sorbate. As(V) solutions with an initial concentration ranging from 5 mg/L to 400 mg/L were selected to investigate the influence of the initial sorbate concentration on the sorption capacity onto raw Mt, T, and J clays and the clays modified with FeOOH. By increasing As(V) concentration, the sorption capacity of the clay samples increased (Figure 3.15. A, B). At lower concentrations sorbent sites are vacant, but at higher concentrations the number of occupied sites increases, thus resulting in increased sorption capacity for As(V) molecules (Srivastava and Sillanpää, 2017).

Effect of sorbent. The modification of clay materials with iron oxy-hydroxide improved the sorption capacity of the 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 the raw Mt clay (Figure 3.15. A, B). 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. The sorption capacity is 63.2%, 47.4% and 41.1% at the initial As(V) concentration of 300 mg/L for Mt-FeOOH, J-FeOOH and T-FeOOH, respectively. It might be possible that the reduction of sorption ability of the sorbent with increasing concentration of metalloid is affected by Fe/As ratio due to reduction of the number of free sorption sites available for As(V) ions (Ozola et al., 2019b).

As(V) sorption capacity of the Fe-modified clays is relatively high in comparison with other adsorbents described in the literature (Mohan and Pittman, 2007). Some of the materials mentioned are pure alumina (13.64 mg/g), activated alumina (9.20–24 mg/g), activated carbon (3.08–30.48 mg/g), bauxsol (1.081 mg/g), activated bauxsol (7.642 mg/g), gibbsite (4.60 mg/g), goethite (12.5 mg/g), kaolinite (<0.23 mg/g), granular ferric hydroxide (2.3–8.5 mg/g), Shirasu zeolite $\mathrm{SZP_1}$ (65.93 mg/g) (Mohan and Pittman, 2007).

Effect of pH. The study on the effect of pH for the sorption of As(V) on the modified Mt clay, J clay, and T clay with iron oxy-hydroxide was investigated in the pH ranging from 2 to 9 with the initial concentration of As(V) of 100 mg/L. The highest sorption of As(V) on modified clays was at the initial pH of 2 being 16.22 ± 0.91, 16.22 ± 0.91 and 14.56 ± 0.82 mg/g for Mt-FeOOH, J-FeOOH and T-FeOOH, respectively (Figure 3.16.). In case of Mt-FeOOH significant reduction in sorption efficiency is observed starting at pH 6 (14.97 ± 0.84 mg/g) down to pH 9 (7.51 ± 0.42 mg/g).

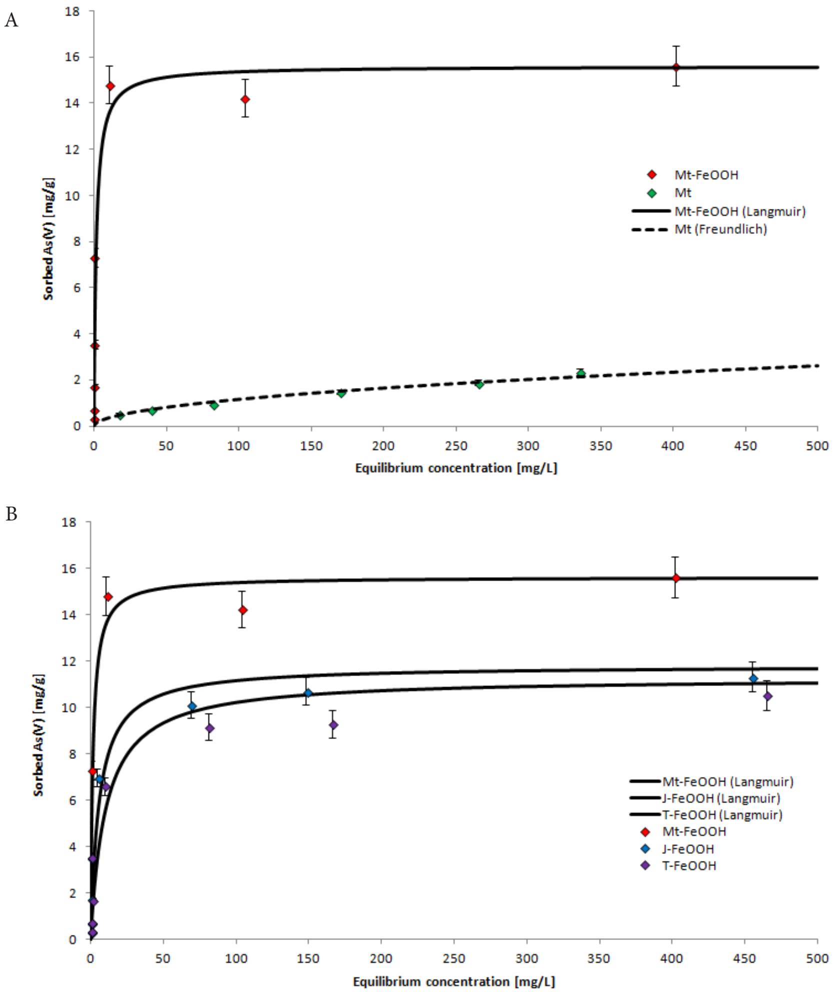


Figure 3.15. **Effect of the initial concentration on the removal of As(V) by (A) raw Mt clay and the clay modified with iron oxy-hydroxide (Mt-FeOOH); (B) Mt, T, and J clay modified with oxy-hydroxide (Mt-Hap; T-Hap; J-Hap) (experimental conditions: Ci = 5–400 mg/L, pH = 6, contact time = 24 h, T = 24 °C).**

Both J-FeOOH and T-FeOOH clays show a continuous sorption efficiency reduction without a clearly defined breaking point.

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 $FeOH_2^+$ surface groups, resulting in the formation of surface complexes (Payne and Abdel-Fattah, 2005; Dupont et al., 2007; Yin et al., 2019; Li et al., 2021).

Sorption isotherms. The obtained Langmuir correlation coefficient (R^2) values for the Mt clay, T clay, J clay, Mt clay modified with FeOOH, the T clay modified with FeOOH, the J clay modified with FeOOH were 0.9105, 0.8620, 0.9675, 0.9994, 0.9974, 0.9993, respectively.

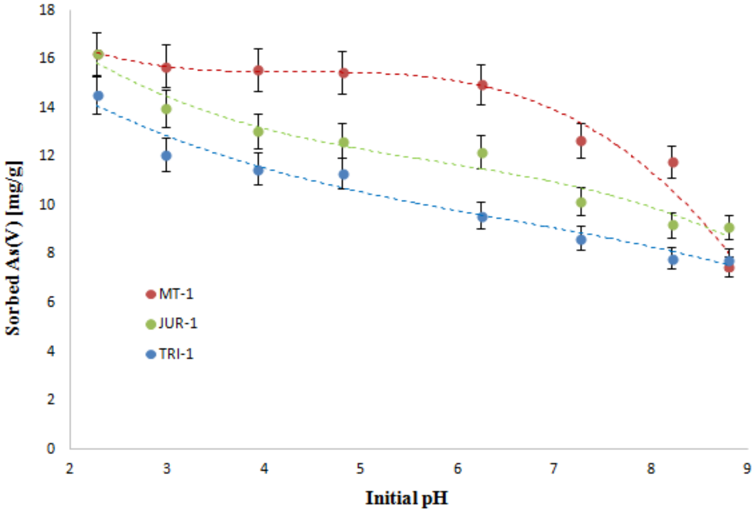


Figure 3.16. **Effect of pH on the removal of As(V) by modified montmorillonite (Mt-FeOOH), Jurassic mixed clay (J-FeOOH) and Triassic smectite dominated clay (T-FeOOH) (experimental conditions: Ci = 100 mg/L, pH = 2–9, contact time = 24 h, T = 24 °C).**

The Freundlich R^2 values for the Mt clay, T clay, J clay, Mt clay modified with FeOOH, the T clay modified with FeOOH, the J clay modified with FeOOH were 0.9838, 0.9995, 0.9867, 0.8024, 0.9794, 0.9548, respectively. Correlation coefficient values (>0.89) indicated that almost for all sorbents (except the 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 both isotherm models for the investigated systems indicates that both monolayer, i.e., only a limited number of surface sorption sites are saturated, and multilayer sorption exist under the experimental conditions studied. Thus, the sorption of As(V) onto these surfaces is complex process, involving more than one mechanism (Freundlich, 1906; Langmuir, 1918; Febrianto et al., 2009). Similar results have been described in the Chapter 3.2.3. for the sorption of PNP onto surfactant modified materials.

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 model rare earth elements (REEs) to investigate the removal efficiency from aqueous solution by the raw Mt clay and the clay modified with synthetic hydroxyapatite (Hap). As the discarded electrical and electronic equipment (EEE) is becoming one of the fastest growing waste streams globally, an ineffective management of EEE can not only cause environmental pollution and affect human health but also means loosing secondary resources such as REEs (Villares et al., 2016; Iannicelli-Zubiani et al., 2017). REEs (including La(III), Ce(III), Nd(III)) are critical raw materials for the European Union (EU); there are no primary sources in the EU territory and they are crucial for renewable energy and battery production (European Commission, 2020b). Clay sorbents, e.g., raw bentonite (Chen et al., 2012) and montmorillonite (Klika et al., 2016), organoclays (Gładysz-Płaska et al., 2014; Iannicelli-Zubiani et al., 2017), heated and acid-treated clays (Gładysz-Płaska et al., 2014) are recognized as prospective solution for the removal of REEs from aqueous solutions due to its cost effectiveness, simplicity of design, high efficiency, reusability, and wide-ranging availability (Iannicelli-Zubiani et al., 2015; Anastopoulos et al., 2016; Iannicelli-Zubiani et al., 2017). After the removal of REEs from aqueous solutions, clay sorbents can be also used to recycle and recover these valuable elements (Iannicelli-Zubiani et al., 2017).

Sorption experiments were conducted as described in the Chapter 2.3. La(III), Ce(III), Nd(III) sorption capacity was investigated by the studying the type and concentration of the sorbate. Physical Langmuir (Langmuir, 1918) and empirical Freundlich (Freundlich, 1906) isotherm models were used to describe the sorption mechanism between the Mt clay samples and the REEs.

Effect of initial concentration of sorbate. The initial concentration of La(III), Ce(III), and Nd(III) in the range of 5 mg/L to 1000 mg/L influenced the sorption of the selected model REEs on the raw and modified Mt clay with hydroxyapatite (Hap). Increasing the initial La(III), Ce(III), and Nd(III) concentration, the sorption capacity of the clay samples improved (Figure 3.17). It can be explained by the number of occupied sorbent sites where at lower concentration sorbent sites are vacant, but at higher concentrations the sorbent sites are occupied, thus resulting in an increased sorption capacity (Srivastava and Sillanpää, 2017).

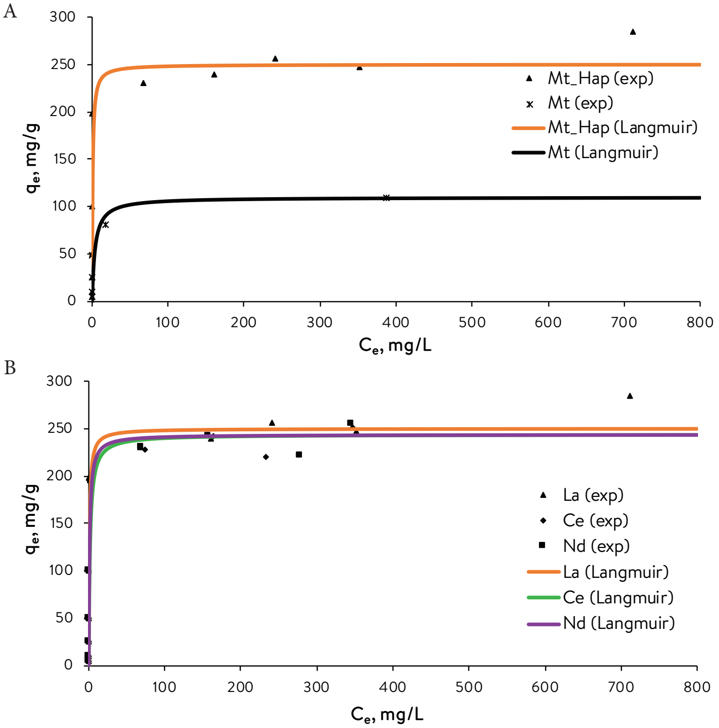


Figure 3.17. **Effect of initial concentration on (A) the removal of La(III) by raw Mt clay and the clay modified with hydroxyapatite (Mt-Hap); (B) comparison of the removal of La(III), Ce(III), Nd(III) (B) by the Mt clay modified with hydroxyapatite (experimental conditions: Ci = 5–600 mg/L, pH = 6, contact time = 24 h, T = 24 °C).**

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, 252 mg/g, and 255 mg/g for La(III), Ce(III), and Nd(III), when the initial concentration of these elements was 1000 mg/L, 600 mg/L, and 600 mg/L, respectively. Modification with Hap increases sorption sites for the positively charged elements. Based on the previous studies, uptake mechanisms of La(III), Ce(III), and Nd(III) can include cation exchange with calcium ions and a surface complexation mechanism exerted by the surface phosphate anion groups (Ramakrishnan et al., 2016; Ferri et al., 2019).

La(III), Ce(III), and Nd(III) sorption capacity on clays modified with hydroxyapatite are relatively high in comparison with other sorbents based on natural materials as described in the literature (in a critical review of sorbents for REEs removal) (Anastopoulos et al., 2016). Some of the materials mentioned in the literature are EDTA-β-cyclodextrin (50.16 mg/g), crab shell (90.9 mg/g) for Ce(III) removal, orange peel (125 mg/g), bone powder (8.70 mg/g) for La(III) removal and calcium alginate (194.73 mg/g), activated biochars from cactus fibres (90 mg/g) for Nd(III) removal (Anastopoulos et al., 2016).

Sorption isotherms. The parameters from the Langmuir and Freundlich isotherms obtained from the experimental data are given in the Table 3.2. The obtained correlation coefficient (R^2) 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 where only a limited number of surface sites are saturated (Langmuir 1918; Febrianto et al., 2009). In the Langmuir model, the values of the dimensionless constant R_L were close to 0, indicating that the sorption of REEs onto Mt- hydroxyapatite composite is strongly favourable at the conditions being studied.

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 the raw Mt, T and J clays and the clays modified with nonionic (DDAO, NMO) and cationic surfactants (BTMAC, DTAC) at various surfactant/CEC ratios. Nonionic surfactants were selected, considering lower toxicity and possibly higher impact on the sorption efficiency as from the widely studied cationic surfactants. Phenols are among the most widespread aquatic contaminants (Nayak and Singh, 2007), and only 96 h exposure to 10–100 mg/L of phenol is lethal for hydrobionts (Lee and Tiwari, 2012). Among different WWT methods, sorption is considered as one of the most effective technologies for the removal of phenols when contaminant concentration is too high for the biological treatment (Park et al., 2013; Luo et al., 2015). Sorbents based on minerals, e.g., modified montmorillonite, zeolite, and silica, are recognized as potential solutions for the removal of phenols, including PNP, from aqueous solutions (Zermane et al., 2010; Xiaohong et al., 2011; Xue et al., 2013; Huong et al., 2016).

Sorption experiments were conducted as described in the Paper II – Ozola et al. (2019a) (see also the Chapter 2.3.). PNP sorption capacity was investigated under various environmental conditions: the concentration of the sorbate, type of sorbent, contact time and pH of the solution.

Table 3.2.

Parameters of Langmuir and Freundlich isotherm models for the sorption of model sorbates on the raw clay samples and the clay samples modified with hydroxyapatite (Hap), various surfactants (BTMAC, DTAC, DDAO, NMO) and ionic liquids (C_4mimCl; C_8mimCl; C_{12}mimCl)

Sample	Langmuir				Freundlich		
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	n	K_F (L/mg)	R^2
	Sorption of La(III)						
Mt	109.89	0.2622	0.008	0.9993	9.15	30.2652	0.1639
Mt_Hap	250.00	1.2903	0.001	0.9992	2.72	34.3156	0.4607
	Sorption of Nd(III)						
Mt_Hap	243.90	0.9318	0.002	0.9938	2.45	29.5919	0.5513
	Sorption of Ce(III)						
Mt_Hap	243.90	0.6119	0.003	0.9948	2.37	28.3719	0.5746
	Sorption of p-nitrophenol						
Mt_BTMAC_2	0.34	0.0340	0.5408	0.2424	1.82	0.0248	0.6809
Mt_DTAC_2	0.63	0.0367	0.5214	0.8964	1.32	0.0287	0.9657
Mt_DDAO_2	0.50	0.1306	0.2345	0.9895	2.03	0.0864	0.9865
Mt_NMO_2	0.04	0.1096	0.2673	0.9818	1.95	0.0064	0.9977
T_DDAO_2	0.19	0.1500	0.2105	0.9921	2.45	0.0423	0.9815
J_DDAO_2	0.02	0.0596	0.4017	0.891	1.53	0.0015	0.9548
	Sorption of Congo red						
Bent	101.01	0.0077	0.8397	0.0432	0.70	0.2898	0.9440
Bent_C_4mimCl	126.58	0.0888	0.0533	0.9319	1.34	8.9165	0.8589
Bent_C_8mimCl	129.87	0.4667	0.0106	0.9857	1.05	5.9895	0.6808
Bent_C_{12}mimCl	158.73	0.3841	0.0128	0.9523	0.92	6.1159	0.6798

Physical Langmuir (Langmuir, 1918) and empirical Freundlich (Freundlich, 1906) isotherm models were used to describe the sorption mechanism between the sorbate and the sorbent. Additionally, Langmuir isotherm dimensionless constant, called the equilibrium parameter (R_L), was calculated with the following equation:

$$R_L = \frac{1}{1 + K_L \cdot C_O} \tag{8}$$

where C_0 is the highest initial sorbate concentration (mg/L) and the value of R_L indicates whether sorption will be favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), irreversible ($R_L = 0$), or linear ($R_L = 1$) (Weber & Chakravorti 1974).

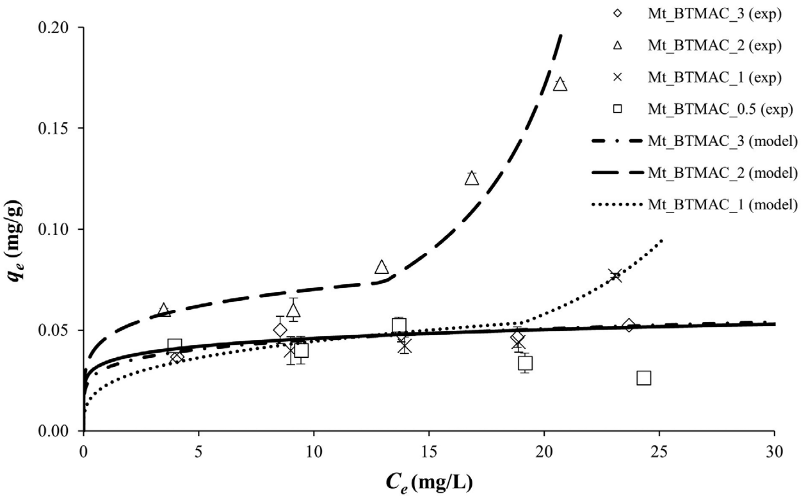


Figure 3.18. **Comparison of PNP sorption for the Mt clay modified with BTMAC at various surfactant/CEC ratios (experimental conditions: Ci = 5–25 mg/L, pH = 7, contact time = 24 h, T = 24 °C).**

Effect of surfactant loading. The obtained results revealed that the sorption capacity of raw Mt clay for PNP was negligible (Figure 3.20.), but after modification of Mt clay with BTMAC the sorption capacity increased at the surfactant/CEC ratio of 2 (Figure 3.18.).

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. Modification of natural clays with other surfactants was made, therefore, at a surfactant/CEC ratio of 2; these results indicated that the sorbed amount of PNP depends strongly on the amount of loaded surfactant and its distribution. Other studies (Zhou et al., 2008; Park et al., 2013) showed that, when surfactant loading is smaller than the CEC of the clay, surfactants replace the exchangeable cations in the interlayer space on montmorillonite. 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. While loaded surfactant molecules attract the dissociated PNP molecules through hydrophobic interaction, dissociated PNP anions bind to surfactant cations on the external surface of the clay through electrostatic interactions.

Effect of initial concentration of sorbate. The initial concentration of PNP in the range of 5 mg/L to 25 mg/L influenced the sorption of PNP on the modified clay materials at a surfactant/CEC ratio of 2 (Figure 3.19., 3.20.). The initial increase in the PNP concentration resulted in an extended PNP sorption by modified clay materials. In the case of Mt_NMO_2, however, this relationship was not observed, because sorption was negligible (~0.02 mg/g) (Figure 3.20.). Increased sorption capacity at higher concentrations of PNP can be explained by the rising number of occupied sites of the sorbent at higher concentrations of contaminant (Srivastava and Sillanpää, 2017).

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 (Figure 3.20.). X-ray diffraction results (see the Chapter 3.1.4.) indicated that the increased interlayer space can be linked to the efficacy of PNP sorption (Park et al., 2013).

The sorption capacity of Mt clay modified with dimethyldodecylamine N-oxide (DDAO) was >18 times greater than that of the raw Mt clay and 3 times greater than fot Mt_Na (Figure 3.20.). Due to the large size of hydrated Na^+ ions (Zhu et al., 2014), the interlayer space was significantly increased enabling ion penetration, thus improving the sorption of organic molecules (Zhou et al., 2008).

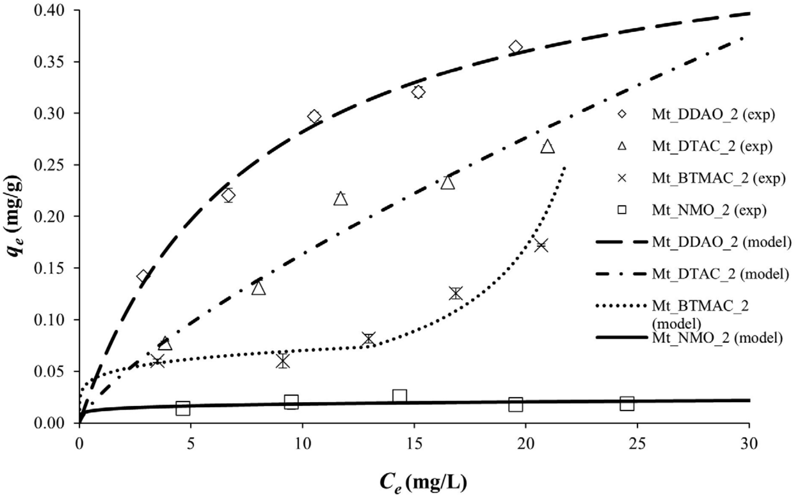


Figure 3.19. **Effect of initial concentration on the removal of PNP by modified Mt clay with various surfactants at surfactant/CEC ratio 2 (experimental conditions: Ci = 5–25 mg/L, pH = 7, contact time = 24 h, T = 24 °C).**

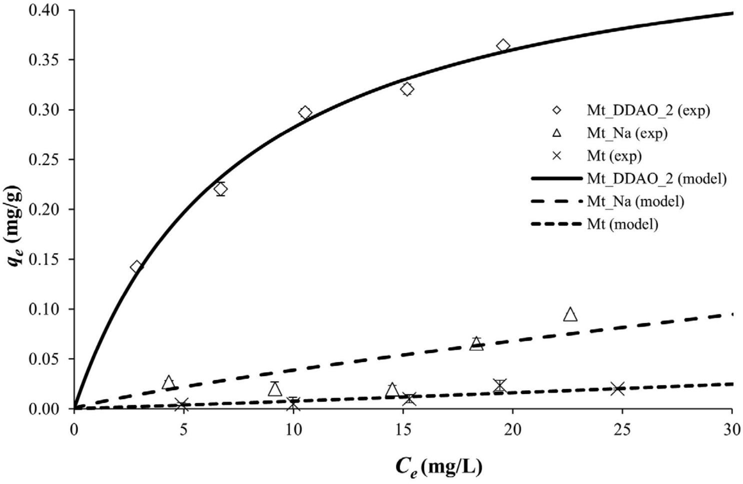


Figure 3.20. **Effect of initial concentration on the removal of PNP by raw Mt clay and the clay modified with dimethyldodecylamine N-oxide (DDAO) at surfactant/CEC ratio 2 (experimental conditions: Ci = 5–25 mg/L, pH = 7, contact time = 24, T = 24 °C).**

A larger BET specific surface area also was determined for samples treated with Na^+ ions (see the Chapter 3.1.4.).

For natural, unmodified T and J clays sorption capacity was negligible when PNP concentration in the solution was 5 to 25 mg/L. The greatest PNP sorption capacity was observed on the T clay modified with dimethyldodecylamine N-oxide (T_DDAO_2), i.e. 0.15 mg/g when the PNP concentration was 25 mg/L. The J clay modified with dimethyldodecylamine N-oxide (J_DDAO_2) sorbed almost no PNP (on average 0.0072 mg/g); therefore, this material was excluded from sorption experiments, where the effect of pH and contact time were estimated (Ozola et al., 2019a).

Effect of contact time. The PNP sorption rate was high at the beginning of the experiment (Figure 3.21.) because sorption sites were initially abundant and PNP molecules were easily sorbed on those sites. 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, afterwards 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 effect of pH on PNP removal by modified Mt clay and T clay with dimethyldodecylamine N-oxide (DDAO) at surfactant/CEC ratio 2 was investigated in the pH range from 2 to 12 with the initial concentration of PNP of 25 mg/L. The highest removal efficiency was obtained in an acidic environment, from pH 2 to 4, for T_DDAO_2 and, from pH 2 to 6, for Mt_DDAO_2 (Figure 3.22.). When the pH exceeded 6, the removal efficiency significantly decreased. Similar results were reported in other works (Zhou et al., 2008; Park et al., 2013; Luo et al., 2015; Zhang et al., 2015) and can be explained by the clay surface charge change and protonation of PNP.

PNP is poorly soluble in water in acidic conditions with a dissociation constant (pKa) of 7.15; when the pH is below pKa (pH < pKa), PNP may be a neutral molecule, but when pH is greater than the pKa (pH > pKa), PNP can exist as an anion. Based on the PNP dissociation conditions, sorption onto modified clay materials is more efficient when PNP is a neutral molecule. In an acidic environment, a surfactant intercalated in the clay interlayer space provides effective contaminants removal due to Van der Waals forces and hydrophobic effects. When the solution is alkaline, PNP sorption decreases due to electrostatic repulsion forces between the negatively charged clay particles and PNP anions.

Sorption isotherms. The parameters from the Langmuir and Freundlich isotherms obtained from the experimental data about the sorption of PNP onto surfactant modified clay samples are presented in the Table 3.2. The correlation coefficient (R^2) 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, meaning that sorption cannot be adequately described by these isotherms. The suitability of both isotherm models for the investigated systems indicates that both monolayer and multilayer sorption exists under the studied experimental conditions. Thus, the sorption of PNP onto these surfaces is complex, involving more than one mechanism (Febrianto et al., 2009). Similar results have been described in the Chapter 3.2.1. for the sorption of As(V) onto FeOOH modified materials and found by Ko et al. (2007) for the sorption of PNP by organo-modified montmorillonite clay.

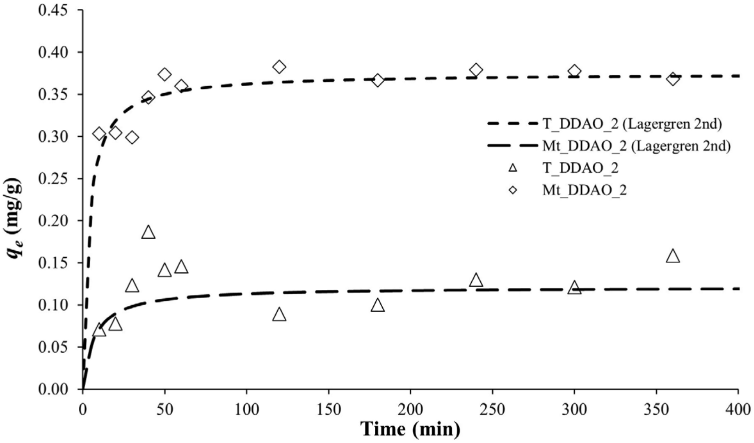


Figure 3.21. **Effect of contact time on the removal of PNP onto modified Mt clay and T clay with dimethyldodecylamine N-oxide (DDAO) at surfactant/CEC ratio 2.0 (Mt_DDAO_2 and T_DDAO_2) (experimental conditions: Ci = 25 mg/L, pH = 7, contact time = 10–360 min, T = 24 °C).**

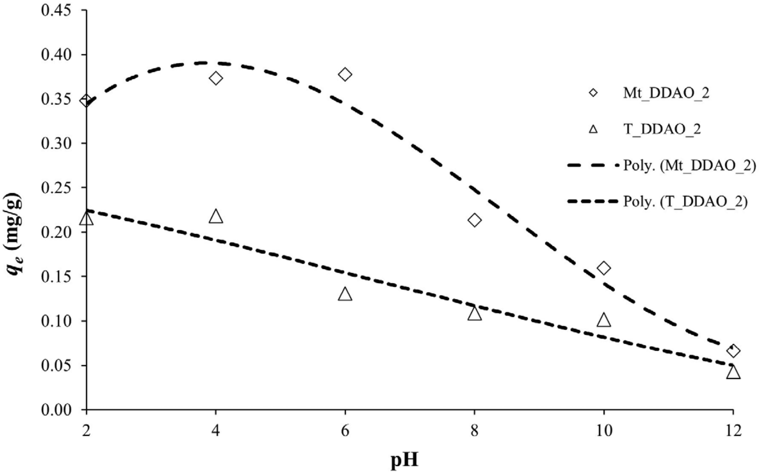


Figure 3.22. **Effect of pH on the removal of PNP by modified Mt clay and T clay with dimethyldodecylamine N-oxide (DDAO) at surfactan/CEC ratio 2 (experimental conditions: Ci = 25 mg/L, pH = 2–12, contact time = 24h, T = 24 °C).**

The Freundlich parameters n and K_F reflect the sorption intensity of PNP and the binding affinity constant providing information about the sorption mechanism. The value of n observed for sorption of PNP solution is >1 (n > 1) indicating that the sorption of PNP onto the clay samples was effective over the entire range of concentrations, and sorption is determined by physical processes (Alkaram et al., 2009; Park et al., 2013). The largest value for the binding affinity constant K_F was obtained in the sorption of PNP on the Mt clay modified with dimethyldodecylamine N-oxide (Mt_DDAO_2) sample and it corresponded to the experimental data.

In the Langmuir model, the values of the equilibrium constant K_L increased in the following order: Mt_BTMAC_2 < Mt_DTAC_2 < Mt_NMO_2 < Mt_DDAO_2 indicating that the affinity of binding sites for PNP increased when clay samples were treated with nonionic surfactants (DDAO and NMO). The dimensionless constant R_L value ranged between 0 and 1, suggesting that sorption of PNP by modified clay samples is favourable (Luo et al., 2015).

3.2.4. Sorption studies of Congo red

Anionic azo dye Congo red (CR) was chosen as a model organic pollutant to investigate the removal efficiency from aqueous solution by the raw Bt clay and the clay modified with imidazolium-based ionic liquids with different lengths of alkyl chains (C_4mimCl, C_8mimCl, C_{12}mimCl). Pollution with dyes is considered one of the major environmental problems as various industries release around 150 tons of dyes each day into water bodies (Tamm et al., 2018; Ismail et al., 2019). Even at low concentrations, dyes can cause threats to human beings and aquatic life due to their high toxicity, low biodegradability and accumulative behaviour (Du et al., 2014; Gupta et al., 2020). Congo red is a mutagen, it affects the reproductive systems and can cause different health issues, e.g., difficulties in breathing, nausea, vomiting and diarrhea (Rani et al., 2017; Gupta et al., 2020). Among various WWT methods, the sorption process is considered as one of the best available technologies for the removal of dyes due to its high efficiency, simplicity of design, ease of operation, wide adaptability and cost-effectiveness (Hu et al., 2006; Zhuang et al., 2009; Gupta et al., 2020). The raw clay minerals and the clays modified with organic compounds can be considered as prospective sorbents for the Congo red removal (Bentahar et al., 2017; Shojaeipoor et al., 2019; Yang et al., 2021).

Sorption experiments were conducted as described in the Paper I – Ozola-Davidane et al. (2021) (see also the Chapter 2.3.). CR sorption capacity was investigated under various environmental conditions: the concentration of the sorbate, type of sorbent, contact time and pH of the solution. Physical Langmuir (Langmuir, 1918) and empirical Freundlich (Freundlich, 1906) isotherm models were used to describe the sorption mechanism between the sorbate and the sorbent. Additionally, Langmuir isotherm dimensionless constant was determined (Weber and Chakravorti, 1974). Lagergren's pseudo-first-order (Lagergren, 1898) and pseudo-second-order (Ho and McKay, 1999) kinetic models were used to analyse the relationship of sorption capacity and contact time. The analytical equations were as follows:

Pseudo-first-order model: $$\log(q_e - q_t) = \log q_e - \frac{K_1}{2{,}303} \qquad (9)$$

Pseudo-second-order model: $$\frac{t}{q_t} = \frac{1}{K_2 q^2_{20}} + \frac{t}{q_{20}} \qquad (10)$$

where q_t is the amount of sorbate sorbed on sorbent (mg/g) at time t, K_1 (1/min) and K_2 (g/mg min) are the rate constants of pseudo-first kinetic model and pseudo-second kinetic model, respectively.

Effect of initial concentration of sorbate. CR solutions of an initial concentration ranging from 0.5 mg/L to 100 mg/L were selected to investigate the influence of the initial dye concentration on the sorption capacity onto raw Bent clay and the clay modified with imidazolium-based ionic liquids with different lengths of alkyl chains.

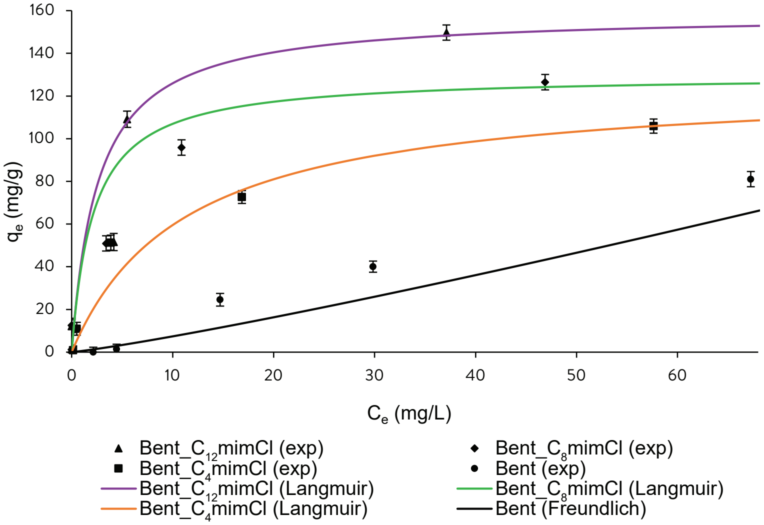


Figure 3.23. **Effect of initial concentration on the removal of Congo red by the raw Bent clay and the clay modified with imidazolium-based ionic liquids with different lengths of alkyl chains (experimental conditions: Ci = 0.5–50 mg/L, pH = 5.5, contact time = 24 h, T = 24 °C).**

Increasing CR concentration, the sorption capacity of clay samples improved (Figure 3.23). As described previously, at lower concentration sorbent sites are vacant but at higher the number of occupied sites increases, thus resulting in increased sorption capacity regards model contaminant (Srivastava and Sillanpää, 2017).

Effect of sorbent. The sorption capacity significantly increased after the Bent clay modification and the highest sorption capacity was 150 mg/g for the Bent clay modified with 1-dodecyl-3-methylimidazolium chloride (Bent_C$_{12}$mimCl) when CR concentration was 100 mg/L. According to the sorption data and XRD results (see the 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 3.23.).

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 the raw Bent clay and the clay modified with 1-dodecyl-3-methylimidazolium chloride (Bent_C$_{12}$mimCl) was 60 min and 240 min, respectively (Figure 3.24.). The high sorption rate of CR at the beginning of experiment is due to the presence of an extensive amount of easily accessible sorbent sites, and dye molecules can rapidly interact with the available active sites. The sorption rate slows down as the number of available sorbent sites for the remaining dye molecules decreases (Lian et al., 2009; Zhang et al., 2015; Srivastava and Sillanpää, 2017).

Sorption kinetics. The parameters from Lagergren's pseudo-first-order and pseudo-second-order kinetic models obtained from the experimental data are given in the Table 3.3. The obtained correlation coefficient (R^2) values indicated that for the raw Bent clay and the clay modified with ionic liquid 1-dodecyl-3-methylimidazolium chloride (Bent_C$_{12}$mimCl) the pseudo-second kinetic model is the most suitable equation to describe the sorption mechanisms between the sorbent and sorbate.

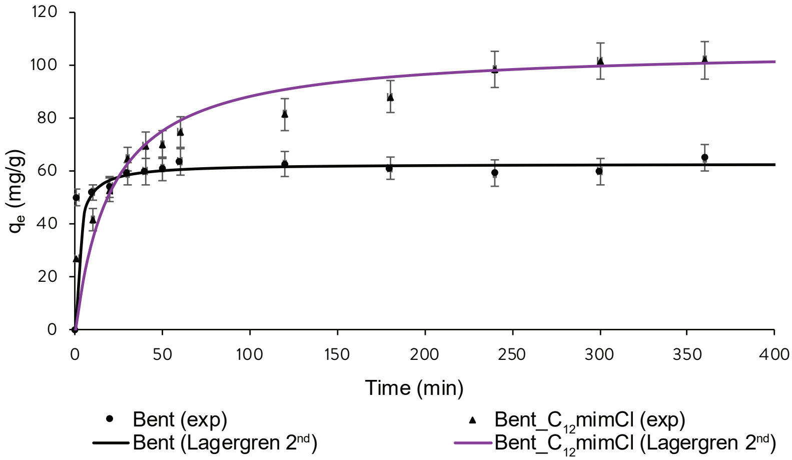


Figure 3.24. **Sorption kinetics of the removal of Congo red by unmodified bentonite (Bent) and modified bentonite with 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl) (experimental conditions: C_i = 50 mg/L, pH = 5.5, contact time = 1–360 min, T = 24 °C).**

Table 3.3.

Parameters of the kinetic models for the sorption of Congo red on the unmodified bentonite and the obtained bentonite-ionic liquid composite

Sample	Pseudo-first order of Lagergren			Pseudo-second order of Lagergren		
	q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg min)	R^2
Bent	6.60	2.10×10^{-3}	0.0941	62.50	7.44×10^{-3}	0.9968
Bent_C_{12}mimCl	75.41	1.50×10^{-2}	0.8858	106.38	4.53×10^{-4}	0.9940

Thus, the sorption kinetics process is governed by the chemisorption mechanism, which involves valence forces between CR anion and Bent_C_{12}mimCl sorbent (Shaban et al., 2018; Alshammari et al., 2020).

Effect of pH. The pH of the dye initial solution influences stability and surface charge of the sorbent and the chemistry of the sorption process (Naik et al., 2019). CR is an example of an azo dye, and the initial pH influences the molecular form of CR in the aqueous solution (Lian et al., 2009). At pH 3 CR appears blue-violet while at pH 5 it changes colour to red, and due to this fact is often used as a pH indicator. CR exists as an anionic species at an alkaline pH but as a cationic species at an acidic pH (Adebayo et al., 2020).

The study on the effect of pH for the sorption of CR on the modified Bent clay with 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl) was investigated in the pH ranging from 2 to 10 with the initial concentration of CR of 50 mg/L. 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% (Figure 3.25.).

A decrease in the removal of CR with the Bent clay with increasing pH is related to the dissociation of sulfonate groups of CR producing anionic dye ions. At lower pH, the negative surface of the Bent clay is neutralized by H^+ thereby promoting the spreading of CR. This is further reinforced by the electrostatic attraction between the Bent clay and the anionic dye ions promoting sorption at low pH. As pH increases, the number of negatively charged sites on the Bent clay increase enhancing the electrostatic repulsion thus hindering sorption (Zhang et al., 2019; Adebayo et al., 2020; Yang et al., 2021). Similar results have been reported for the CR sorption on different sorbents (Lian et al., 2009; Lawal et al., 2017; Bentahar et al., 2017; Litefti et al., 2019; Shojaeipoor et al., 2019; Yang et al., 2021).

Nevertheless, the sorption efficiency of CR is significantly high even at alkaline pH suggesting that besides electrostatic attraction there is another sorption mechanism. Since the Bent_C_{12}mimCl sorbent is hydrophobic due to the modification with 1-dodecyl-3-methylimidazolium chloride, the hydrophobic interaction is likely to be the main sorption mechanism that interacts through π-π reactions between the ionic liquid on the sorbent and the aromatic rings in the CR (Lawal et al., 2017).

Sorption isotherms. The parameters from the Langmuir and Freundlich isotherms obtained from the experimental data are given in the Table 3.2. The obtained correlation coefficient (R^2) values indicated that for the raw Bent clay Freundlich isotherm model is the most suitable equation to describe the sorption behaviour. While in the case of the Bent-ionic liquid composites Langmuir isotherm model is the most relevant. This suggests that for the raw Bent clay sorption of CR has a multilayer character, while for the modified Bent samples sorption is monolayer (i.e., only a limited number of surface sites are saturated) (Freundlich, 1906; Langmuir, 1918; Alkaram et al., 2009).

In the Langmuir model, the values of the equilibrium constant K_L were between 0 and 1, indicating that the sorption of CR onto Bent-ionic liquid composites is favourable under the conditions being studied. By using a modifier with longer alkyl chain, the q_{max} increased from 126.58 mg/g to 158.73 mg/g.

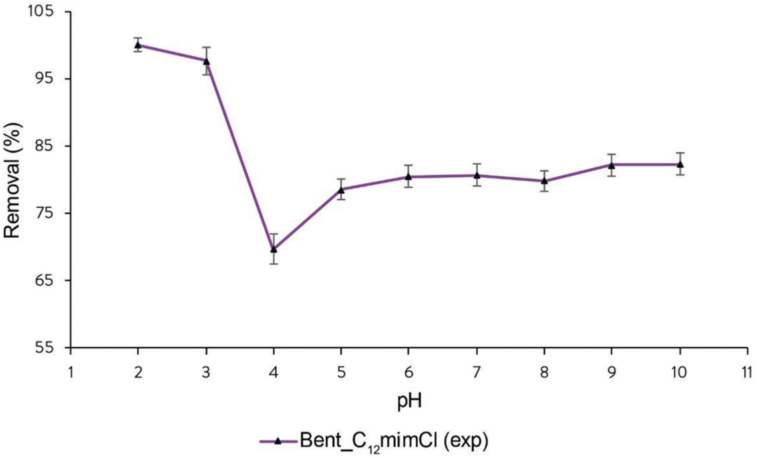


Figure 3.25. **Effect of pH on the removal of Congo red by the modified Bent clay with 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl) (experimental conditions: Ci = 50 mg/L, pH = 2–10, contact time = 24 h, T = 24 °C).**

Additionally, the dimensionless constant R_L value decreased (Table 3.2.), indicating that sorption is more favourable when ionic liquid is with a longer alkyl chain.

In the Freundlich model, the constant K_F indicates the sorption capacity of the sorbent, while the parameter ‘n’ reflects the sorption intensity of CR. In the case of the raw Bent clay, the value of n is lower than 1, indicating that the sorption system is more favourable at higher concentrations of CR and sorption is determined by the chemical process (Jiang et al., 2002; Park et al., 2013).

The raw Bent clay follows Freundlich whereas the modified Bent clay sorbents follow Langmuir behaviour. The reason for this is not obvious, but it could be linked to a difference in the sorption mechanism between the raw Bent clay and the modified material. A similar transition from Freundlich to Langmuir was found also for other modified aluminosilicate sorbents (Krauklis, 2017). According to the results, sorption is more favourable when ionic liquid is introduced and is increasing with regard to the length of the alkyl chain of the introduced ionic liquid in bentonite.

3.2.5. Sorption studies of other sorbates

Working on this thesis, additional sorbates were used for a preliminary search of new application possibilities. Montmorillonite modified with iron oxy-hydroxide and hydroxyapatite was used for silver(I) and aluminum(III) uptake experiments from nitric acid-treated solar cells waste (SoliTek, Lithuania) solution. Solar photovoltaic (PV) energy technologies are one of the most important resources of renewable energy and it is an eco-friendly and feasible approach for energy generation. Nevertheless, inappropriate disposal practices of solar cell end-of-life can cause a significant damage to the environment, if they are not recovered or disposed of properly (Chowdhury et al., 2020). The European Union has included PV waste into the Waste of Electrical and Electronic Equipment directive (2012/19/EU) to limit the negative influence of the persistent growth in PV waste volume and to implement its recycling (Chowdhury et al., 2020). The solar cell waste contains valuable elements, like silver (Ag), silicon (Si), aluminum (Al), that can be recovered, for example by chemical leaching, and used for new applications related to catalysts, metal alloys, drug delivery, lithium-ion batteries (Yousef et al., 2019; Chen et al., 2020).

The experiments were carried out at the Hamburg University of Technology, Institute of Environmental Technologies and Energy economics (Germany) and one of the focuses was to use the clay sorbents for the uptake of silver and aluminum from solar cells’ waste leachate with future potential to recover elements by release mechanism from the clay material solid phase. The obtained results indicated that the raw and modified clay composites can sorb aluminum and silver ions from the filtrate of solar cell wastes (Figure 3.26.).

The most efficient sorbent was montmorillonite modified with oxy-hydroxide, where more than 99% of silver ions were removed. The sorption mechanism can include cation exchange with silver ions and a surface adsorption mechanism. Uptake of aluminum by clay composites was negligible, thus further experiments are necessary. The future studies could focus on the alkalization of filtrate from solar cells before the sorption experiments with clays. Based on other studies (Chen et al., 2012; Iannicelli-Zubiani et al., 2017), the alkalization of filtrate from solar cells before the sorption experiments with clays could increase sorption capacity.

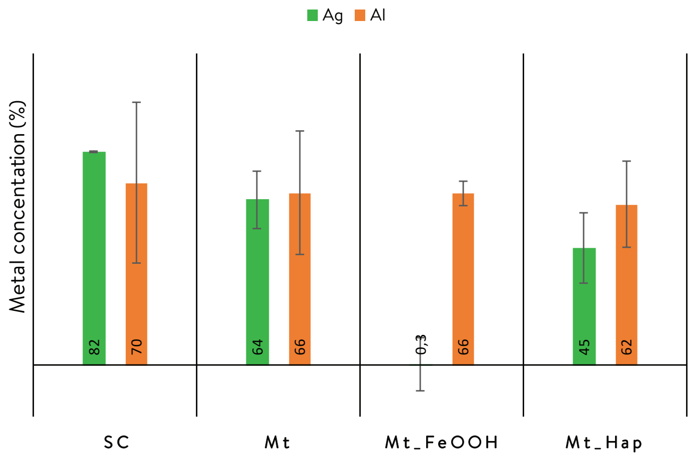


Figure 3.26. **Percentages of silver (Ag) and aluminum (Al) before and after uptake by clay samples (SC – leachate of solar cells; Mt – raw montmorillonite; Mt_FeOOH – montmorillonite modified with iron oxy-hydroxide; Mt_Hap – montmorillonite modified with hydroxy-apatite).**

Anthocyanin sorption onto clays was also thoroughly tested under various environmental conditions: the concentration and type of the sorbate, type of sorbent, contact time, pH of the mixture, etc. As it is planned to commercialize the clay-anthocyanin composites and the patent is pending, detailed information is not provided in this thesis.

3.3. Prospective applications of newly developed materials and future outlook

Sorbents are a group of materials with high application potential in environmental management (for solving such problems as remediation of contaminated areas, treatment of wastewater, air, and others), 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, gel filtration media, polyester, polypropylene and polyurethane pads and others) and despite the 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 to develop environmentally friendly technologies and to increase the usage of safe and sustainable materials which do not harm people and the environment (European Commission, 2020a). Results of this study demonstrate that clays can be successfully used to replace synthetic sorbents. Clays are natural, versatile, abundant and low-cost material, but elaborated modified clay-based materials support possibilities to design sorbents with the necessary properties to target some specific problems.

In this study purposeful modification of the clay minerals was conducted to change their physical and chemical properties and to design innovative materials for the environmentally friendly technologies. Detailed characterization of developed clay composites demonstrated alteration in interlayer space, specific surface area, pore volume, particle morphology, charge properties and new sorption centres (see the Chapters 3.1. and 3.2.). Thus, modified clay materials obtained 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 3.27.).

Materials elaborated in this study can find diverse application possibilities. Based on the discussion above and the results obtained in this study (see the Chapter 3.2.), 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 emerging pollutants removal; 2) pre-treatment installations of industrial wastewaters; 3) constructed wetland treatment systems; 4) in situ filter system to remove pollutants from water streams. While clay-anthocyanin composites are more appropriate for innovative application in the food industry as freshness indicators that detect perishable food quality.

Separation of contaminants from the liquid phase by a solid material (sorbent) is one of the most common treatment methods used in the conventional clean-up technologies. In wastewater treatment process several types of sorption systems can be used for both industrial scale and lab-scale treatment, e.g., batch reactor, fixed-bed reactor, pulsed beds, moving mat filters and fluidized beds. However, the most frequently used technical solutions applied in solid-liquid sorption processes are **fixed bed reactors or columns and batch reactors**. Fixed bed reactors are continuous flow systems where sorbent is continuously in contact with wastewater, while in the batch reactors the amount of sorbent is continuously changing due to the sorbate being sorbed (Crini et al., 2018).

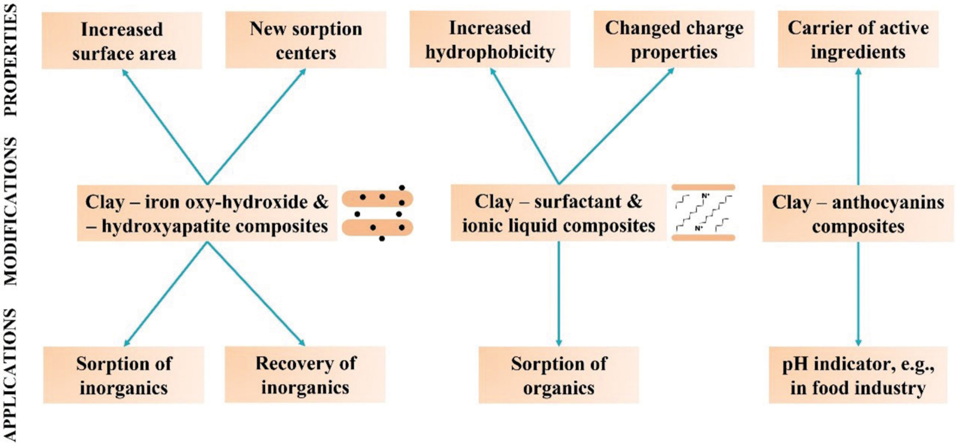


Figure 3.27. **Scheme of modified clay composites' connections with their properties and environmental applications prospects in this study.**

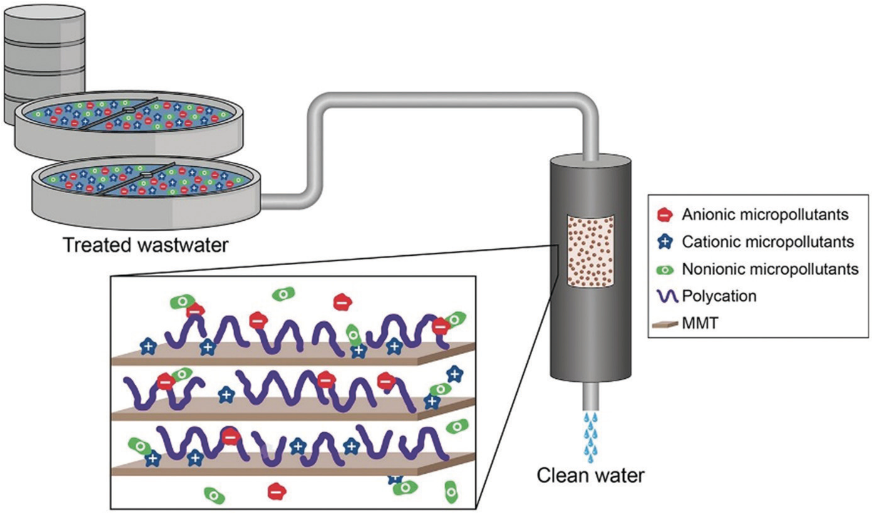


Figure 3.28. **Visualization of filtration system consisting of a column filled with montmorillonite (MMT)-polymer nanocomposite (Zusman et al., 2021).**

Fixed bed reactors can be also installed as the final treatment step at a municipal or industrial wastewater treatment plant with the purpose to recycle treated water. **Reuse of treated wastewater** (TWW) for agricultural irrigation, industrial processes (i.g. cooling, processes, cleaning), groundwater recharge, landscaping and drinking water, has increased over the past decades due to technological improvements, reduced treatment costs and actions toward circular economy (Gadipelly et al., 2014; Salgot and Folch, 2018). However, the main problem is that the conventional treatment plants are insufficiently effective in respect to the need to remove emerging pollutants. including pharmaceuticals, antibiotics and hormones, nanomaterials, microplastics and others, resulting in their occurrence not only in treated wastewater but also in ground water and drinking water (Kosek et al., 2020; Zusman et al., 2021). Clay composites have a high potential to be used as sorbents for the removal of emerging pollutants and can be more efficient than the presently used sorbents, for example, granular activated carbon (GAC). In a recent study, clay polymer nanocomposites have been applied to filtration columns for the removal of chemically diverse organic micropollutants, metoprolol (cationic), diclofenac (negative), and lamotrigine (neutral) from TWW (Figure 3.28.). The results showed that the filtration of the micropollutants and effluent organic matter by the clay polymer nanocomposites column was more cost-effective (total removal /sorbent price) in comparison to the activated carbon column (Zusman et al., 2021).

Similar filtration system has been tested on the pilot-scale where raw clays (ElBastamy et al., 2021) and polymer-, surfactant-clay composites (Lelario et al., 2017) have been used as sorbents in columns to remove organic and inorganic pollutants from wastewater for its reuse in irrigation.

Sorbents can be also used for the pre-treatment processes to remove harmful pollutants from industrial wastewater before being discharged into a municipal sewer system. Heiderscheidt et al. (2020) has proposed an innovative purification system for mineral and biomass-based **sorbent system in the pre-treatment installation of industrial wastewaters**. In the study, a continuous-flow continuous stirred tank reactor (CSTR), followed by a sedimentation unit for sorbent/water separation was designed (Figure 3.29.). The designed system consisted of three separate units: 1) dosing tank; 2) stirred tank reactor; 3) sedimentation tank (Figure 3.29.). 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 later 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 innovative 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.

Sorbents are used outside wastewater treatment plants in engineered ecosystems – **constructed wetland (CW) treatment systems.** Constructed wetlands are specifically designed basins to remove pollutants from wastewaters by optimizing the biological, physical, and chemical processes that occur in natural wetland systems, e.g., bogs, swamps, and marshes (EPA, 1993; Mareddy, 2017). Commonly they are used in rural sections of the country mainly for the treatment of domestic and municipal wastewaters (Xu et al., 2018; Uzun et al., 2021). Based on the wastewater flow path there are three main types of constructed wetlands: free water surface CW, horizontal flow CW and vertical flow CW (Figure 3.30.) (Mlih et al., 2020).

In constructed wetland basins, substrate materials are used to remove pollutants through filtration and sorption onto material surfaces. Commonly sand and gravel are used as substrate materials that have a well rooting media but inefficient treatment performance (Uzun et al., 2021). Thus, clay composites as substrates with high sorption capacity can provide a significant contribution to the design of constructed wetland systems and improve the removal performance of pollutants, especially phosphorus and nitrogen. There have been some studies already, where phyllosilicate materials, such as zeolites and lightweight expanded clay aggregate, are used in laboratory and pilot-scale constructed wetland systems to eliminate nutrient concentration in effluents (Mateus and Pinho, 2010; Mlih et al., 2020; Uzun et al., 2021).

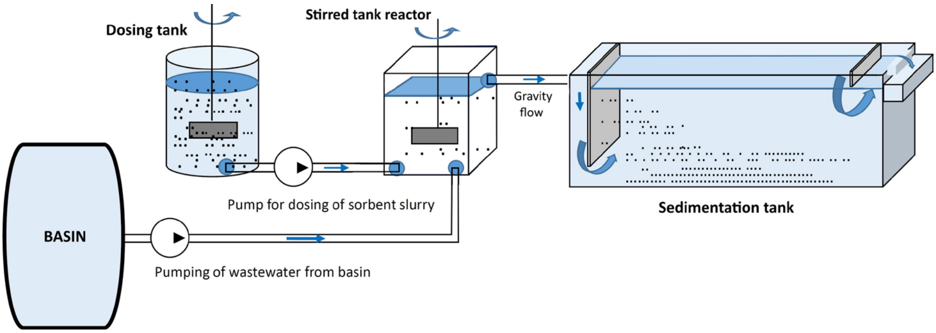


Figure 3.29. **Visualization of the continuous-flow continuous stirred tank reactor system and sedimentation unit for mineral based sorbents application in wastewater treatment systems** (Heiderscheidt et al., 2020).

Mineral-based sorbents can also be used for **in situ filter systems to remove inorganic pollutants from mine drainage waters**. A team of researchers from the University of Oulu (Finland) proposed the pilot-scale filter system where the main principle is that treated water via gravity flows through a box filled with the sorbent and is afterwards discharged downstream of the ditch (Figure 3.31.).

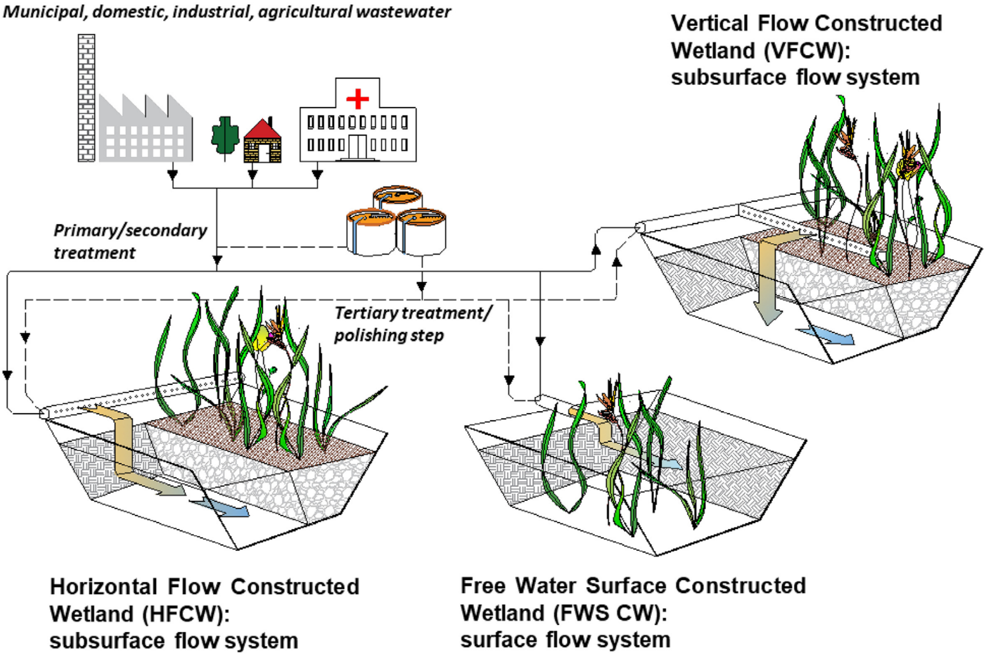


Figure 3.30. **Visualization of types of constructed wetland treatment systems and their possible integration places in wastewater streams** (Mlih et al., 2020).

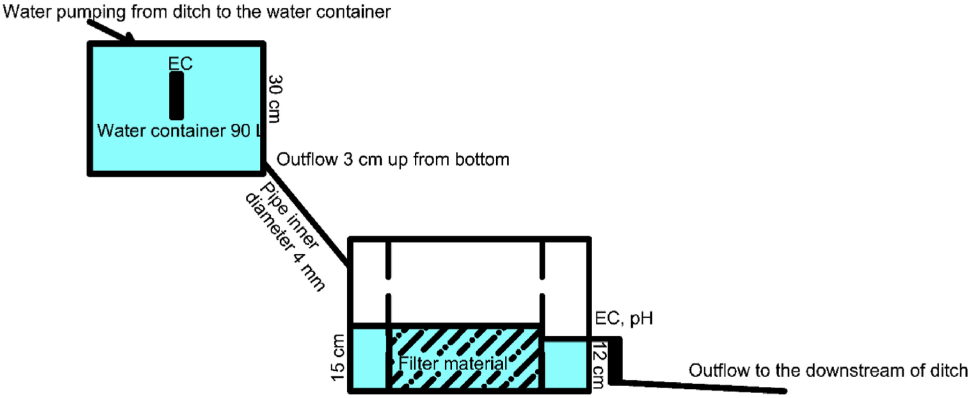
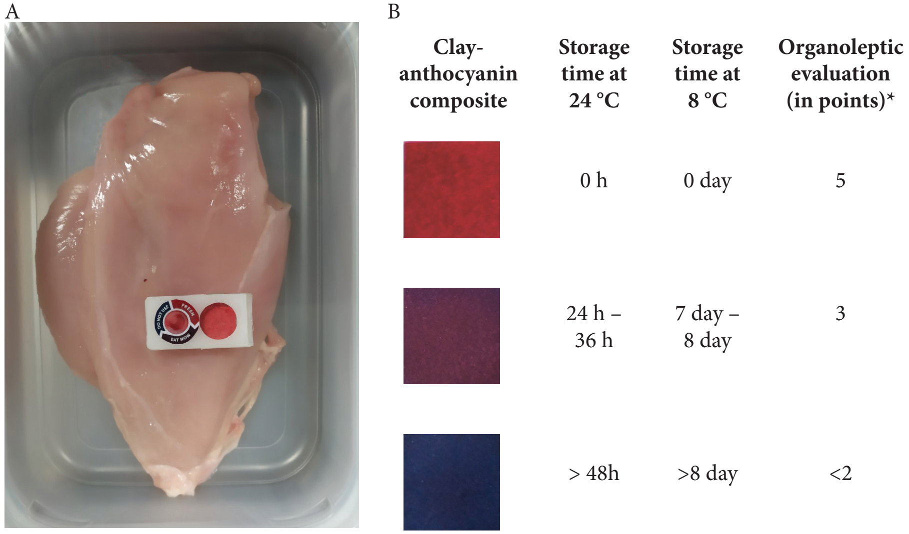


Figure 3.31. **Schematic visualization of pilot-scale in situ filter system with water flow routes** (Postila et al., 2019).

The study showed that mineral-based sorbents can be used to significantly remove inorganic pollutants (lead, copper, cadmium, vanadium etc.) not only from mine drainage waters but prospectively also from the polishing phase of treatment for wastewaters from active mine sites and urban stormwater (Postila et al., 2019; Zhang et al., 2021).

In this study application of **clay-anthocyanins composites** in the food industry was investigated. Anthocyanins (in Greek *anthos* – flower and *kyanos* – blue) are water-soluble natural pigments, that can be extracted from different fruits and vegetables. One of the important characteristics are colour change of anthocyanins depending on the pH level of the environment due to structural changes in their structure. When the pH is less than 3, the flavylium cation is the predominant species and colour of the anthocyanins is red. At a slightly acidic to neutral pH, flavylium cation undergoes a rapid deprotonation reaction to form the purple quinonoidal base as the kinetic product. At the pH of more than 7 neutral quinonoidal base transforms into an anionic quinonoidal base that has a blue colour (Wrolstad, 2006; Rose et al., 2018). Nevertheless, anthocyanins are unstable under several conditions – storage temperature variations, presence of solvents, light irradiation, and other factors (Castañeda-Ovando et al., 2009). Intercalation of anthocyanins into clay structure enhances active compound stability (Kohno et al., 2009; Hamedi and Koosha, 2020) and expands the possibility to use these materials, e.g., as pH-sensitive indicators to detect food quality. There is a close relationship between the pH value of perishable food products and their spoilage degree. The increase in the pH value of most meat products indicates spoilage due to the action of microorganisms and the formation of ammonia and amino sugar complexes because of the decomposition of proteins and lipids (Choi et al., 2017; Luchese et al., 2018).



Clay-anthocyanin composite	Storage time at 24 °C	Storage time at 8 °C	Organoleptic evaluation (in points)*
🟥	0 h	0 day	5
🟪	24 h – 36 h	7 day – 8 day	3
🟦	> 48h	>8 day	<2

Figure 3.32. **(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.

Spoilage tests of fresh chicken fillets were conducted partly at the Latvia University of Life Sciences and Technologies to evaluate clay-anthocyanins composites' performance as smart sensors in food packaging. Spoilage tests were conducted in a laboratory environment placing meat samples in commercially available polypropylene containers with film sealing in the air (Figure 3.32. A), 100% nitrogen (N_2) environment and in a protective atmosphere (30% CO_2/70% N_2), then kept at room temperature and a temperature of cold showcases (8 °C) that are used in stores for the storage of raw meat products. The experimental results showed that 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 3.32.B); and before bacterial contamination exceeds the threshold values set by the Commission Regulation on microbiological criteria for food stuffs No. 2073/2005.

In the European Union, around 88 million tons of food waste are generated annually, with associated costs estimated at 143 billion euros (FUSIONS, 2016). Today many customers throw away food simply because they are unsure of its freshness. It is estimated that 10% of food waste is related to date labels. This means that in total, 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. Smart sensors change colour from red to blue, thus demonstrating food quality and in a very simple way explaining levels of bacterial and microbial contamination. Smart sensor technology enables individuals to make informed decisions reassuring required food quality. The simplicity of the colour change in the sensor will reduce avoidable food waste. Additionally, this technology is following the Green Deal 'Farm to Fork Strategy' that highlights the importance of the reduction of food loss and waste, and the revision of the European rules on data markings.

In the future studies it is planned to test prospective clay-based composites not only in laboratory-scale experiments but also in pilot-scale experiments. Additionally, new modification methods and application possibilities are planned, e.g., sorption of greenhouse gases, i.e., carbon dioxide (Krūmiņš et al., 2022); intelligent drug carriers of clay-polyphenol composites with immuno-modulating properties (Hamedi and Koosha, 2020; Shakoor et al., 2021); clay-based materials as electrodes, electrolytes, separators, or nanofillers in energy storage and conversion devices (Lan et al., 2021); magnetic clays in wastewater treatment (Salinas et al., 2018) and even clay materials in aerospace industry (Rathod et al., 2017).

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 (γ-Fe_2O_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), CeIII), Nd(III),** with clay-hydroxyapatite sorbents under various environmental conditions revealed that the highest sorption capacity of La(III), CeIII), 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_C_{12}mimCl) 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 their turn can be used in the food industry as freshness indicators that ensure perishable food quality.

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APPENDICES

APPENDIX A

PAPER I

Ozola-Davidane, R., Burlakovs, J., Tamm, T., Zeltkalne, S., Krauklis, A. E., Klavins, M.

BENTONITE – IONIC LIQUID COMPOSITES FOR CONGO RED REMOVAL FROM AQUEOUS SOLUTION

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Bentonite-ionic liquid composites for Congo red removal from aqueous solutions

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ABSTRACT

Clay-organic composites have attracted great interest due to their ability to remove various contaminants from wastewater. The surfactants are the most commonly used organic compounds for clay modification. However, cationic surfactants are toxic and can be environmentally hazardous. Ionic liquids are a new promising alternative to the cationic surfactants due to lesser toxicity and appropriate thermal stability. The research aim is to prepare an environmentally friendly new class of clay sorbents modified with ionic liquids for potential applications in wastewater treatment from the textile industry. Imidazolium-based ionic liquids with different lengths of alkyl chains were intercalated in the interlayer space of sodium bentonite via an ion exchange reaction. X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric (TG) analysis, and Brunauer-Emmett-Teller (BET) method for the specific surface area (SSA) analysis provided evidence of successful modification of the bentonite. The removal of model organic contaminant, Congo red dye, from aqueous solutions was investigated using the modified clays under different experimental conditions, i.e., reaction time, pH and sorbate concentration. Detailed isotherm studies showed that the modified clays have much higher Congo red sorption capacity compared to unmodified bentonite. The maximum Congo red sorption capacity of 150 mg/g was observed for bentonite modified with 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl) with d-value of 17.7 Å. This study shows that ionic liquids enhance bentonite capacity for Congo red sorption with different trends based on the ionic liquid structure. Bentonite-ionic liquid composites are eco-friendly and effective sorbents and due to a substantial increase in their capacity for the removal of textile dyes, they are expected to diminish the environmental impact of industrially used dyes.

1. Introduction

Within the development of circular economy and environmental protection paradigms, the textile industry is considered as one of the most polluting industries as it consumes large quantities of water resources and produces huge volumes of wastewater. Treatment planning involves intensive planning efforts, modelling, and innovation in environmental technologies taking also account long term changes in climate and land use [1]. Wastewaters containing dyes with no special treatment are considered hazardous waste [2]. 10–20% of dyes are directed to industrial wastewaters [3]. Since dyes are complex and have relatively stable structures, resistant toxicity, and low biodegradability, methods that are needed for their removal are complex; a few of currently used methods include coagulation or flocculation, biological treatment, chemical oxidation, membrane filtration [4–8]. However, still, the sorption treatment is considered one of the best available technologies so far [9,10].

The use of clay-organic composites for the removal of organic and inorganic contaminants from soil and water might be one of the solutions to the challenge posed by flourishing green chemistry during the last decades [11]. These composites are created (synthesized) by intercalating specific organic molecules through an ion exchange reaction in the interlayer space [12 –14]. Modified

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kaolinite with hexadecyltrimethylammonium bromide (HDTMA-Br) can be used as a sorbent for the removal of nitrates, arsenate, and chromates [15]. Additionally, montmorillonite modified with octadecyltrimethylammonium bromide (ODTMA-Br) is another example that has been successfully used as an efficient sorbent for the treatment of various pesticides [16]. However, those might be toxic to soil and aquatic organisms [17,18]. Modified clay materials are useful for the treatment of pollutants that are toxic and carcinogenic to humans and hazardous in the aquatic environment [19]. E.g., montmorillonite modified with the 1-hexadecyl-3-methylimidazolium bromide is an effective sorbent for a hydrophobic organic contaminant (polychlorinated biphenyls) with 80% of efficiency for wastewater treatment. Pharmaceutically active substances are also target contaminants that are treated by montmorillonite modified with imidazolium-based ionic liquids providing selective and rapid separation of four estrogenic hormones: estrone, 17β-estradiol, estriol, and ethynylestradiol from river water samples [20].

Ionic liquids are organic salts with an advantage of lower toxicity compared to surfactants, nearly no vapour pressure at room temperature, and melting points below 100 °C positionings in green chemistry with enhanced activity, stability, and selectivity [21]. Cai et al. [22], Lou et al. [23], Arce et al. [24], and many others successfully demonstrated various outperformance properties of ionic liquids for different industries.

These green solvents are synthesized in concert with a variety of cations and anions. Some ionic liquids that are based on phosphonium or tetra-alkylammonium cations include $[BF_4]^-$, $[PF_6]^-$ and $[CF_3COO]^-$, etc. Ionic liquids are eco-friendly alternatives to the commonly used surfactants due to their unique thermal, physical, chemical, and biological properties [25,26].

Recent studies have shown successful synthesis of ionic liquid-clay composites consisting of smectite type clay minerals, imidazolium cation with variational alkyl chain lengths and different anions [27 –33]. These studies are in general focused on the characterization of ionic liquid-clay composites' properties, e.g., sorption [30,33], structure and thermal behaviour [29], rheological and swelling properties [31] and interlayer configuration of intercalated ionic liquids [27]. Thus, excluding the application aspect of newly developed materials.

In this study modification of clay minerals using eco-friendly modifiers - ionic liquids are performed, and application as innovative sorbents for the removal of the model organic pollutant - Congo red dye, is studied. Moreover, no study has focused on the removal of Congo red dye from aqueous solutions using the laboratory synthesized ionic liquids. The objective of this study is to investigate the sorption of Congo red dye using modified smectite type mineral, bentonite, by imidazolium-based ionic liquids. In this research, three types of imidazolium-based ionic liquids with variational alkyl chain lengths were synthesized and used for modifying sodium bentonite. The obtained products were characterized using complementary techniques such as XRD, TG analysis, FTIR, the specific surface determined by the BET method, and adsorption isotherms including Langmuir and Freundlich. Throughout this work, the influence of synthesized ionic liquid-clay composites on the Congo red sorption from aqueous solution under different experimental conditions, i.e., reaction time, pH and sorbate concentration were studied.

2. Materials and methods

2.1. Materials

Bentonite (Bent), trade name: *Bentonite, sodium form* was purchased from Alfa Aesar (Ward Hill, United States). According to the product's specification bentonite has the appearance of cream to brown or grey powder, exhibited a mass loss upon drying from 10% to 15 wt% and swelling volume from 20 mL to 40 mL (2 g in 100 mL water) (according to the product's specification). The cation exchange capacity is 0.98 ± 0.03 mmol/g (determined by the methylene blue test).

The ionic liquids (ILs) used for the modification of bentonite were 1-butyl-3-methylimidazolium chloride (C_4mimCl), 1-octyl-3-methylimidazolium chloride (C_8mimCl), and 1-dodecyl-3-methylimidazolium chloride (C_{12}mimCl), which were obtained by alkylation of 1-methylimidazole with corresponding alkyl chlorides in an ethyl acetate solution at 80 °C for 72 h, according to a recently published method [34]. Congo Red (CR) dye used as a model contaminant in sorption experiments was obtained from Sigma-Aldrich (St. Louis, United States). The molecular size of Congo red is 2.3 nm [35]. The chemical structures of the used ionic liquids and Congo red are depicted in Fig. 1. All solutions were prepared using high purity deionized water (10–15 MΩ cm) obtained with a Millipore Elix 3 (Burlington, United States).

The motivation of the study is to prepare a novel environmentally friendly sorbent material for wastewater applications, where contamination with azo dyes is an increasing problem. The authors successfully obtained and characterized a bentonite – ionic liquid composite. Furthermore, the final properties of the sorbent were related to the type of ionic liquid used in modification. These aspects are presented in detail further in the manuscript.

2.2. Synthesis of bentonite-ionic liquid composites

The modified clay has been prepared by the cation exchange method, which is a reaction between the sodium cation of bentonite and imidazolium ions of ionic liquids as the intercalating agent. 5 g of bentonite was added to the ionic liquid solution and the mixture was stirred for 10 min using a magnetic stirrer. Then the bentonite-ionic liquid solution was placed in a shaker overnight at room temperature. The mixture was centrifuged at 3000 rpm for 15 min and washed several times with deionized water until no chloride ions were detected by the addition of 0.1 M silver nitrate. The modified bentonite samples were dried in Gallenkamp Plus II (London, United Kingdom) oven overnight at 60 °C. The corresponding mass of the ionic liquid was calculated in a similar way as described in Ozola et al. [13]; using the following equation:

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

where m_s is the mass of the ionic liquid (g), m_c is the mass of the used clay sample (g), CEC is the cation exchange capacity of bentonite (mmol/g), Q_{CEC} value is 1 and corresponds to the proportion between the added ionic liquid and cation exchange capacity of bentonite; M is the molecular mass of the ionic liquid (g/mol).

Bentonite samples prepared with 1-butyl-3-methylimidazolium chloride, 1-octyl-3-methylimidazolium chloride and 1-dodecyl-3-methylimidazolium chloride were designated as Bent_C_4mimCl, Bent_C_8mimCl and Bent_C_{12}mimCl, respectively.

2.3. Characterization methods

The thermal stability of samples was studied by thermogravimetric analysis and was performed on a TA Instruments – Waters LLC SDT Q600. 5 mg of the sample was heated from room temperature to 900 °C at the heating rate of 20 °C/min under nitrogen flow (100 mL/min). The X-ray diffraction (XRD) analysis with Bruker D8 Advance diffractometer (CuKα radiation in the 2θ range from 3° to 15° at a scanning rate 0.02°/s) was used to calculate d-space and

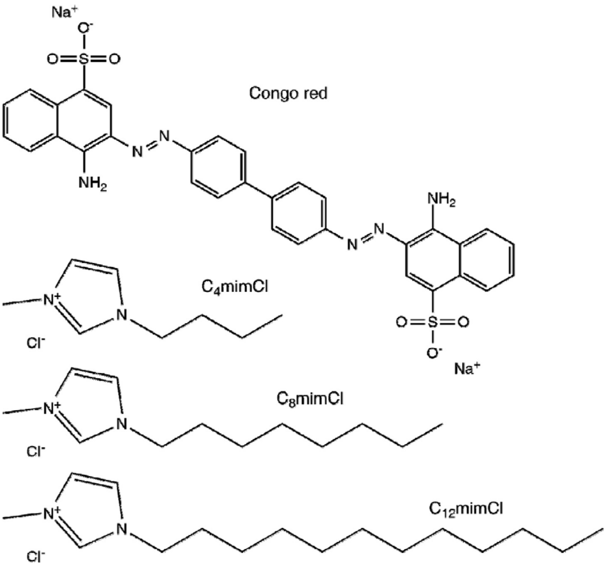

Fig. 1. Chemical structures of the textile dye Congo red and the ionic liquids used for modifying bentonite.

describe the mineral composition of clay samples. The Fourier-transform infrared spectroscopy (FTIR) was performed using a Shimadzu IR-Tracer 100 spectrophotometer in KBr pellets in the scanning range of 400 – 4000 cm^{-1}, using 20 scans per spectrum with a resolution of 2 cm^{-1}. The specific surface area was measured using the BET-N_2 absorption method (the Brunauer-Emmett-Teller isotherm) on a Quantachrome Quadrasorb S1 surface area and pore size analyzer using the gas sorption technique. The pore size was obtained using the built-in Quantachrome Quadrasorb S1 Density Functional Theory (BJH) model method. Before the measurements, samples were pre-heated at 80 °C in the nitrogen atmosphere overnight.

2.4. Sorption experiments

Sorption experiments were conducted using a batch system. 0.01 g of samples and 25 mL of Congo red solution were mixed for 24 h at room temperature in a multi-functional orbital shaker Biosan PSU-20 with a shaking speed of 170 rpm. After shaking, the mixtures were centrifuged at 3000 rpm for 12 min and filtered. Then the concentration of Congo red in the supernatant was analysed using a UV–Vis spectrophotometer (Shimadzu UV 1800) at 500 nm, and the sorption amount (q_e, mg/g) was calculated using the following equation:

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

where 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 the mass of sorbent used (g). The percentage removal (%) of Congo red dye by the sorbent was calculated using the following equation:

$$\text{Removal}(\%) = \frac{(C_i - C_e)}{C_i} \cdot 100 \tag{3}$$

The experiments of contact time (1, 10, 20, 30, 40, 50, 60, 120, 180, 240, 300 and 360 min) and the initial concentration of Congo red (0.5, 5, 25, 50 and 100 mg/L) were carried out. The pH of the Congo red solution was adjusted to values ranging from 2 to 10 by adding either 0.1 M HCl or 0.1 M NaOH. Standard deviations of the results were reported based on 3 experimental parallels.

3. Results and discussions

3.1. Characterization of composite materials

FTIR. The intense absorption bands in the FTIR spectra at 3622 cm^{-1}, 3429 cm^{-1}, 1038 cm^{-1}, 716 cm^{-1}, 781 cm^{-1}, and 848 cm^{-1} and ranging from 428 cm^{-1} to 513 cm^{-1} are observed for both unmodified and modified bentonite; and are related to the structure of bentonite (Fig. 2). The sharp bond observed at 3622 cm^{-1} and broadband at 3429 cm^{-1} was assigned to OH stretching vibrations which may arise from isomorphic substitution in the tetra and octahedral layers in bentonite [36,37]. The band at 1038 cm^{-1} is assigned to the asymmetric stretching vibration of Si-O-Si. Also, bonds at 716 cm^{-1}, 781 cm^{-1}, and 848 cm^{-1} are the most typical for quartz and the bands ranging from 428 cm^{-1} to 513 cm^{-1} can be attributed to O-Si-O bending vibrations [36,38,39].

The FTIR spectra of the modified bentonite indicated the occurrence of new signals. The appearance of the additional absorbance bands with wavenumber at 2927 cm^{-1} and 2847 cm^{-1} are corresponding to asymmetric and symmetric C–H stretching vibrations of the methylene groups (CH_2). The bands occurring at 1462 cm^{-1}

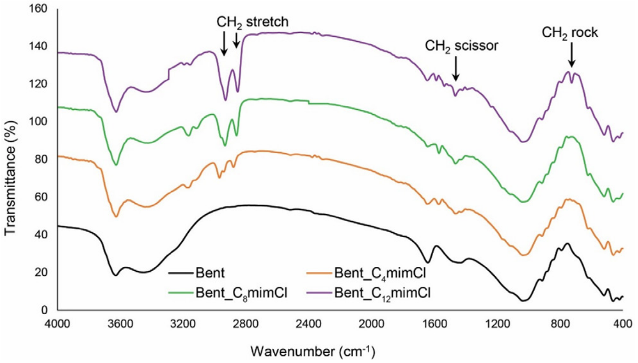

Fig. 2. FTIR spectra of the unmodified bentonite and the obtained bentonite-ionic liquid composites.

and 721 cm^{-1} are indicating scissoring and rocking vibrations of methylene groups, respectively (Fig. 2) [38]. The presence of bands in the range of 3000 – 2840 cm^{-1} is an indication of the presence of the ionic liquid cations on both bentonite surface and basal space [40 –42].

XRD. The X-ray diffraction pattern showed that after the modification of bentonite the 001 reflection was shifted to lower angular values (Fig. 3), leading to an increase of the interlayer space (Table 1).

The height of interlayer space was estimated from d001-value and the thickness of the sheet of phyllosilicate (9.6 Å) using the following equation [43]:

$$\text{Interlayer space height}(\text{Å}) = \text{Distance}(d_{001}) - 9,6\text{Å} \quad (4)$$

The interlayer space 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. For the Bent_C$_4$mimCl, Bent_C$_8$mimCl and Bent_C$_{12}$mimCl samples interlayer space expansions were 1.3 Å, 1.8 Å, and 5.1 Å, respectively. Similar results are also found in other studies [42,44 –46] confirming that the shift of basal reflection to lower values is a signature of successful intercalation of ionic liquid cations into the interlayer of the bentonite platelets.

TG analysis. The thermal gravimetric (TG) and differential thermal gravimetric (DTG) analysis curves are given in Fig. 4 for unmodified and modified bentonite samples. The TG spectrum of the unmodified bentonite revealed mass loss (8.19%) from room temperature up to 100 °C due to the release of the adsorbed water molecules in the interlayer of the clay mineral. In this temperature range, a small mass loss of a maximum of 2% was observed for bentonite-ionic liquid composites, indicating that the intercalation of ionic liquids provided hydrophobic properties for the clay samples. The decomposition of the structural hydroxyl groups in the aluminosilicate occurred around 700 °C, as reported by Schroeder [39], Takahashi et al. [45], and He et al. [47]. The decomposition of ionic liquids (C$_4$mimCl and C$_8$mimCl) was observed around 480 °C (Fig. 4b,c), while in the case of Bent_C$_{12}$mimCl the decomposition of C$_{12}$mimCl was observed in multiple steps in the range of 395 °C and 580 °C (Fig. 4d). The peaks between 395 °C and 580 °C in the DTG curves correspond to evaporation and decomposition of the intercalated ionic liquid species between clay mineral layers [48 –51]. Mass loss of Bent_C$_4$mimCl, Bent_C$_8$mimCl, and Bent_C$_{12}$mimCl, which is attributed to the decomposition of the

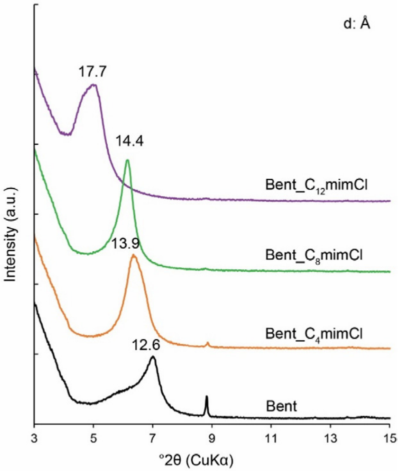

Fig. 3. XRD diffractograms of the unmodified bentonite and the obtained bentonite-ionic liquid composites. The numbers above the peaks represent d001-values.

Table 1
Interlayer space of the unmodified bentonite and the obtained bentonite-ionic liquid composites.

Sample	$d_{(001)}$ (Å)	Interlayer space (Å)	Interlayer space expansion (Å)*
Bent	12.6	3.0	–
Bent_C$_4$mimCl	13.9	4.3	1.3
Bent_C$_8$mimCl	14.4	4.8	1.8
Bent_C$_{12}$mimCl	17.7	8.1	5.1

[*] Calculated by Eq. (3).

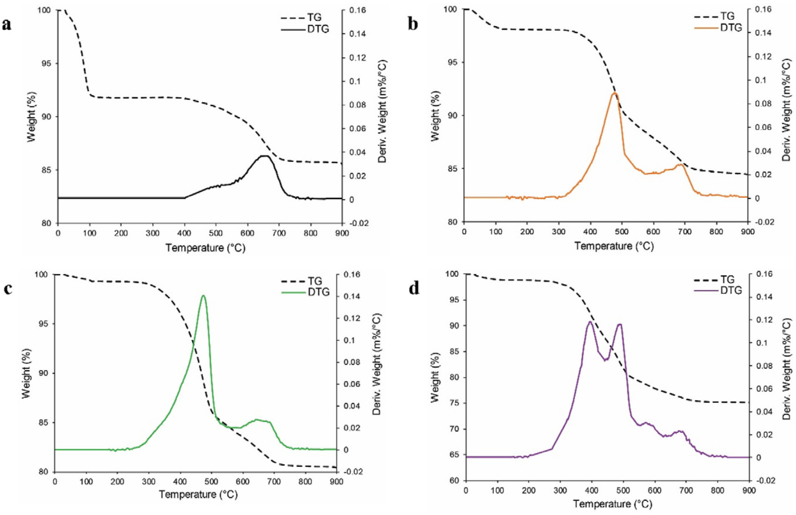

Fig. 4. TG and DTG curves of the unmodified bentonite (Bent) (a) and the modified bentonite with ionic liquids: 1-butyl-3-methylimidazolium chloride (Bent_C_4mimCl) (b); 1-octyl-3-methylimidazolium chloride (Bent_C_8mimCl) (c) and 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl) (d).

ionic liquids, were 8.30%, 13.59%, and 18.61%; and total mass loss were 15.51%, 19.59%, and 24.88%, respectively.

SSA measurements. The BET method was used to study the porosity and textural properties of unmodified and ionic liquid-modified bentonite samples. The SSA and pore volume values of the unmodified bentonite decreased after the addition of ionic liquids. However, the average pore diameter of modified bentonite gradually enlarged by 0.84 nm, 1.55 nm, and 11.72 nm for Bent_C_4mimCl, Bent_C_8mimCl, and Bent_C_{12}mimCl respectively, compared to unmodified bentonite. Furthermore, it was also found that the SSA and pore volume of the modified clay samples decreased with an increasing length of the alkyl chain of the ionic liquid. Thus, the sample prepared with C_{12}mimCl (Bent_C_{12}mimCl) exhibited the lowest SSA (more than 6 times lower as compared to Bent) and the lowest pore volume (3 times lower as compared to Bent) (Table 2).

Similar results were reported also in other studies by Zhang L et al. [37], Srivastava et al. [52], Zhou et al. [53], Park et al. [54]. The adsorption capacity is increased as the ionic liquid is introduced into the clay, and is increasing with the length of the alkyl chain of the ionic liquid. However, ionic liquid cations not only enter the bentonite interlayer space but also are adsorbed on the exterior surface, occupying pores in the clay particles. Since pores are occupied by the ionic liquid, the measured specific surface area is smaller. From these results, it was assumed that the specific surface area and pore size are not determining factors for the improvement of the sorption capacity of organic pollutants.

3.2. Congo red sorption studies

Equilibrium sorption experiments. Congo red solutions of an initial concentration ranging from 0.5 mg/L to 100 mg/L were selected to investigate the influence of the initial dye concentration on the sorption of Congo red onto unmodified and modified bentonite samples. Increasing initial dye concentration, the sorption capacity of clay samples improved (Fig. 5). At lower concentration sorbent sites are vacant, but at higher - the number of occupied sorbent sites increases thus resulting in increased sorption capacity regards Congo red [55].

Table 2
Textural properties of the unmodified bentonite and the obtained bentonite-ionic liquid composites.

Sample	Specific surface area (m^2/g)	Pore volume (m^3/g)	Average pore diameter (nm)
Bent	45.21	0.092	9.53
Bent_C_4mimCl	29.83	0.066	10.37
Bent_C_8mimCl	18.80	0.045	11.08
Bent_C_{12}mimCl	6.89	0.029	21.25

The sorption capacity significantly increased after bentonite modification and the highest sorption capacity was 150 mg/g for bentonite modified with 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl) when Congo red concentration was 100 mg/L. According to results removal efficiency of Congo red is linked to the size of the interlayer space of bentonite-ionic liquid composites. Modified bentonite samples that had the largest interlayer space (according to XRD results, Table 1) sorbed the highest amount of Congo red molecules (Fig. 5). Similar results have been found in previous studies [13] where *p*-nitrophenol sorption onto modified clay samples was investigated.

Sorption isotherms. The classic physical Langmuir [56] and empirical Freundlich [57] isotherm models were used to describe the sorption mechanism between the sorbate and the sorbent. The analytical equations were as following:

$$\text{Langmuir}: q_e = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (5)$$

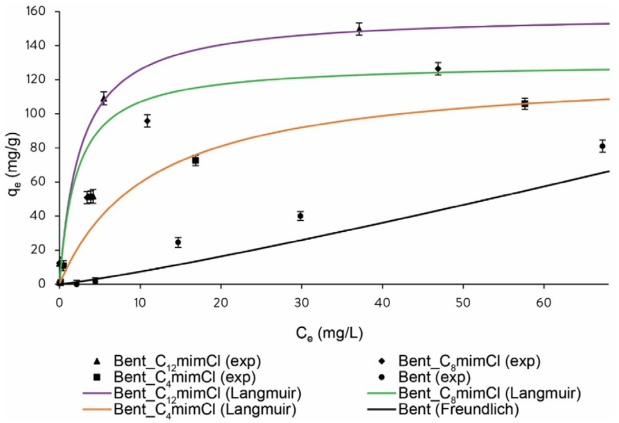

Fig. 5. Effect of initial concentration on the removal of Congo red by unmodified and modified bentonite samples (experimental conditions: Ci = 0.5–50 mg/L, pH = 5.5, contact time = 24 h, T = 24 °C).

Table 3
Langmuir and Freundlich isotherm model parameters for the adsorption of Congo red on the unmodified bentonite and the obtained bentonite-ionic liquid composites.

Sample	Langmuir				Freundlich		
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	n	K_F (L/mg)	R^2
Bent	101.01	0.0077	0.8397	0.0432	0.70	0.2898	0.9440
Bent_C$_4$mimCl	126.58	0.0888	0.0533	0.9319	1.34	8.9165	0.8589
Bent_C$_8$mimCl	129.87	0.4667	0.0106	0.9857	1.05	5.9895	0.6808
Bent_C$_{12}$mimCl	158.73	0.3841	0.0128	0.9523	0.92	6.1159	0.6798

$$\text{Freundlich}: q_e = K_F \cdot C_e^{1/n} \tag{6}$$

Where q_{max} (mg/g) is the theoretical monolayer capacity of Langmuir equation, K_L (L/mg) is the Langmuir equilibrium constant and C_e (mg/L) is the equilibrium solution concentration (Eq. (2)). K_F (L/mg) and n are Freundlich constants defining relative capacity and sorption intensity, respectively (Eq.6). Additionally, from Langmuir isotherm dimensionless constant (R_L) was calculated by the following equation:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{7}$$

where C_0 (mg/L) is the highest initial sorbate concentration and the value of R_L indicates whether sorption will be favourable ($0 < R_L < 1$), unfavourable (R_L greater than 1), irreversible ($R_L = 0$), or linear ($R_L = 1$) [58].

The parameters from the Langmuir and Freundlich isotherms obtained from experimental data are given in Table 3. Obtained correlation coefficient (R^2) values indicated that for unmodified bentonite Freundlich isotherm model is the most suitable equation to describe the sorption behaviour. While in the case of the bentonite-ionic liquid composites Langmuir isotherm model is the most relevant. This suggests that for unmodified bentonite sorption of Congo red is of multilayer character, while for modified bentonite samples sorption - monolayer (i.e. only a limited number of surface sites are sorbed) [36,56,57].

In the Langmuir model, the values of K_L were between 0 and 1, indicating that the sorption of Congo red onto bentonite-ionic liquid composites is favourable at the conditions being studied. As the longer alkyl chain of the modifier used, the q_{max} increases from 126.58 mg/g to 158.73 mg/g. Additionally, the R_L value decreases, indicating that sorption is more favourable when ionic liquid is with a longer alkyl chain.

In the Freundlich model, the constant K_F indicates the sorption capacity of the sorbent. Parameter n reflects the sorption intensity of Congo red. In the case of the unmodified bentonite, the value of n is obtained lower than 1, indicating that the sorption system is more favourable at higher concentrations of Congo red and sorption is determined by the chemical process [54,59].

Unmodified bentonite follows Freundlich whereas modified Bentonite follows Langmuir behaviour. The reason for this is not obvious, but the authors think that this may be linked to a difference in the sorption mechanism between unmodified clay and the modified material. A similar transition from Freundlich to Langmuir was found also for other modified aluminosilicate sorbents [13,60,61]. According to the results, sorption is more favourable when ionic liquid is introduced and is increasing regarding the length of the alkyl chain of the introduced ionic liquid in bentonite.

Sorption kinetics. At the initial stage the removal of Congo red is relatively fast; with 10 mg of sorbents used approximately 50% of dye molecules were sorbed in the first 30 min. Congo red sorption equilibrium time on unmodified bentonite and modified bentonite with 1-dodecyl-3-methylimidazolium chloride was 60 min and 240 min, respectively (Fig. 6). The high sorption rate of Congo red at the beginning of the experiment is due to the presence of an extensive amount of easily accessible sorbent sites, and dye

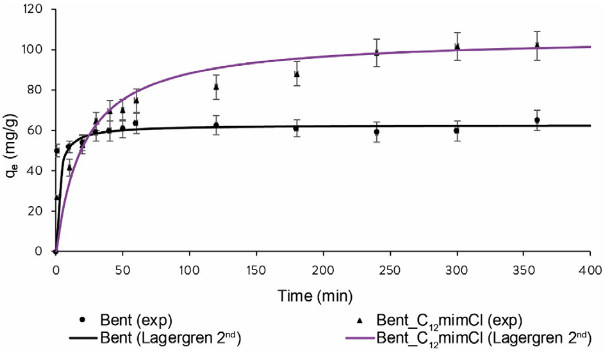

Fig. 6. Sorption kinetics of the removal of Congo red by unmodified bentonite (Bent) and modified bentonite with 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl) (experimental conditions: C_i = 50 mg/L, pH = 5.5, contact time = 1–360 min, T = 24 °C).

Table 4
Parameters of the kinetic models for the sorption of Congo red on the unmodified bentonite and the obtained bentonite-ionic liquid composite.

Sample	Pseudo-first order of Lagergren			Pseudo-second order of Lagergren		
	q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg min)	R^2
Bent	6.60	2.10×10^{-3}	0.0941	62.50	7.44×10^{-3}	0.9968
Bent_C_{12}mimCl	75.41	1.50×10^{-2}	0.8858	106.38	4.53×10^{-4}	0.9940

molecules can rapidly interact with the available active sites. The sorption rate slows down as the number of available sorbent sites for the remaining dye molecules decreases [37,62,55].

Lagergren's pseudo-first-order [63] and pseudo-second-order [64] kinetic models were used to analyze the relationship of sorption time and sorption capacity. The analytical equations were as following:

$$\text{Pseudo} - \text{first} - \text{ordermodel}: \log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (8)$$

$$\text{Pseudo} - \text{second} - \text{ordermodel}: \frac{t}{q_t} = \frac{1}{K_2 q_{2e}^2} + \frac{t}{q_{2e}} \quad (9)$$

where q_t is the amount of dye sorbed on sorbent (mg/g) at time t, K_1 (1/min) and K_2 (g/mg min) are the rate constants of pseudo-first kinetic model and pseudo-second kinetic model, respectively.

The parameters from Lagergren's pseudo-first-order and pseudo-second-order kinetic models obtained from experimental data are given in Table 4. Obtained correlation coefficient (R^2) values indicated that for unmodified bentonite and bentonite-ionic liquid composite (Bt_C_{12}mimCl) the 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 chemisorption mechanism which involves valence forces between Congo red anion and Bt_C_{12}mimCl sorbent [65,66].

Effect of pH. The pH of the dye initial solution influences stability and surface charge of the sorbent and the chemistry of the sorption process [67]. Congo red is an example of diazo dye, and the initial pH influences the molecular form of Congo red in the aqueous solution [62]. At pH 3 Congo red appears blue-violet but at pH 5 changes its colour to red and due to this is often used as a pH indicator. Congo red exists as an anionic species at an alkaline pH but as a cationic species at an acidic pH value [68].

The study on the effect of pH of the sorption of Congo red on the modified bentonite with 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl) was investigated in the pH ranging from 2 to 10 with the initial concentration of Congo red of 50 mg/L at room temperature. 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% (Fig. 7.).

A decrease in the removal of Congo red by bentonite with increasing pH is related to the dissociation of sulfonate groups of Congo red producing anionic dye ions. At lower pH, the negative surface of bentonite is neutralized by H^+ thereby promoting the spreading of Congo red. This is further reinforced by the electrostatic attraction between bentonite and the anionic dye ions promoting sorption at low pH. As pH increases, the number of negatively charged sites on the bentonite increase enhancing the electrostatic repulsion thus hindering sorption [68–70]. Similar results have been reported for the Congo red sorption on different sorbents [62,70 –74].

Nevertheless, the sorption efficiency of Congo red is significantly high even at alkaline pH suggesting that besides electrostatic attraction there is another sorption mechanism. Since the Bent_C_{12}mimCl is hydrophobic due to the modification with 1-dodecyl-3-methylimidazolium chloride, the hydrophobic interaction is likely the main sorption mechanism that interacts through π-π reactions between the ionic liquid on the sorbent and the rings in the Congo red [73].

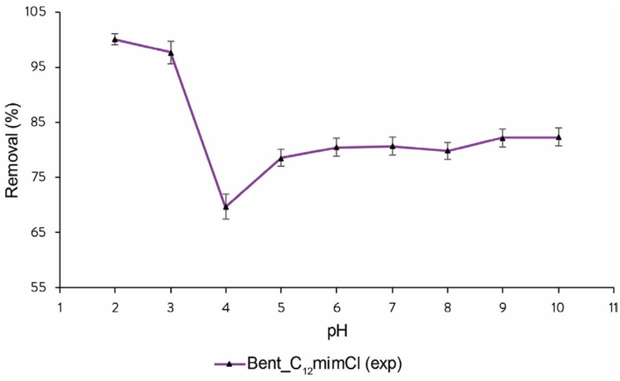

Fig. 7. Effect of pH on the removal of Congo red by modified bentonite with 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl) (experimental conditions: Ci = 50 mg/L, pH = 2–10, contact time = 24 h, T = 24 °C).

4. Conclusions

The experimental results and property characterization for newly developed modified bentonite sorbents with ionic liquids show that sorption capacity has improved significantly as well as the performance of clay-composite material in general. Modified bentonite samples that had the largest interlayer space according to XRD results sorbed the highest amount of Congo red molecules. For bentonite-ionic liquid composites description with the Langmuir isotherm model is the most relevant, while for unmodified bentonite Freundlich isotherm model is the most suitable. Final sorptive properties and interlayer space of the composites are related to the type of ionic liquid used in modification and to the length of the alkyl chain, in particular. Sorption is more favourable when ionic liquid is introduced in a system and is increasing in regards to the length of the alkyl chain of the introduced ionic liquid in bentonite. 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}-mimCl) had the highest sorptive properties in the ionic liquid-bentonite composite. The maximum adsorption capacity of a new sorbent reached up to 150 mg/g for bentonite modified with 1-dodecyl-3-methylimidazolium chloride (Bent_C_{12}mimCl) when Congo red (model contaminant) concentration was 100 mg/L. Newly created wastewater treatment sorbents of clay composites with ionic liquids are expected to diminish the environmental impact of industrially used dyes and are perspective tools for textile dye removal.

CRediT authorship contribution statement

Ruta Ozola-Davidane: Writing - original draft, Visualization, Methodology, Investigation, Validation, Formal analysis, Data curation, Writing - review & editing. **Juris Burlakovs:** Writing - original draft, Supervision, Project administration. **Toomas Tamm:** Supervision. **Sindija Zeltkalne:** Investigation, Resources. **Andrey E. Krauklis:** Formal analysis, Writing - review & editing, Supervision. **Maris Klavins:** Conceptualization, Methodology, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.116373.

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APPENDIX B

PAPER II

Ozola, R., Burlakovs, J., Krauklis, A., Hogland, W., Klavins, M.

SURFACTANT MODIFIED CLAY SORBENTS FOR THE REMOVAL OF P-NITROPHENOL

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SURFACTANT-MODIFIED CLAY SORBENTS FOR THE REMOVAL OF *p*-NITROPHENOL

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Abstract—Organic pollutants are widespread and a known problem for the environment. *p*-nitrophenol (PNP) is one such pollutant found in effluents from various industries involved with pesticides, pharmaceuticals, petrochemicals, plastic, paper, and other materials. The objective of this research was to prepare and test organically modified clays using four different surfactants and to evaluate the removal efficiency of PNP from aqueous solutions. Organically modified clays have attracted great interest due to their wide applications in industry and environmental protection as sorbents for organic pollutants. Two natural smectite-dominated clay types from outcrops in Latvia and Lithuania as well as industrially manufactured montmorillonite (Mt) clay were modified using different nonionic (4-methylmorpholine N-oxide (NMO) and dimethyldodecylamine N-oxide (DDAO)) and cationic (benzyltrimethyl ammonium chloride (BTMAC) and dodecyltrimethyl ammonium chloride (DTAC)) surfactants. Modified clay materials were characterized by Fourier-transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and the Brunauer-Emmett-Teller method (BET) for surface area analysis. Sorption of PNP was investigated under various conditions, e.g. surfactant loading, initial PNP concentration, contact time, and pH. The novelty of the present study was to prepare innovative organo-sorbents based on manufactured as well as natural clay samples using cationic surfactants and nonconventional nonionic surfactants as modifiers. The sorption data combined with FTIR and XRD supplementary results suggests that nonionic organo-clay (Mt-DDAO_2) is the most effective sorbent and may serve as a low-toxicity immobilizer of pollutants such as phenols.

Keywords—Cationic and Nonionic Surfactants · Clay Sorbents · *p*-nitrophenol · Sorption · Water Treatment

INTRODUCTION

Clay minerals are aluminosilicates that include 1116 crystalline minerals and comprise ~80% of the sedimentary rocks in the Earth's crust (Seglins, 2010). Known properties such as plasticity, fire resistance, cation exchangeability, and wide distribution make them a resource used widely in industry (Murray, 2007). From the point of view of environmental engineering, the key properties of aluminosilicates are cation exchange capability, structure, texture, and surface area (Brovkina et al. 2012). Over recent decades, interest has increased the use of clay minerals as a potential sorbent material for organic (Ruiz-Hitzky et al. 2010) and inorganic pollutants (Anirudhan & Ramachandran 2015). Most modified clays are used as environmentally friendly or neutral sorbent materials (Brovkina et al. 2012). Clay modification with surfactants increases the ability of clay minerals to exchange metallic ions with other cationic, anionic-cationic, and nonionic molecules (Gamoudi et al. 2015). The generalized formula describing surfactants of interest is:

$$\left[(\mathrm{CH_3})_3\mathrm{N}R'\right]^+ \mathrm{or} \left[(\mathrm{CH_3})_2\mathrm{N}R'R''\right]^+ \qquad (1)$$

where R' refers to aliphatic compounds and R'' to aliphatic or aromatic compounds (Yariv & Cross, 2002; Guégan et al. 2015). Inorganic cations are exchanged with surfactant cations and, thus, a hydrophilic surface of clay becomes hydrophobic; the derived material can then be referred to as organoclay (Guégan et al. 2015; Zhang, Zhang et al. 2015).

Organoclays are created mostly using smectite-group clay minerals that have a large surface area and a large cation exchange capacity – these properties are very important when characterizing sorbents (Seliem et al. 2011; Bertuoli et al. 2014). The choice of surfactant with chemical and textural properties that best fit the purpose is also of great importance (Guégan et al. 2015). Organoclay synthesis can be performed successfully by using surface-active organic (substituted) ammonium ions containing long alkyl chains (Paiva et al. 2008). Synthesis can be performed by various methods, e.g.: (1) cation-exchange reactions; (2) solid-state reactions; and (3) microwave irradiation (Paiva et al. 2008; Gamoudi et al. 2015).

Most chemical pollutants consist of organic compounds of which phenols are among the most widespread aquatic contaminants (Nayak & Singh, 2007) as they are used widely in oil, petroleum, coal, pharmacy, plastic, rubber, paper, dye, herbicide, pesticide, and many other industries (Nayak & Singh, 2007; Yan et al. 2007; Park et al. 2011; Lee & Tiwari, 2012; Luo et al. 2015).

In the aquatic environment a 96 h exposure to a phenolic concentration of >2 mg/L is toxic to fish, but exposure to 10–100 mg/L for the same period is lethal to all hydrobionts (Lee & Tiwari, 2012). Furthermore, human exposure, depending on the concentration, may lead to a variety of health risks, e.g. poisoning, eye and skin irritation, and damage to kidneys and liver (Xue et al. 2013; Zhang et al. 2015). Contamination by

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derivatives such as *p*-nitrophenol (PNP) and *p*-chlorophenol (PCP) in drinking water causes bad odors even at very low concentrations (Park et al., 2013).

Various wastewater-treatment methods for phenolic contaminants are available, such as biological and chemical treatment, catalytic oxidation, ion exchange, solvent extraction, membrane filtration, and sorption methods (Luo et al. 2015). Sorption is considered to be more effective when the phenolic concentration is too high for biological treatment (Park et al. 2013; Luo et al. 2015). Nitrophenols are important chemical intermediates that serve as precursors for many pharmaceuticals and pesticides (Zhang et al., 2006). A range of industries, such as the plastics and paper industries, use nitrophenols extensively in their products. Significant amounts of nitrophenols are commonly present in the effluents of these industries and need to be treated before being discharged into the environment (Orshansky & Narkis, 1997; Li et al. 2002).

Various types of sorbents can be used for the removal of phenols (including PNP) from water: humic substances (Yang & Koopal, 1999), composite geomaterials (Houari et al. 2014), Mt modified with surfactants (Xue et al. 2013), and magnetic materials (Han et al. 2013). For instance, Fe-nano-zeolite was characterized as a sorbent, and its potential applications and efficacy at removing *o*-, *m*-, and *p*-nitrophenols from water was studied by Huong et al. (2016). Removal of nitrophenols from aqueous solutions using cationic ß-cyclodextrin-modified zeolite as an adsorbent was investigated by Xiaohong et al. (2011) and using magnetic porous silica-graphene oxide hybrid composite by Liu et al. (2016). Zermane et al. (2010) modified hydroxyiron-Mt with cetyltrimethylammonium bromide (CTAB) and showed that the newly developed sorbent can remove both basic dye yellow 28 and PNP, and the presence of yellow 28 enhanced the uptake of PNP. Several authors have studied organically modified clay minerals (dominantly Mt) and their use for the removal of a wide variety of contaminants, including hydrophobic organic contaminants, heavy-metal cations, radioactive nuclides, etc. (Zhu et al. 2016).

In most research, cationic surfactants are used to produce organoclay sorbents, but, as an alternative, nonionic surfactants can be used. The main difference between cationic surfactants and nonionic surfactants is not only charge, but also low toxicity and potential biodegradability (Shen 2001). The present research focused on development of nonionic organoclay using 4-methylmorpholine N-oxide and dimethyldodecylamine N-oxide, comparing them to raw Mt clay, natural clay samples, and cationic organo-clays. The sorption properties of sorbent materials were studied by focusing on an organic pollutant – PNP.

MATERIALS AND METHODS

Materials and Chemicals

The following natural and manufactured clay samples were used in the experiments: (1) natural smectite-dominated clay of Triassic age from the Saltiski deposit (Saltiski, Lithuania) – further labeled as T clay; (2) clay mixed with organic matter of Jurassic age from the Legernieki deposit (Nikrace, Latvia) – J clay; and (3) montmorillonite K 10 industrially produced clay, purchased from Sigma-Aldrich (Taufkirchen, Germany) – Mt clay.

The T clay contained mostly smectite-group minerals (66%) in the <0.001 mm fraction. The J clay was a mixture of equal amounts of illite-smectite, illite, smectite, chlorite, and kaolinite with admixture of ancient organic matter (3%); the amount of clayey fraction (<0.001 mm) varied between 15% and 20%. The Mt clay consisted mainly of montmorillonite (65%) with specific weight 300–370 kg/m^3 and surface area 220–270 m^2/g (according to the product's specification). The cation exchange capacities (CEC) of the Mt clay, T clay, and J clay were: 0.50 ± 0.03 mmol/g, 0.33 ± 0.03 mmol/g, and 0.25 ± 0.02 mmol/g, respectively.

The PNP ($C_6H_5NO_3$) used for sorption experiments was provided by Alfa Aesar (Haverhill, Massachusetts, USA). Two types of surfactants which operated as examples of nonionic and cationic surfactants, respectively: (1) dimethyldodecylamine N-oxide (DDAO, $C_{14}H_{31}NO$, M = 229.40 g/mol), 4-methylmorpholine N-oxide (NMO, $C_5H_{11}NO_2$, M = 117.15 g/mol); and (2) benzyltrimethylammonium chloride (BTMAC, $C_{10}H_{16}ClN$, M = 185.69 g/mol) and dodecyltrimethylammonium chloride (DTAC, $C_{15}H_{34}ClN$, M = 263.89 g/mol) were purchased from Sigma-Aldrich (Taufkirchen, Germany). All solutions were prepared using high purity deionized water (15 MΩ cm) obtained with a Millipore Elix 3 (Billerica, Massachusetts, USA) purification system.

Method of Clay Modification

Raw clay samples were saturated with sodium ions (Na^+) by stirring 100 g of clay with 1 L of 0.5 M NaCl solution at 60°C for 24 h. Subsequently, the Na^+-saturated clay sample was washed three or four times with deionized water until chloride ions were not detected by addition of 0.1 M $AgNO_3$; then the sample was dried in a Gallenkamp Plus II Oven (London, UK) at 60°C overnight. Such treated clay samples were labeled as Mt_Na, J_Na, and T_Na, respectively.

Modification of the Na^+-saturated clay samples for the preparation of organoclays was performed as follows: 10 g of Na^+-saturated clay sample was dispersed in 400 mL of deionized water using a Jenway 1000 hotplate/stirrer (Stone, Staffordshire, UK) for 30 min. A selected amount of each surfactant was dispersed in 100 mL of deionized water and stirred for 30 min. Dissolved surfactant was added slowly to the clay suspension at 60°C. The mixtures were stirred for 24 h at 60°C. The suspension was then washed several times with deionized water until no chloride ions were detected by addition of 0.1 M $AgNO_3$, filtered, dried at room temperature, and dried at 60°C overnight. Dried organoclays were triturated in an agate mortar and stored in a desiccator.

The BTMAC-modified Mt clay samples obtained were labeled as Mt_BTMAC_0.5, Mt_BTMAC_1, Mt_BTMAC_2, and Mt_BTMAC_3, where the number means the proportion of added surfactant/CEC; and the corresponding weight of the surfactant was calculated using the following equation:

$$m_s = m_c \cdot \mathrm{CEC} \cdot 10^{-3} \cdot Q_{\mathrm{CEC}} \cdot M \quad (2)$$

where m_s is mass of the surfactant (g), m_c is mass of the clay sample used (g), CEC is cation exchange capacity of the clay samples used (mmol/g), Q_{CEC} is the proportion of surfactant added/CEC, and M is molecular weight of the surfactant (g/mol).

Characterization Methods of OrganoClay Sorbents

The modified clay materials obtained were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller surface area analysis (BET method), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The XRD data describing the mineralogy of sorbents were collected using a Bruker D8 Advance diffractometer (Billerica, Massachusetts, USA) using CuKα radiation. Surface area measurements were performed using a Micromeritics Gemini 2360 surface area and porosity analyzer (Norcross, Georgia, USA). The FTIR spectra were recorded using a Shimadzu IR-Tracer 100 spectrophotometer (Kyoto, Japan). The SEM images were obtained using a scanning electron microscope FE-SEM Hitachi S4800 (Tokyo, Japan).

Sorption Experiments

Sorption experiments were carried out to investigate the sorption capacity of raw and modified clays for the removal of PNP from aqueous solutions. For the sorption-isotherm studies, 0.3 g of a prepared sorbent material (organo-clays) was placed in a 100 mL glass vessel and supplemented with 20 mL of PNP at a concentration of 5, 10, 15, 20, or 25 mg/L. The mixture was agitated continuously on a multi-functional orbital shaker Biosan PSU-20i (Riga, Latvia) for 24 h at room temperature. After shaking, the mixture was centrifuged at 3000 rpm for 12 min and the supernatants were analyzed using a UV-Vis spectrophotometer (Shimadzu UV 1800, Kyoto, Japan) at 318 nm.

To undertake the sorption kinetics studies, 0.3 g of each of the sorbents (Mt_DDAO_2 and T_DDAO_2) was added to 20 mL of PNP solution (25 mg/L). The mixtures were agitated for 10–60 min with 10 min intervals and for 120–360 min with 60 min intervals. The pH of the PNP solution was adjusted to values ranging from 2 to 12 by adding either 0.1 M HCl or NaOH.

The quantity of the PNP sorbed on the organoclays was calculated using the following equation:

$$q_e = \frac{(C_i - C_e)}{m} \cdot v \quad (3)$$

where q_e is the amount of PNP sorbed on the sorbent (mg/g), C_i and C_e are initial and equilibrium liquid-phase concentrations of PNP (mg/L), respectively, v is the volume of solution (mL), and m is mass of sorbents used (g).

RESULTS AND DISCUSSION

Characterization of Organoclay Sorbents

XRD X-ray diffraction patterns for clay sorbents modified with various proportions of BTMAC/CEC of Mt clay (Fig. 1a) revealed that the d_{001} peak for the Na-exchanged montmorillonite at 1.34 nm shifted to greater values as a result of the exchange of Na^+ ions with surfactant cations. For clay samples that were treated with surfactant/CEC ratios of 0.5, 1.0, 2.0, and 3.0, the interlayer distances increased by 0.17, 0.17, 0.18, and 0.18 nm, respectively (Table 1). Cation exchange by the other surfactants yielded a maximum increase in interlayer distance also with a surfactant/CEC ratio of 2.0, and did not change significantly when the surfactant concentration was increased.

Clay modification with the various surfactants at a surfactant/CEC ratio of 2 showed clearly an increase in the d_{001} spacing in every case (Fig. 1b, Table 1), indicating a successful intercalation by the organic molecules. The largest increase in interlayer spacing occurred with surfactant DDAO

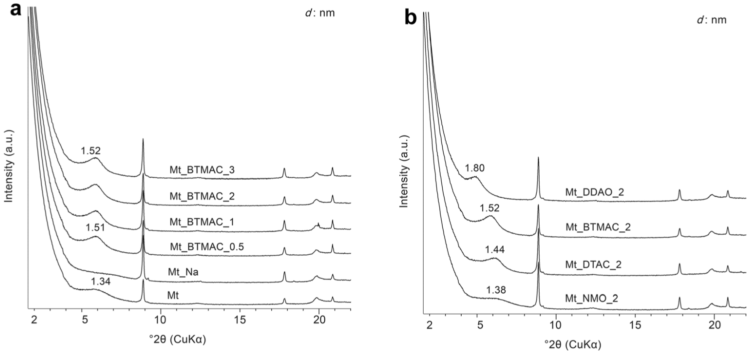

Fig. 1 XRD patterns of (**a**) Mt clay modified with BTMAC at various surfactant/CEC ratios and (**b**) modified with various surfactants at a surfactant/CEC ratio of 2.0

Table 1 Interlayer spacing of raw Mt clay and modified with various surfactants

Sample	d_{001} (nm)	Interlayer spacing (nm)	Interlayer space expansion (nm)
Mt	1.34	0.38	–
Mt_BTMAC_0.5	1.51	0.55	0.17
Mt_BTMAC_1	1.51	0.55	0.17
Mt_BTMAC_2	1.52	0.56	0.18
Mt_BTMAC_3	1.52	0.56	0.18
Mt_NMO_2	1.38	0.42	0.04
Mt_DTAC_2	1.44	0.48	0.10
Mt_DDAO_2	1.80	0.84	0.46

(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 (n_c, number of carbon atoms) (He et al. 2014). In the case of NMO, the value of n_c is 5, which is short compared to DDAO where n_c is almost three times longer at 14. In these organoclay samples, the alkyl chains of NMO, DTAC, and BTMAC formed only one parallel layer in the interlayer, as the basal 001 reflection was ≤1.5 nm, while in the case of DDAO, the alkyl chains were ordered in two parallel layers between the montmorillonite plates, indicated by the basal 001 reflection at 1.80 nm (Fig. 1a, b, Table 1) (Yariv & Cross, 2002; Zhu et al. 2007; Zhang et al. 2015).

Specific Surface Area Measurements Modification products were characterized also by their specific surface area, as this parameter is often used for sorption interpretation (Haydar et al. 2003). The specific surface area of Mt clay decreased from 245.88 m^2/g (according to the one-point method) to 231.10 m^2/g and 218.42 m^2/g after treatment with 0.5 and 3.0 BTMAC/CEC ratios, respectively (Table 2). Similar results were achieved also in other studies (Zhou et al. 2008; Wu et al. 2012; Park et al. 2013; Parolo et al. 2014; Zhang et al. 2015).

Surfactant intercalation not only obstructs the clay mineral interlayer space, but also arranges a monolayer on the outer surface, creating a `house of cards structure,' occupying pores among the clay particles. This process results in a reduction of pore size and molecular nitrogen adsorption, thus decreasing reported values via BET of the specific surface area with an increasing degree of modification (Parolo et al. 2014; Zhang et al. 2015). As for clays treated with surfactants, the interlayer space is increased significantly; one might assume, therefore, that the specific surface area and pore size are not determining factors for the improvement of sorption capacity (Park et al. 2013; Zhang et al. 2015).

FTIR The functional groups and structural changes in clay after modification were determined by infrared spectroscopy. The characteristic bonds of montmorillonite that appear at 3621 cm^{-1} as a sharp peak are assigned to OH-stretching vibrations of the structural OH group in the clay, whereas the broad band at 3428 cm^{-1} is ascribed to hydrogen-bonded water molecules adsorbed within the interlayer space of the clay (Zhang et al. 2015). The bands at 1040 cm^{-1} and 920 cm^{-1} indicate the Si–O and Al–O bending vibrations (Zhou et al. 2011). The bands of quartz at 798 cm^{-1}, 515 cm^{-1}, and 460 cm^{-1} are typical bending vibrations of O–Si–O (Alkaram et al. 2009).

After modification of Mt clay with surfactants, a pair of strong bands at 2930 cm^{-1} and 2854 cm^{-1} was observed which is assigned to the asymmetric and symmetric stretching vibrations of the methylene groups (CH_2), and their bending vibrations were detected at 1466 cm^{-1} (Fig. 2) (Alkaram et al. 2009; Zhou et al. 2011; Wu et al. 2012; Zhang et al. 2015). These observations of the changes in the IR spectra confirmed the presence of surfactant molecules in Mt clay modified with BTMAC, DTAC, and DDAO.

SEM Irregular crystal morphology was observed for Mt clay (Fig. 3a). The surface of the particles was rough and the presence of a layer structure was revealed (Fig. 3b). Compared with Na clay, the SEM images showed similar irregular morphology, but in the case of Mt_BTMAC_2 aggregates were smaller (Fig. 3g, h). Although, in samples Mt_NMO_2 (Fig. 3c, d), Mt_DTAC_2 (Fig. 3e, f), and Mt_DDAO_2 (Fig. 3i, j), particles were bound into larger agglomerations.

Studies of removal of p-nitrophenol

Effect of Surfactant Loading Experimental results revealed that the sorption capacity of Mt clay for PNP was negligible (Fig. 6), but after modification of Mt clay with

Table 2 Specific surface area (by the BET method) of raw Mt clay and modified with BTMAC at various surfactant/CEC ratios

Sample	Multi-point method (m^2/g)	One-point method (m^2/g)	According to the Langmuir isotherm (m^2/g)
Mt	252.03	245.88	423.24
Mt_Na	262.16	256.04	439.76
Mt_BTMAC_0,5	238.41	231.10	402.05
Mt_BTMAC_1	236.98	229.52	399.95
Mt_BTMAC_2	235.75	228.79	396.78
Mt_BTMAC_3	224.46	218.42	376.58

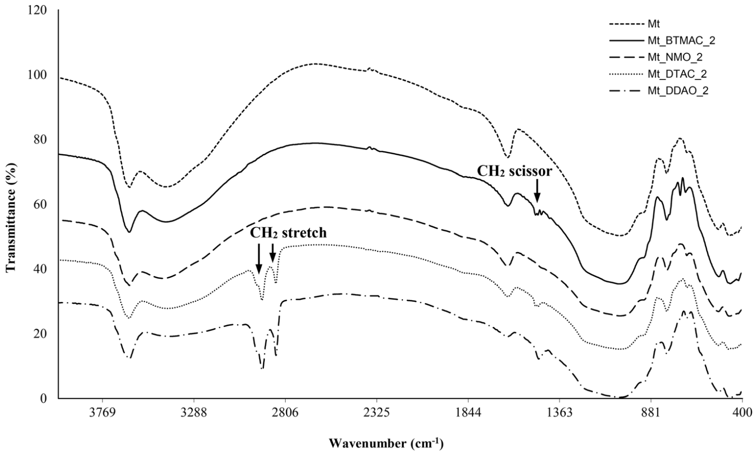

Fig. 2 FTIR spectra of Mt clay and modified with various surfactants at a surfactant/CEC ratio of 2.0

BTMAC the sorption capacity increased under a surfactant/CEC ratio of 2 (Fig. 4). The sorption capacities of the newly developed materials for PNP at surfactant/CEC ratios 0.5, 1.0, and 3.0 were relatively small (Fig. 4), however. Modification with natural clays and other surfactants was made, therefore, at a surfactant/CEC ratio of 2; these results indicated that the sorbed amount of PNP depends strongly on the amount of loaded surfactant and its distribution. Other studies (Zhou et al. 2008; Park et al. 2013) showed that, when surfactant loading is less than the CEC of the clay, surfactants replace the exchangeable cations in the interlayer space on montmorillonite. 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. While loaded surfactant molecules attract the dissociated PNP molecules

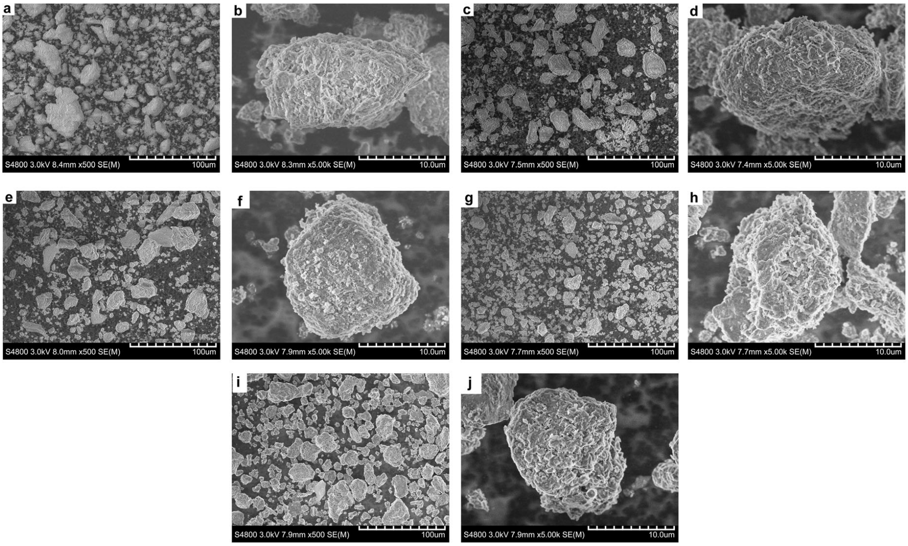

Fig. 3 SEM images of (**a, b)** Mt clay, (**c, d**) Mt_NMO_2, (**e, f**) Mt_DTAC_2, (**g, h**) Mt_BTMAC_2, (**i, j**) Mt_DDAO_2

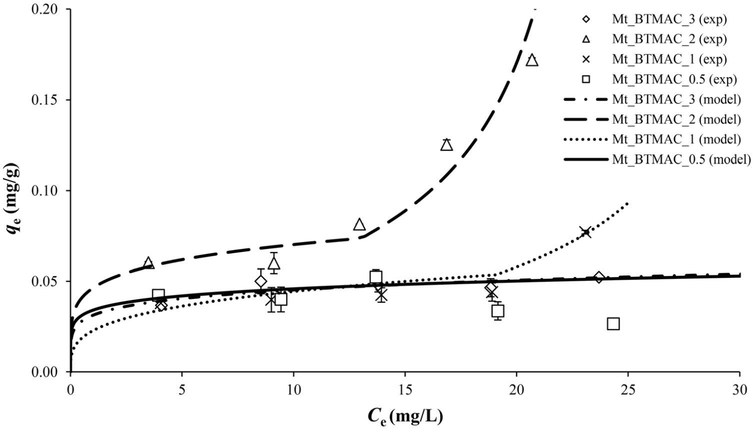

Fig. 4 Comparison of PNP sorption for Mt clay modified with BTMAC at various surfactant/CEC ratios (experimental conditions: initial PNP concentration = 5–25 mg/L, pH = 7, contact time = 24 h at room temperature)

through hydrophobic interaction, dissociated PNP anions bind to surfactant cations on the external surface of the clay through electrostatic interactions.

Effect of Initial Solution Concentration The initial concentration of PNP in the range 5–25 mg/L influenced the sorption of PNP on the modified clay materials at a surfactant/CEC ratio of 2 at room temperature and pH 7 (Figs. 5, 6 and 7). Initial increase in the PNP concentration resulted in an extended PNP sorption by modified clay materials. In the case of Mt_NMO_2, however, this relationship was not observed, because sorption was small (~0.02 mg/g) (Fig. 5). The largest PNP sorption capacity was observed on Mt_DDAO_2 (0.36 mg/g) when the PNP concentration was 25 mg/L (Fig. 6). X-ray diffraction results (Fig. 2, Table 1) indicated that the largest interlayer space can be linked to the efficacy of PNP sorption (Park et al. 2013). The sorption capacity of Mt clay modified with DDAO was >18 times greater than that of raw Mt clay and three times greater than Mt_Na (Fig. 6). Due to the large size of hydrated Na^+ ions (Zhu et al. 2014), the interlayer space during penetration was increased significantly, thus improving

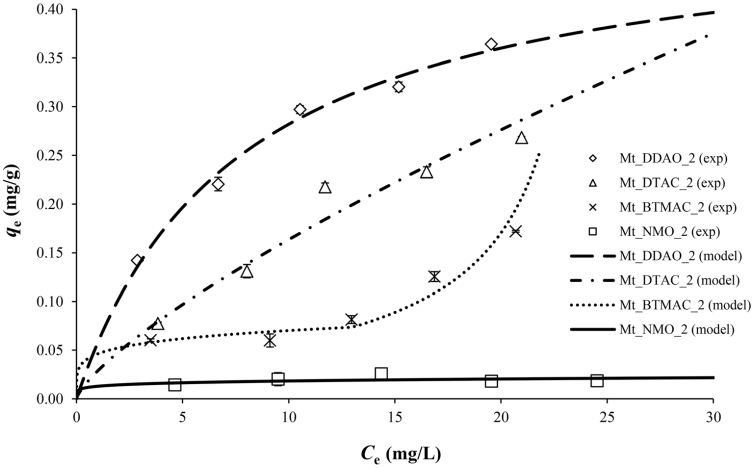

Fig. 5 Comparison of PNP sorption for modified Mt. clay with various surfactants at a surfactant/CEC ratio of 2.0 (experimental conditions: initial PNP concentration = 5–25 mg/L, pH = 7, contact time = 24 h at room temperature)

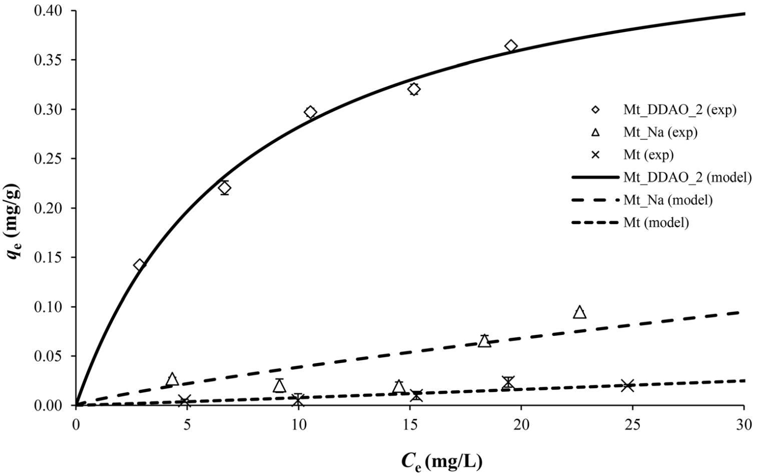

Fig. 6 Comparison of PNP sorption for raw Mt clay, Mt_Na, and modified with DDAO at organic phase loading of 2.0 (experimental conditions: initial PNP concentration = 5–25 mg/L, pH = 7, contact time = 24 h at room temperature)

sorption of organic molecules (Zhou et al., 2008). A larger BET specific surface area also was determined for samples treated with Na^+ ions (Table 2).

According to results obtained previously, natural clay was modified with DDAO at a surfactant/CEC ratio of 2. For natural, unmodified clays the sorption capacity was very small when the PNP concentration in the solution was 5 to 25 mg/L (Fig. 7). The greatest PNP sorption capacity was observed on T_DDAO_2, i.e. 0.15 mg/g, when the PNP concentration was 25 mg/L. J clay modified with DDAO sorbed almost no PNP (on average 0.0072 mg/g); therefore, this material was excluded from sorption experiments in which the effect of pH and contact time were estimated.

Effect of Contact Time The PNP sorption rate was high at the beginning of the experiment (Fig. 8) because sorption sites were initially abundant and PNP molecules were easily sorbed on those sites. The sorption capacity of the PNP onto Mt_DDAO_2 and T_DDAO_2 reached a maximum within

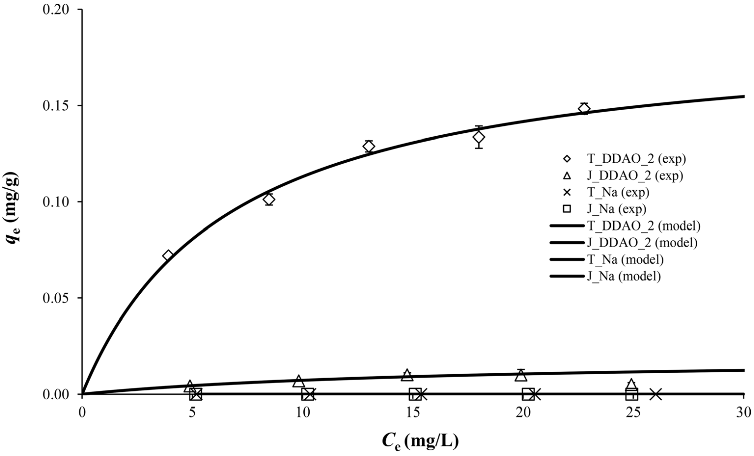

Fig. 7 Comparison of PNP sorption for J clay and T clay modified with DDAO at organic phase loading of 2.0 (experimental conditions: initial PNP concentration = 5–25 mg/L, pH = 7, contact time = 24 h at room temperature)

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 effect of pH on PNP removal was investigated in the pH range 2 to 12 with the initial concentration of PNP of 25 mg/L at room temperature. High removal efficiency was obtained in an acidic environment (pH 2 to 4) for T_DDAO_2 and from pH 2 to 6 for Mt_DDAO_2 (Fig. 9). When the pH exceeded 6, the removal efficiency decreased significantly. Similar results were reported by other scientists (Zhou et al. 2008; Luo et al. 2015; Zhang et al. 2015; Park et al., 2013) and were explained by the clay surface charge and dissociation level of PNP. PNP is poorly soluble in water in acidic conditions with a dissociation constant (pK_a) of 7.15; when the pH is below pK_a ($pH < pK_a$), PNP may be a neutral molecule, but when pH is greater than the pK_a ($pH > pK_a$), PNP can exist as an anion. Based on the PNP dissociation conditions, sorption onto modified clay materials is more efficient when PNP is a neutral molecule. In acidic environments, a surfactant intercalated in the clay interlayer space provides effective environmental pollution removal due to Van der Waals forces and hydrophobic effects. When the solution is alkaline, PNP sorption decreases due to electrostatic repulsion forces between the negatively charged clay particles and PNP anions.

Sorption Isotherms

In this study, Langmuir and Freundlich isotherms were used to describe the relationship between the amount of sorbed PNP and its equilibrium concentration in the solution at room temperature and pH 7.

The Langmuir isotherm assumes that sorption occurs at specific homogenous sites on the surface of a sorbent. When a site is occupied by a sorbate molecule, no future sorption can occur at this site. The Langmuir isotherm is expressed by the following equation:

$$q_e = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{4}$$

where q_{max} is the theoretical monolayer capacity (mg/g), K_L is the Langmuir equilibrium constant (L/mg) related to the affinity of binding sites, and C_e is the equilibrium solution concentration (mg/L) (Langmuir, 1918).

One of the essential characters of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter (R_L) and which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{5}$$

where C_0 is the highest initial PNP concentration (mg/L) and the value of R_L indicates whether sorption will be favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), irreversible ($R_L = 0$), or linear ($R_L = 1$) (Weber & Chakravorti, 1974).

The Freundlich isotherm is an empirical equation based on sorption on heterogeneous surfaces, and is given by the following equation:

$$q_e = K_F \cdot C_e^{1/n} \tag{6}$$

where K_F (L/mg) and n are Freundlich constants defining relative capacity and sorption intensity, respectively (Freundlich, 1906).

The Langmuir and Freundlich isotherm constants and correlation coefficients (R^2) for the sorption of PNP onto modified clay samples at a surfactant/CEC radio of 2 at a constant temperature and pH values are presented in Table 3. The R^2 values are >0.89 (Alkaram et al., 2009), indicating that both the

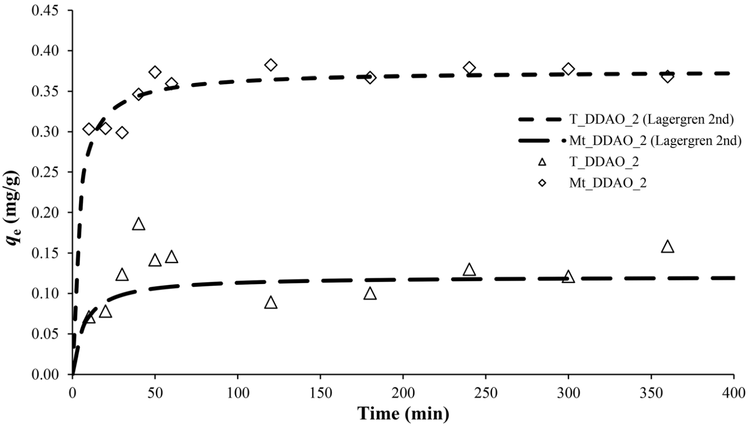

Fig. 8 Effect of contact time on the sorption of PNP onto modified Mt. clay and T clay (experimental conditions: initial PNP concentration = 25 mg/L pH = 7, at room temperature)

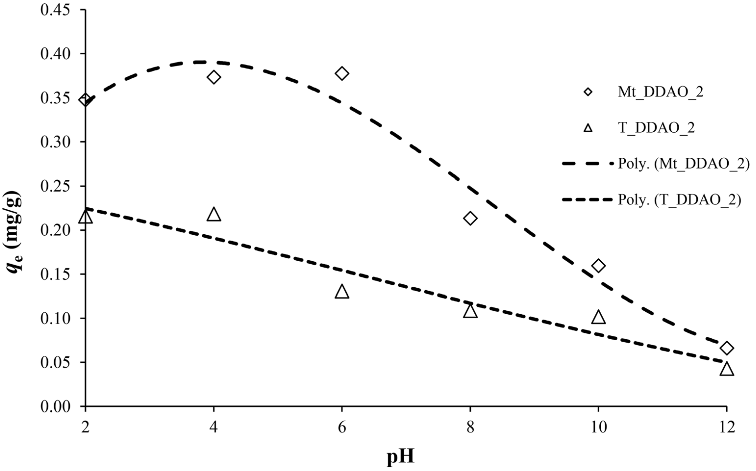

Fig. 9 Effect of pH on the sorption of PNP onto modified Mt. clay and T clay (experimental conditions: initial PNP concentration = 25 mg/L, contact time = 24 h at room temperature)

Langmuir and Freundlich isotherms can describe sorption data adequately. However, in the case of Mt_BTMAC_2, R^2 is < 0.89, meaning that sorption cannot be described adequately by these isotherms. The suitability of the two isotherm models for the systems investigated indicates that both monolayer and multilayer sorption exist under the experimental conditions studied. The sorption of PNP onto these surfaces is thus complex, involving more than one mechanism (Febrianto et al. 2009). Similar results have been reported by Ko et al. (2007) for the sorption of PNP by organo-modified montmorillonite clay.

The Freundlich parameters n and K_F reflect the sorption intensity of PNP and the binding affinity constant and provide information about the sorption mechanism. The value of n observed for sorption of PNP solution is >1 ($n > 1$) and this indicated that the sorption of PNP onto the clay samples was effective over the entire range of concentrations, and sorption is determined by physical processes (Alkaram et al. 2009; Park et al. 2013). The largest value for the binding affinity constant, K_F, was obtained in the sorption of PNP on the Mt_DDAO_2 sample and it fitted well with the experimental data.

In the Langmuir model, the values of K_L were 0.0340, 0.0367 and 0.1306, 0.1096 for Mt_BTMAC_2, Mt_DTAC_2 and Mt_DDAO_2, Mt_NMO_2, respectively. K_L values indicated that the affinity of binding sites for PNP increased when clay samples were treated with nonionic surfactants. R_L values ranged between 0 and 1; this also suggested that sorption of PNP by modified clay samples was favorable (Luo et al. 2015).

CONCLUSIONS

Organoclays prepared by intercalating cationic or nonionic surfactants are able to interact with organic molecules of a different polarity and serve as immobilizers for organic molecules and toxicants, e.g. phenols and nonionic organic compounds (NOCs). The sorbents developed revealed significantly improved performance in comparison to their unmodified counterparts, with a significant increase in *p*-nitrophenol

Table 3 Parameters of Langmuir and Freundlich isotherms for sorption of PNP onto modified clay samples at surfactant/CEC ratio of 2

Sample	Langmuir					Freundlich	
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	n	K_F (L/mg)	R^2
Mt_BTMAC_2	0.34	0.0340	0.5408	0.2424	1.82	0.0248	0.6809
Mt_DTAC_2	0.63	0.0367	0.5214	0.8964	1.32	0.0287	0.9657
Mt_DDAO_2	0.50	0.1306	0.2345	0.9895	2.03	0.0864	0.9865
Mt_NMO_2	0.04	0.1096	0.2673	0.9818	1.95	0.0064	0.9977
T_DDAO_2	0.19	0.1500	0.2105	0.9921	2.45	0.0423	0.9815
J_DDAO_2	0.02	0.0596	0.4017	0.891	1.53	0.0015	0.9548

(PNP) sorption capacity up to 25 and 30.5 times in the cases Mt_DDAO_2 and Mt_DTAC_2, respectively. For a modified natural smectite dominated Triassic clay (T clay) and a mixed-content clay containing organic matter (J clay), sorption capacity with respect to PNP in aqueous solution significantly increased. The pH level dominates the efficiency of PNP sorption – an acidic environment promotes sorption for all modified clays, e.g. T_DDAO_2 was the most efficient within pH 2–4 and Mt_DDAO_2 within pH 2–6. The hypothesis that organoclays are more efficient sorbents than raw clays has been proved; furthermore, organoclays based on natural montmorillonite may be used for the removal of PNP, but with less efficacy than manufactured montmorillonite. Further studies must be performed to reveal improved properties in order to benefit wastewater treatment engineering and environmental remediation.

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APPENDIX C

PAPER III

Ozola, R., Krauklis, A., Leitietis, M., Burlakovs, J., Vircava, I., Ansone Bertina, L., Bhatnagar, A., Klavins, M.

FeOOH-MODIFIED CLAY SORBENTS FOR ARSENIC REMOVAL FROM AQUEOUS SOLUTIONS

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FeOOH-modified clay sorbents for arsenic removal from aqueous solutions

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HIGHLIGHTS

- Clays were modified with iron oxy-hydroxide and properties compared.
- As(V) sorption capacity of clays significantly increased after modification.
- Effect of pH on As(V) sorption was investigated.
- FeOOH-modified natural clays from Baltic region are of interest for further testing.

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ABSTRACT

The presence of arsenic (As) in natural and anthropogenic soils causes severe pollution of groundwater due to its harmful carcinogenic effects. The present work describes the research activities for searching of appropriate innovative sorbents based on clay material for As sorption using iron oxy-hydroxide modification. Natural and manufactured clay was chosen for comparison of modification efficiency in order to obtain best sorption results for As(V). The results of pilot testing were obtained and the sorption was studied as a function of initial arsenic concentration. Obtained results indicate that modification of clay with Fe compounds significantly improves the sorption capacity of a newly developed material used for sorption of As(V). Efficiency of sorption for Fe-modified clay is highly dependent on clay type as well as iron content in it. Further perspectives of investigations are recovered during this study in order to create more efficient and relatively cheap sorbents for As removal from aqueous solutions.

1. Introduction

The growing attention is devoted to environmental pollution with metalloids including arsenic (As) (Ansari and Sadegh, 2007; Ceriotti and Amarasiriwardena, 2009; Filella et al., 2002; Nemade et al., 2009; Zhang et al., 2010; Mondal et al., 2013). According the legislation of many countries, e.g., The Agency for Toxic substances and Disease Registry of the USA, As is

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included in the Priority List of Hazardous Substances (Agency for Toxic Substances and Disease Registry, 2014). It is a well-known carcinogen often announced as one of the world's most hazardous chemicals (Environmental Protection Agency, 2001). It is important to study the occurrence of As speciation forms in the environment as well as associated environmental sources and possible solutions for environmental remediation.

Arsenic is a well known toxic element that can be found in drinking water in areas affected by the problem, Americas, Europe, Australia and Africa, but most in South and South Eastern Asia (Fendorf et al., 2010). Concentration of As in these areas exceeds maximum allowed levels and in distinct geological regions termed the "largest mass poisoning of a population in history" (Nemade et al., 2009; Dupont et al., 2007; Negrea et al., 2011; Zhang and Itoh, 2005a; Smith et al., 2000). As can enter natural water systems naturally, but also due to anthropogenic sources from end-of-pipe, as well as diffusive sources. Weathering of rocks and minerals is a typical example of a natural process for releasing As into the environment – one of the most controversially disputed mechanisms of As release is the oxidative dissolution of gray sulfide minerals that contain this element. This process is well described, e.g., in Muehe and Kappler (2014). In addition, anthropogenic sources include inflows of As from smelting industries, petroleum refinement works, glass, insecticides and fertilizers, production and more (Muehe, 2009; Anirudhan and Unnithan, 2007; Mohan and Pittman, 2007).

Arsenic exists in many oxidation states, however, most commonly known are -3, 0, $+3$, and $+5$ which exist both in inorganic and organic speciation forms. Inorganic As is the most commonly found form in contaminated waters as As(III) and As(V) depending on pH and redox conditions (Singh et al., 2015; Pokhrel and Viraraghavan, 2006). In media with pH 3–9, the dominant species of As(III) is neutral H_3AsO_3, while those of As(V) are negatively charged $HAsO_4^{2-}$ and $H_2AsO_4^-$ (Nemade et al., 2009). As(V) is adsorbed more easily onto solid surfaces than As(III), and therefore oxidation of As(III) from anoxic conditions followed by adsorption is effective for the removal of As in general (Ghurye et al., 2004; Leupin and Hug, 2005). Therefore, in this work, sorption of As(V) is studied, as it is considered of primary importance for water treatment purposes in engineering systems where oxidation processes already had taken place.

Different treatment methods for As decontamination: conventional and advanced have been proposed under both laboratory and field conditions. Most commonly reported include oxidation, adsorption, coagulation–flocculation, ion exchange as well as use of membranes. However, these primary technologies are to be referred as reference ones in order to define the need and feasibility of advanced methods as each of them has advantages and disadvantages (Dupont et al., 2007; Negrea et al., 2011; Zhang and Itoh, 2005a; Anirudhan and Unnithan, 2007). The main disadvantage is high costs and therefore authors considered research of innovative sorbents from cheap local resources as primary for gaining the highest efficiency and affordability.

Kaolinite, montmorillonite and illite are often used typical clay minerals used for As adsorption (Goldberg, 2002; Mohapatra et al., 2000) and it is reported that As is adsorbed on surface of clay through inner sphere surface complexation (Mondal et al., 2013; Mohapatra et al., 2000). However, the rate of reaction and the efficiency of adsorption of As on clay is comparably low and therefore unsuitable for the remediation process. In order to improve the adsorption of As on clay, surfactant modification converted clay surface from negatively charged to a positively charged one, and thus organoclay became a potential sorbent of As from aqueous solution (Li and Bowman, 2001). Also, efficiency of activated carbon has been studied by Payne and Abdel-Fattah (2005) and considered not sufficient to reach drinking water quality. Activated alumina, zirconium oxide, bauxol and granular ferric hydroxides have also been used for the removal of As(V) before (Mondal et al., 2013; Altundoğan et al., 2002). Among all sorbents—iron based ones are most widely used for the remediation process from As. Iron based technologies can act as immobilizers or reductants. Previous studies have shown that As(V) and As(III) form relatively strong inner sphere complexes on the ferrihydrite surface, which acts as sorption surface (Waychunas et al., 1996; Manning et al., 1998). Natural iron containing minerals, such as magnetite, siderite and hematite, have been studied as sorption agents (Jönsson, 2008). Metallic iron, a zero valent iron, was used in past for the treatment of groundwater in permeable reactive barrier systems (Mondal et al., 2013; Bang et al., 2005). There, zero valent iron forms spontaneously Fe(II) and Fe(III) oxides and hydroxides and As(III) and As(V) are forming complexes with the resulting corrosion products (Farrell et al., 2001; Manning et al., 2002).

Natural iron oxides, as described in many reports, have shown considerably low sorption efficiency for with As contaminated aqueous solutions (0.02–0.4 mg/g) mainly due to low specific surface area (Singh et al., 2015; Zhang et al., 2004; Guo et al., 2007b,a).

Zhang (2003) have studied nanoparticles for As removal from aqueous solutions. High specific surface area and reactivity of nanoparticles are considered as enough efficient (Huber, 2005), but free release of the nanoparticles to the environment has a potential impact on human health as well have not been studied enough so far (Colvin, 2003).

As mentioned above in literature analysis, clay is widely known perspective material for sorption, but mainly for heavy metals that are positively charged (Abollino et al., 2008), however, arsenic sorption requires the process of binding anionic type of pollutant. Clay is a widespread natural material in Central and Eastern Europe and elsewhere in all continents. Advantages of clay-based sorbents are as follows: it is environmentally friendly and relatively cheap sorbent, it has a comparatively low cost and can be treated for secondary use. Considering affinity of metalloids to interact with Fe-containing compounds, studies of As sorption can be promoted in direction of using iron modified clay sorbents.

The purpose of this work is to prove that natural clays from Baltic region (Latvia and Lithuania) can be successfully modified with iron oxy-hydroxide in order to improve sorption properties in respect to arsenic as well as to compare the modification process for these materials to commercially available montmorillonite material.

The aim of the study is to provide preliminary results of As(V) sorption onto modified clay with iron oxy-hydroxides.

2. Material and methods

2.1. Materials

The natural smectite dominated clay of Triassic (T) from Saltiski deposit (Lithuania), mixed content clay with organic matter of Jurassic (J) from Legernieki deposit (Latvia) and montmorillonite industrial production clay (Mt) *Montmorillonite K* 10 purchased from Sigma-Aldrich Co. (Germany) were used in this study. Cation exchange capacity (CEC) of montmorillonite, Triassic and Jurassic clay were 0.13 mmol/g, 0.27 mmol/g and 0.11 mmol/g, respectively.

Triassic clay contains 66% smectite group minerals in fraction <0.001 mm (Pipira, 2010), Jurassic clay is mixed of proportionally equal content of illite–smectite, illite, smectite, chlorite and kaolinite with admixture of ancient organic matter (3%), amount of clayey fraction (<0.001 mm) varies between 15% and 20% (Burlakovs et al., 2015). Industrial K10 clay is mainly composed of montmorillonite (65%).

All chemicals were of analytical grade and used without further purification. All solutions were prepared from high purity deionized water (10–15 MΩ cm) obtained with a Millipore Elix 3 (Millipore Co.) purification system. The arsenate stock solution was prepared from disodium hydrogen arsenate heptahydrate $Na_2HAsO_4 \cdot 7H_2O$ (Sigma-Aldrich, purity 98%).

2.2. Modification of clay

The modification method was based on impregnation of the material with iron oxy-hydroxide (DeMarco et al., 2003; Zhang and Itoh, 2005b). For $Fe(OH)_3$ preparation, 250 mL of 0.25 M $FeCl_3 \cdot 6H_2O$ were mixed with 250 mL 3M NaOH and leaved for 3 h. Then, the formed precipitates were washed and decanted three times in a 1 L vessel. The dispersion of 0.125 M $Fe(OH)_3$ was mixed in 100 g of homogenized clay sample. After filtration, the reaction product was washed with approximately 0.5 L deionized water, filtered, dried and heated for 4 h at 60 °C. As a result, iron oxy-hydroxide modified montmorillonite (Mt-FeOOH), Jurassic period mixed clay (J-FeOOH) and Triassic period smectite dominated clay (T-FeOOH) were obtained.

2.3. Characterization of sorbents

Modified clay sorbents were characterized using different methods such as scanning electron microscopy (SEM), X-ray powder diffraction (XRD), cation exchange capacity (CEC) and specific surface area determination by Brunauer–Emmett–Teller (BET) as well as analysis of Fe_2O_3 by flame atomic absorption spectrometry (FAAS).

Cation exchange capacity (CEC) has been estimated using barium chloride extraction method (Ciesielski et al., 1997). SEM images were obtained by a scanning electron microscope Tescan Mira/LMU. Samples were measured in the backscattered electron regime, with the SEM operating voltage of 15 kV. Specific surface area (SSA) of sorbents was measured using a surface area pore size analyzer Gemini2360 in Poland at J.S. Hamilton International. The BET method was used for the specific surface area measurements. The mineral composition was carried out by X-ray diffraction (XRD) method, using Bruker D8 Advance diffractometer with Cu$K\alpha$ radiation vario1 focusing primary monochromator and two 2.5 ° Soller slits and LynxEye line positive sensitive detector, scanned in 2°–55° 2θ range with 0.02 step size and total counting time 1 s per step. Textured samples from bulk rock pasta for modified with FeOOH and unmodified clay specimens were prepared due to high non-clays phase admixture and for the better clay phase resolution.

Content of Fe_2O_3 was determined in samples after heating at 550 °C. Samples were mineralized using concentrated HCl and conc. HNO_3, and heated at 120 °C for 2 h. In corresponding filtrates after dilution Fe was analyzed using an atomic absorption spectrometer with flame atomization (FAAS) (Perkin-Elmer Analyst 200 atomic absorption spectrometer). Content of iron (III) oxide ($w_{Fe_2O_3}$) in the sorbent was calculated according to the following equation (Eq. (1)):

$$w_{Fe_2O_3} = \gamma_{Fe} \cdot \frac{M_{Fe}}{M_{Fe_2O_3}} \cdot \frac{v}{m} \tag{1}$$

where γ_{Fe}—concentration of iron in the sample (mg/g), M_{Fe} and M_{Fe2O_3}—molecular weight of Fe and Fe_2O_3 (g/mol), v—volume of the sample (L), and m—mass of sorbent (g).

2.4. Sorption experiments

Sorption experiments were conducted using batch system. $Na_2HAsO_4 \cdot 7H_2O$ was used for preparation of arsenic stock solutions at various concentrations (400, 300, 200, 100, 50, 25, 10 and 5 mg/L). 0.5000 g of a sorbent material was weighed in each 100 mL glass vessel. 40 mL of an As(V) solution was then added to every vessel with the adsorbent. Vessels were then shaken for 24 h at room temperature at 150 rpm using orbital shaker BioSan PSU U-20 to ensure sorption equilibrium was achieved. Suspensions were filtered into 50 mL test-tubes, and concentration of As(V) in the filtrate was then analyzed using PerkinElmer AAnalyst 200 with flame atomization (FAAS—Flame Atomic Absorption Spectrometry). Measurements were performed 3 times and standard deviations were determined.

Table 1
Characterization of oxy-hydroxide modified clay sorbents: montmorillonite (Mt-FeOOH), Jurassic mixed clay (J-FeOOH) and Triassic smectite dominated clay (T-FeOOH).

Sample	Respective unmodified material's CEC (mmol/g)	CEC (mmol/g)	Fe_2O_3 (mg/g)	Specific surface area by BET (m^2/g)
Mt-FeOOH	0.13 ± 0.01	0.98 ± 0.06	31.50 ± 1.58	245.63
T-FeOOH	0.27 ± 0.02	1.01 ± 0.06	39.75 ± 1.83	91.75
J-FeOOH	0.11 ± 0.01	0.84 ± 0.05	43.22 ± 2.33	63.79

Experiments with different pH were conducted using batch system. $Na_2HAsO_4 \cdot 7H_2O$ solution of 100 mg/L was used. pH values of arsenate solution were set using 0.4 M NaOH and 7% HNO_3 solutions. 0.2500 g of a sorbent material was weighed in each 100 mL glass vessel. 40 mL of an As(V) solution was then added to every vessel with the adsorbent. Vessels were then shaken for 24 h at room temperature at 150 rpm using orbital shaker BioSan PSU U-20 to ensure sorption equilibrium was achieved. Suspensions were filtered into 50 mL test-tubes, and concentration of As(V) in the filtrate was then analyzed using PerkinElmer AAnalyst 200 with flame atomization (FAAS). Measurements were performed 3 times and standard deviations were determined.

In order to ensure arsenic analysis quality control, experiments were performed systematically as described, accurate As(V) concentration of stock solutions was measured 3 times and standard deviation was determined, which then was taken into account when describing sorption capacity of the materials.

3. Results and discussion

3.1. Characterization of sorbents

The SEM images clearly indicate that the surface morphology of clay materials changed evidently after modification. For example, Triassic smectite dominated clay shows characteristic layer structure (Fig. 1(A)). After modification, T-FeOOH shows coated surface with iron compounds (Fig. 1(B)). Similar changes are observed in Jurassic clay (Fig. 1(C),(D)) and montmorillonite clay (Fig. 1(E),(F)).

Also other characteristics of sorbents are given in Table 1 to describe changes after modification process. The CEC values significantly increased after modification of clay materials. The highest CEC was established for T-FeOOH (1.0076 mmol/g), followed by Mt-FeOOH (0.9752 mmol/g) and J-FeOOH (0.8379 mmol/g). The highest specific surface area determined by BET in turn, was observed for oxy-hydroxide modified montmorillonite (245.63 m^2/g).

The obtained results indicated that the applied method of modification was effective as content of Fe_2O_3 significantly increased after modification. For example, the raw montmorillonite contained 1.4 mg/g of Fe_2O_3 while the Fe_2O_3 content reached 31.50 mg/g after modification. Considering, that metalloids have high affinity to interact with iron compounds, one can predict that sorbents with the highest content of iron oxide will also have the highest sorption capacity. In this case, modified Triassic and Jurassic natural clays from Lithuania and Latvia has relevant properties ensuring possibly higher sorption capacities and thus could improve As removal.

Natural clay specimens are rich with non-clays phases as quartz, calcite, dolomite, feldspars etc. (Fig. 2). Content of clay phases in bulk samples vary and is around 65% w.t. in Montmorillonite K10 and 45% w.t. in Triassic clays to 30% w.t. in Jurassic clays. XRD patterns shows noticeable decrease in intensity and smoothing of the first basal peak of smectite (15–15.5 Å) in clay sorbents with iron oxy-hydroxide (Fig. 2). Also the roentgen-line light shifting in modified clay specimens between 10 and 15 Å indicate sorbent influence on smectite phases in all samples.

XRD diffractograms of raw and FeOOH-modified clays (Fig. 2) 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. In addition, increased background noise of modified clays, while not unambiguous, is an indication of increase in amorphous phase.

The diffractograms also suggest presence of the following (Fig. 2): (A) montmorillonite, quartz, muscovite and kaolinite phases for Mt and Mt-FeOOH clays; (B) montmorillonite, illite, quartz, dolomite, kaolinite, calcite, chlorite, muscovite, dolomite as well hematite for T and T-FeOOH clays; (C) quartz, chlorite, illite, kaolinite, dolomite, muscovite, calcite and feldspar phases for J and J-FeOOH clays.

Hematite present in raw Triassic smectite dominated clays is expected to contribute positively to the sorption of As(V).

3.2. Arsenic removal studies

The modification of clay materials with oxy-hydroxide improved the sorption capacity of the materials. Three different types of clay materials were used for As(V) sorption during experiments. Sorbed amount of As differs, but in all cases it was considerably higher for oxy-hydroxide modified clay in comparison with raw clay materials, e.g., the raw montmorillonite sorbed 2.36 mg/g of As(V), while after modification, sorbed amount increases more than six times (15.62 mg/g) (Fig. 3(A)). It was found that Langmuir model fits arsenic sorption experimental data better for iron oxy-hydroxide modified materials, while Freundlich model fits better for sorption using raw materials; this was observed for all materials used. Model

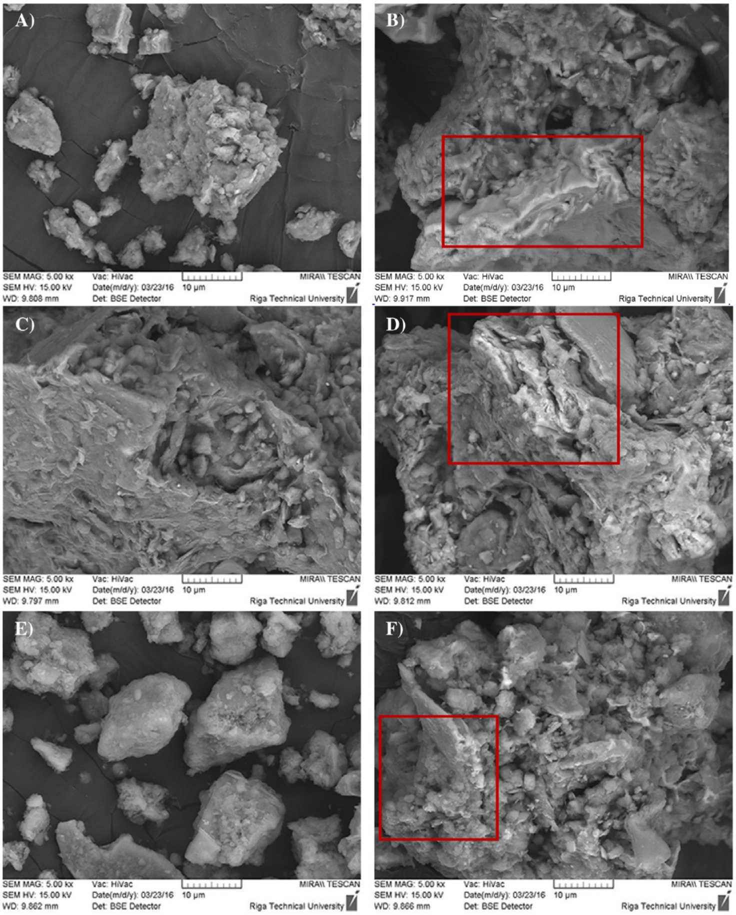

Fig. 1. SEM images of (A) raw Triassic smectite dominated clay; (B) FeOOH-modified Triassic smectite dominated clay; (C) raw Jurassic mixed clay; (D) FeOOH-modified Jurassic mixed clay; (E) raw montmorillonite clay; (F) FeOOH-modified montmorillonite clay.

comparison was performed plotting experimental data in linearized Langmuir and Freundlich forms with a further comparison of determination coefficients R^2. Values of respective determination coefficient are presented in Table 2.

Obtained data indicated that sorption capacity depends on the clay material of used sorbent—the highest sorption capacity was established for Mt-FeOOH, followed by J-FeOOH and T-FeOOH (Fig. 4). The sorption capacity of Mt-FeOOH, J-FeOOH and T-FeOOH reached up to 15.62, 11.84 and 11.40 mg/g (Fig. 3), 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. Ability for sorption is 63.2%, 47.4% and 41.1% at the initial As(V) concentration of 300 mg/L for Mt-FeOOH, J-FeOOH and T-FeOOH, respectively. It might be possible that reduction of sorption ability of the sorbent with increasing concentration of metalloid is affected by Fe/As ratio due to increasing reduction of the number of free sorption sites caused by metalloids. Initial stage of sorption studies allow concluding that further studies of kinetics and thermodynamics of sorption reactions are needed to evaluate full potential of modified natural clay resources in Baltic States for removal of arsenic from aqueous media.

As(V) adsorption capacity of Fe-modified clays is relatively high in comparison with other adsorbents described in literature, in a critical review of adsorbents for arsenic removal (Mohan and Pittman, 2007). Some of the materials mentioned

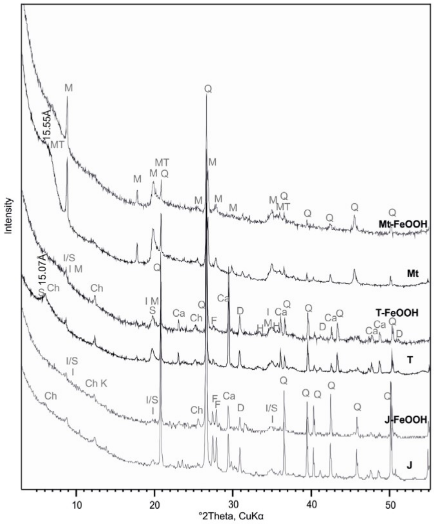

Fig. 2. XRD diffractograms of raw (Mt) and modified montmorillonite (Mt-FeOOH) clays, raw (T) and modified Triassic smectite dominated (T-FeOOH) clays, raw (J) and modified Jurassic mixed (J-FeOOH) clays. Mineral denotations: M—muscovite, MT—montmorillonite, Q—quartz, S—smectite, I—illite, F—feldspar, Ca—calcite, Ch—chlorite, D—dolomite, K—kaolinite, H—hematite.

Table 2
Comparison of Langmuir and Freundlich models and determination coefficients for As(V) sorption on raw (Mt) and modified montmorillonite (Mt-FeOOH) clays, raw (T) and modified Triassic smectite dominated (T-FeOOH) clays, raw (J) and modified Jurassic mixed (J-FeOOH) clays.

Sample	R^2(Langmuir)	R^2(Freundlich)
J-FeOOH	0.9993	0.9548
T-FeOOH	0.9974	0.9794
Mt-FeOOH	0.9994	0.8024
J	0.9675	0.9867
T	0.8620	0.9995
Mt	0.9105	0.9838

are pure alumina (13.64 mg/g), activated alumina (9.20–24 mg/g), activated carbon (3.08–30.48 mg/g), bauxsol (1.081 mg/g), activated bauxsol (7.642 mg/g), gibbsite (4.60 mg/g), goethite (12.5 mg/g), kaolinite (<0.23 mg/g), granular ferric hydroxide (2.3–8.5 mg/g), Shirasu zeolite SZP_1 (65.93 mg/g) (Mohan and Pittman, 2007).

3.3. *Effect of initial pH on As(V) removal*

Effect of initial pH on As(V) removal was investigated using different oxy-hydroxide modified clay samples (montmorillonite (Mt-FeOOH), Jurassic mixed clay (J-FeOOH) and Triassic smectite dominated clay (T-FeOOH)) at the initial As(V) concentration in solution of 100 mg/L (Fig. 5). In all cases, sorption of As(V) on modified clays is highest at the lowest initial pH of 2 and is 16.22 ± 0.91, 16.22 ± 0.91 and 14.56 ± 0.82 mg/g for Mt-FeOOH, J-FeOOH and T-FeOOH, respectively. In case of Mt-FeOOH significant reduction in sorption efficiency is observed starting at pH 6 (14.97 ± 0.84 mg/g) down to pH 9 (7.51 ± 0.42 mg/g). Both J-FeOOH and T-FeOOH clays show a continuous sorption efficiency reduction without a clearly defined breaking point.

4. Conclusions

Clay sorbents modified with iron oxy-hydroxides have been developed for testing the potential of effective removal of arsenic from aqueous solutions and screened under laboratory conditions. The physical and chemical properties of innovative modified clay sorbents developed from natural clay resources in Latvia and Lithuania have been investigated and

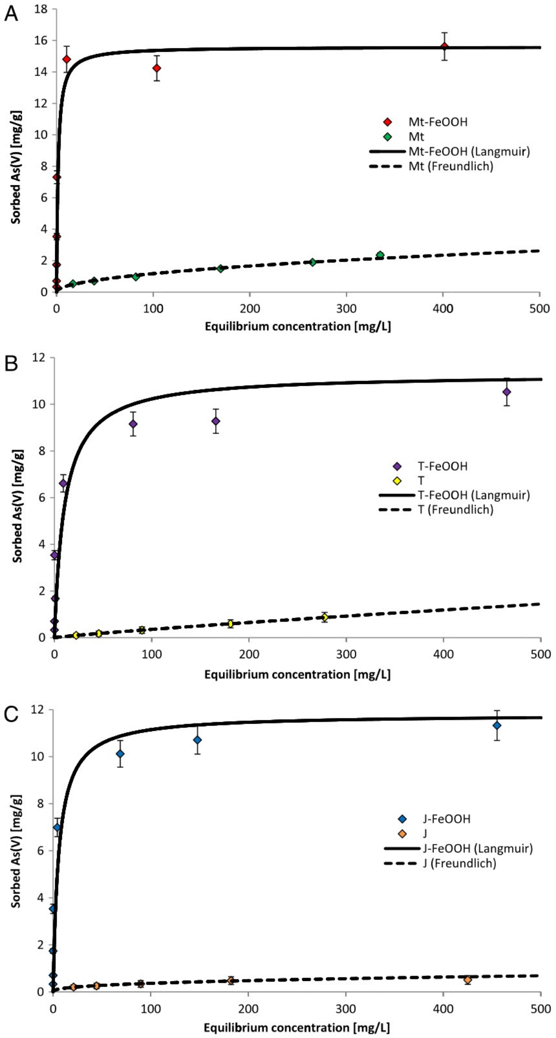

Fig. 3. Removal of As(V) using: (A) oxy-hydroxide modified (Mt-FeOOH) and raw montmorillonite (Mt); (B) oxy-hydroxide modified (T-FeOOH) and raw Triassic smectite dominated clay (T); (C) oxy-hydroxide modified (J-FeOOH) and raw Jurassic mixed clay (J).

compared with raw and modified industrial montmorillonite based clay. The results of batch tests revealed that modified clays with iron oxy-hydroxide are effective agents for immobilization of arsenic compared to raw clays. Sorption capacity of modified natural smectite dominated Triassic and mixed mineralogical content Jurassic clay significantly increases in respect to arsenic in aqueous solutions. Further studies of kinetics and thermodynamics of sorption processes are needed to evaluate full potential of modified natural clay resources in Baltic States in order to use them for production of industrial sorbents.

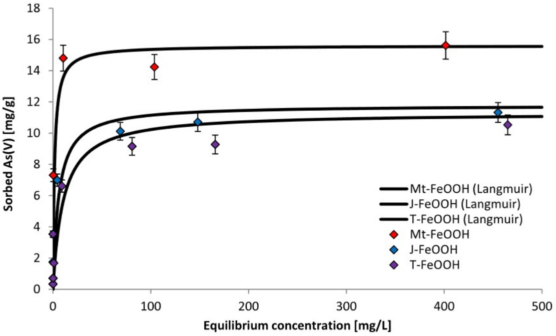

Fig. 4. As(V) sorption using different oxy-hydroxide modified clay samples (montmorillonite (Mt-FeOOH), Jurassic mixed clay (J-FeOOH) and Triassic smectite dominated clay (T-FeOOH)).

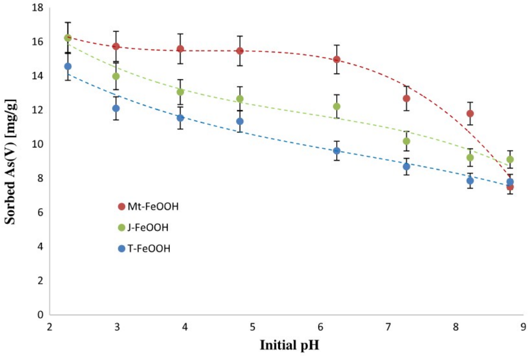

Fig. 5. Effect of initial pH on As(V) sorption using different oxy-hydroxide modified clay samples (montmorillonite (Mt-FeOOH), Jurassic mixed clay (J-FeOOH) and Triassic smectite dominated clay (T-FeOOH)). As(V) initial concentration in solution was 100 mg/L.

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Rūta Ozola-Davidāne

MĀLA KOMPOZĪTMATERIĀLU IZSTRĀDE UN RAKSTUROŠANA INOVATĪVAM UN VIDEI DRAUDZĪGAM PIELIETOJUMAM

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ANOTĀCIJA

Eiropas Zaļā kursa aktivitāte “Ilgtspēju sekmējoša ES ķimikāliju stratēģija” uzsver videi draudzīgu tehnoloģiju izstrādāšanas nozīmīgumu un tāda droša un ilgtspējīga materiāla izmantošanas palielināšanu, kas nekaitē cilvēkiem un videi. Promocijas darbs piedāvā risinājumu, kas sintētiskās un toksiskās vielas vides tehnoloģijās ļauj aizstāt ar dabiskiem, plaši pieejamiem un lētiem materiāliem – māla minerāliem. Pētījuma mērķis ir izstrādāt un raksturot ar organiskām un neorganiskām vielām modificētus māla minerālus un eksperimentāli pārbaudīt sintezēto kompozītmateriālu pielietojumu inovatīvās un videi draudzīgās tehnoloģijās. Smektīta tipa māla minerāli tika modificēti, balstoties uz diviem principiem: 1) mālus pārklājot ar citu neorganisku materiālu (dzelzs oksihidroksīdu vai hidroksilapatītu) un tādējādi nodrošinot jaunu sorbcijas centru izveidi; 2) panākot organisku modifikatoru (virsmaktīvo vielu vai jonu šķidrumu) interkalāciju māla minerālu starpslāņa telpā, lai nodrošinātu hidrofobas īpašības. Māla kompozītmateriāli tika raksturoti, izmantojot daudzfaktoru metodes pieeju, kas ietvēra modificēto materiālu strukturālo, morfoloģisko un ķīmiskā sastāva izmaiņu analīzi. Papildus tika pētīta jaunizstrādāto materiālu sorbcijas veiktspēja, lai noteiktu pielietojuma iespējas vides tehnoloģijās.

Rezultāti atklāj, ka modifikācijas metodes sniedz iespēju mērķtiecīgi mainīt mālu īpašības, integrējot to struktūrā jaunas funkcionālās grupas, mainot fizikālās un ķīmiskās īpašības un tādējādi nodrošinot jaunu pielietojuma iespēju attīstību. Māla-hidroksilapatīta un māla-dzelzs oksihidroksīda materiāliem ir augsta sorbcijas kapacitāte neorganisko piesārņotāju (arsēna), retzemju elementu (lantāna, neodīma, cērija) un citu vērtīgu elementu (sudraba, alumīnija) saistīšanai. Māla-virsmaktīvo vielu un māla-jonu šķidrumu materiāli uzrādīja augstu toksisko organisko piesārņotāju (Kongo sarkanā, *p*-nitrofenola) saistīšanas spēju, pateicoties iegūtām hidrofobām īpašībām. Rezultāti liecina, ka māla minerālus, kas modificēti ar jonu šķidrumiem, virsmaktīvām vielām, dzelzs oksihidroksīdu un hidroksilapatītu, var veiksmīgi izmantot cietu vielu-šķidrumu sorbcijas sistēmās, lai saistītu piesārņotājus vai atgūtu vērtīgus elementus no atkritumu plūsmām. Turklāt māla-antociānu kompozītmateriālus var izmantot pārtikas rūpniecībā kā svaiguma indikatoru pārtikas kvalitātes kontrolei.

Atslēgvārdi: māli, smektīta minerāli, māla modifikācija, organiskie un neorganiskie modifikatori, sorbenti, organiskie un neorganiskie piesārņotāji, elementu atgūšana, ūdens un notekūdeņu attīrīšana, svaiguma indikatori.

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DARBĀ LIETOTIE SAĪSINĀJUMI

AIPEA	(angļu val. *Association Internationale pour l'Etude des Argiles*) Mālu pētniecības starptautiskā asociācija
Bent māli	*Bentonite, sodium form* iegādāts no *Alfa Aesar*
BET	*Brunauer*, *Emmett* un *Teller* metode
BTMAC	benziltrimetilamonija hlorīds
C_{12}mimCl	1-dodecil-3-metilimidazolija hlorīds
C_4mimCl	1-butil-3-metilimidazolija hlorīds
C_8mimCl	1-oktil-3-metilimidazolija hlorīds
CMS	(angļu val. *the Clay Minerals Society*) Māla minerālu biedrība
DDAO	N,N-dimetildodecilamīna N-oksīds
DTAC	dodeciltrimetilamonija hlorīds
FeOOH	dzelzs oksihidroksīds
FTIS	Furjē transformācijas infrasarkanā spektroskopija
Hap	hidroksilapatīts
ĪVL	īpatnējais virsmas laukums
J clay	juras sistēmas māli no Lēģernieku atradnes
KAK	katjonu apmaiņas kapacitāte
KS	Kongo sarkanais
LDH	(angļu val. *layered double hydroxide*) slāņaini dubulthidroksīdi
Mt clay	*Montmorillonite K10* iegādāts no *Sigma-Aldrich*
NMO	4-metilmorfolīna N-oksīds
PNF	*p*-nitrofenols
SEM	skenējošā elektronmikroskopija
T clay	triasa sistēmas māli no Saltišķu atradnes
TG	termogravimetrija
XRD	rentgenstaru difraktometrija

IEVADS

Ir pieaugošs pieprasījums pēc dabas materiāliem, ko varētu izmantot rūpniecībā, vides tehnoloģijās un citās jomās, lai samazinātu sintētisko vielu izmantošanu. Piemēram, vides tehnoloģijās aizvien plaši izmanto sintētiskos materiālus kā pildvielas, sorbentus, materiālus vides sanācijai un citās jomās. Viena no šādām perspektīvām materiālu grupām izmantošanai vides tehnoloģijās ir māli (Sverdrup un Ragnarsdóttir, 2014).

Saskaņā ar Starptautisko mālu pētniecības asociāciju (*Internationale pour l'Etude des Argiles*, AIPEA) un Māla minerālu biedrības (CMS) apvienoto nomenklatūras komiteju jēdziens "māls" ir definēts kā "dabiskas izcelsmes materiāls, kura galvenie komponenti ir sīkdispersi māla minerāli, kas parasti noteiktā ūdens daudzumā paliek plastiski un pēc apdedzināšanas vai žāvēšanas iegūst akmens cietību" (Guggenheim and Martin, 1995). Latvijā ir ievērojams daudzums dažādu māla minerālu, kas atrodami 287 atradnēs (Stinkule, 2014, LEGMC, S.a.). Neskatoties uz to, māliem ir vairāki būtiski ierobežojumi, kas saistīti ar to virsmas īpašībām, fizisko formu un ķīmisko sastāvu. Risinājums mālu pielietojuma potenciāla paplašināšanai ir to pārveidošana, izmantojot mērķtiecīgu pasākumu kopumu, lai izveidotu materiālus ar nepieciešamajām īpašībām.

Šādas modifikācijas metodes piemērs ir organomālu sintēze (Guégan, 2019). Organomālus iegūst, modificējot māla minerālus (galvenokārt smektītus) ar organiskiem savienojumiem (galvenokārt virsmaktīvām vielām), izmantojot interkalācijas procesu un virsmas adsorbciju (Park et al., 2011; He et al., 2014; Guégan, 2019). Modifikācija maina māla virsmas īpašības no hidrofilām uz hidrofobām un palielina māla minerāla starpslāņu telpu. Iegūtos materiālus var efektīvi izmantot kā sorbentus organisko un neorganisko piesārņotājvielu saistīšanai augsnē un ūdenī (Li and Bowman, 2001; Rodríguez-Cruz et al., 2007; Aftafa et al., 2014; Fiscal-Ladino et al., 2017).

Vēl viena māla modifikācijas metode ir neorganisku vielu, piemēram, dzelzs oksihidroksīda, izmantošana māla virsmas impregnēšanai (Lenoble et al., 2002; Krauklis et al., 2017; Ozola et al., 2019b). Neapstrādātus mālus plaši izmanto katjonu piesārņotājvielu sorbcijai, bet mālu modificēšana ar dzelzs savienojumiem nodrošina arī tādu negatīvi lādētu piesārņotājvielu kā arsēna, fosfora un antimona sorbciju (Boujelben et al., 2008; Singh et al., 2015). Procesi, kas nosaka šo elementu saistīšanas spēju, ir adsorbcija uz virsmas hidroksilgrupām, anjonu apmaiņa un nogulsnēšanās (Smedley un Kinniburgh, 2002). Taču svarīgas var būt arī citas īpašību grupas, tāpēc aktuāla ir nepieciešamība izstrādāt mālu modifikācijas metodes un rast pielietojumu vides problēmu risināšanā.

Promocijas **darba mērķis** ir izstrādāt un raksturot ar organiskām un neorganiskām vielām modificētus māla minerālus un eksperimentāli pierādīt sintezēto māla kompozītmateriālu pielietojumu inovatīvās un videi draudzīgās tehnoloģijās. No mērķa izriet šādi **uzdevumi**:

1. Modificēt dabiskas izcelsmes un rūpnieciski ražotus māla paraugus, attīstot jaunus modifikācijas risinājumus, izmantojot organiskus un neorganiskus savienojumus.
2. Raksturot iegūto kompozītmateriālu īpašības ar multiparametru metodēm.

3. Analizēt jaunizveidoto materiālu sorbcijas veiktspēju dažādos apstākļos, kā, piemēram, atkarībā no sorbāta koncentrācijas, sorbenta daudzumu, pH, temperatūras un kontakta laika.
4. Izpētīt un apspriest pielietojuma iespējas vides tehnoloģijās.

Darbā izvirzīta **hipotēze**, ka modifikācija būtiski palielina māla minerālu pielietošanas potenciālu vides tehnoloģijās.

Promocijas darba novitāte

1. Izstrādātas inovatīvas metodes mālu modificēšanai: smektīta tipa minerālu modifikācija veikta ar virsmaktīvām vielām, jonu šķidrumiem un antociāniem jonu apmaiņas reakcijā, un izstrādāta modifikācija ar dzelzs oksihidroksīdu un hidroksilapatītu virsmas adsorbcijas procesā.
2. Iegūtie kompozītmateriāli raksturoti, izmantojot multiparametru analītiskās metodes, un ir pārliecinoši pierādīta modifikācijas efektivitāte.
3. Izstrādāta rīcības koncepcija, lai veidotu materiālus konkrētam mērķim vides problēmu risināšanai, pamatojoties uz sorbenta-sorbāta mijiedarbību kombinācijā ar matricas ietekmi.
4. Modifikācija nosaka unikālas iegūtas māla materiālu īpašības: mālu kompozītmateriālus, kas modificēti ar jonu šķidrumiem, virsmaktīvām vielām, dzelzs oksihidroksīdu un hidroksilapatītu, var izmantot kā efektīvus sorbentus notekūdeņu attīrīšanā; savukārt mālus, kas modificēti ar antociāniem, var izmantot pārtikas rūpniecībā kā inteliģentus sensorus pārtikas kvalitātes kontrolei.

Promocijas darba praktiskā nozīme

1. Mālu modifikācija ļauj izstrādāt inovatīvus materiālus ar paplašinātu darbības sfēru un potenciālo pielietojumu vides jomā.
2. Māla materiālu modificēšana būtiski paplašina Latvijas dabas resursu praktisko pielietojumu dažādās nozarēs, izmantojot pieejas, kas iekļautas jaunāko tehnoloģiju sarakstā (Top 10 Emerging Technologies.., 2019).
3. Modificētos māla materiālus var uzskatīt par perspektīviem dabas materiāliem, kas pielietojami vides tehnoloģijās, pirmām kārtam kā sorbenti piesārņojošo vielu saistīšanai no notekūdeņiem.

Promocijas darba rezultātu aprobācija

Pētījuma rezultāti publicēti 9 rakstos (6 no tiem iekļauti *Web of Science* un/vai *Scopus* datubāzēs); kopumā autorei ir 20 publikācijas (17 no tām iekļautas *Web of Science* un/vai *Scopus* datubāzēs). Darba rezultāti tika prezentēti 27 ziņojumos starptautiskās un 18 ziņojumos nacionālajās konferencēs. Publikācijas VIII darba rezultāti ir ziņoti žurnāla *Nature Sustainability* sadaļā "Burnside 2018". Koncepcija par mālu-antociānu kompozītmateriālu izmantošanu viedajos pārtikas iepakojumos kvalitātes kontrolei ieguva Eiropas Inovāciju un tehnoloģiju institūta reģionālās inovācijas shēmas inovācijas balvu Latvijā (1. vieta), kā arī tiek izstrādāts viens patents par šo tēmu. Promocijas darba izstrādes ietvaros autore vadījusi divus bakalaura darbus un sniegusi konsultācijas viena maģistra darba izstrādē. Turklāt studenti tika aktīvi iesaistīti Latvijas Mālu zinātniskās apvienības organizētajos pasākumos, t. sk. izglītojošos semināros par māla zinātni, un tika aicināti piedalīties starptautiskā simpozijā "Clays & Ceramics".

Ar promocijas darbu saistītās zinātniskās publikācijas (piezīme: no 2020. gada uzvārds mainīts no "Ozola" uz "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, IF_{2020} = 6.165) (turpmāk tiek apzīmēta kā **Publikācija 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, IF_{2020} = 1.609) (turpmāk tiek apzīmēta kā **Publikācija II**).
3. **Ozola, 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. (Web of Science/SCOPUS, Q2/Q1, IF_{2019} = 3.356) (turpmāk tiek apzīmēta kā **Publikācija 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, IF_{2018} = 0.24) (turpmāk tiek apzīmēta kā **Publikācija 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, IF_{2019} = 7.246) (turpmāk tiek apzīmēta kā **Publikācija V**).
6. Krauklis, A., **Ozola, R.**, Burlakovs, J., Rugele, K., Kirillov, K., Trubaca-Boginska, A., Rubenis, K., Stepanova, V., Klavins, M. 2017. FeOOH and $Mn_8O_{10}Cl_3$ 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, IF_{2019} = 2.750) (turpmāk tiek apzīmēta kā **Publikācija 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 (turpmāk tiek apzīmēta kā **Publikācija 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 (turpmāk tiek apzīmēta kā **Publikācija VIII**).
9. Burlakovs, J., **Ozola, R.**, Kostjukovs, J., Klavins, I., Purmalis, O., Klavins, M. 2015. Properties of the Jurassic clayey deposits of southwestern Latvia and northern Lithuania. *Materials Sciences and Applied Chemistry*. 32, 5–12 (turpmāk tiek apzīmēta kā **Publikācija IX**).

Citas zinātniskās publikācijas (piezīme: no 2020. gada uzvārds mainīts no "Ozola" uz "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, IF_{2020} = 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, IF_{2020} = 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, IF_{2020} = 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., Bełdowska, M., Bełdowski, J., Bhatnagar, Amit, 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., Kataržytė, 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, IF_{2020} = 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, IF_{2019} = 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. Ansone-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, IF_{2018} = 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., Kriipsalu, 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, IF_{2019} = 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, IF_{2019} = 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, IF_{2019} = 0.69)
11. Lama, E., **Ozola, R**., Rudovica, V., Bavrins, K. and 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, IF_{2018} = 0.24)

Patents: Ozola-Davidāne, R. 2022. Preparation method and application of freshness indicators for meat quality monitoring [apstiprinājuma procesā] (turpmāk tiek apzīmēts kā Patents).

Ziņojumi starptautiska un vietēja mēroga zinātniskās konferencēs (15 no 45) (piezīme: no 2020. gada uzvārds mainīts no "Ozola" uz "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"*. Rīga, Latvija, 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 (hibrīda: tiešsaistē un klātienē).
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.* Rīga, Latvija (Tiešsaistē), 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 (Tiešsaistē), 35.
5. Salmiņa, 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.* Rīga, Latvija (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.* Tiešsaistē, 85.
7. **Ozola-Davidane, R.,** Klavins, M., Jemeljanova, M., Ansone-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.* (Tiešsaistē), 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*. Kalmāra, Zviedrija (Tiešsaistē), n/a.
9. Burlakovs, J. Kriipsalu, M., Bhatnagar, A., Ansone-Bertina, L., **Ozola-Davidane, R.,** Klavins, M. 2020. Modified clay composites as potential landfill covering material. *Goldschmidt 2020 Virtual Conference. Goldschmidt2020 Abstract*, (Tiešsaistē), 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.* Rīga, Latvija, 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.* Parīze, Francija, 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.* Parīze, Francija, 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.* Kalmāra, Zviedrija, 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.* Rīga, Latvija, 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, Spānija, 602.

Promocijas darba struktūra

Promocijas darbs ir veidots kā 9 zinātnisku publikāciju un 1 patenta apkopojums. Pētīto kompozītmateriālu savstarpējā saistība ar zinātniskām publikācijām ir attēlota 1. tabulā.

1. tabula

Ar promocijas darbu saistīto zinātnisko publikāciju apskats

		Darbā ietvertās sadaļas			
Kompozītmateriāli	**Zinātnisko publikāciju Nr.**	**Mālu un māla minerālu īpašības**	**Modifikācijas metodes**	**Kompozītmateriālu raksturojums**	**Kompozītmateriālu pielietojuma izpēte**
Neapstrādāti māli	IX	×			
Māli-virsmaktīvās vielas	II		×	×	×
	IV	×			×
	VIII		×	×	×
Māli-dzelzs oksihidroksīdi	III		×	×	×
	VIII		×		
	VI		×	×	×
Māli-hidroksilapatīts	V				×
	VII		×	×	×
	Promocijas darbā			×	×
Māli-jonu šķidrumi	I		×	×	×
	IV	×			×
Māli-antociāni	Patents				×

Promocijas darba kopsavilkums sastāv no 34 lappusēm, kas papildinātas ar ilustrācijām – 10 attēliem un 4 tabulām.

1. TEORĒTISKAIS PAMATOJUMS

1.1. Mālu un māla minerālu terminoloģija

Saskaņā ar Starptautisko mālu pētniecības asociāciju (franču val. *Internationale pour l'Etude des Argiles, AIPEA*) un Māla minerālu biedrības (CMS) apvienoto nomenklatūras komiteju jēdziens "māls" zinātnē tiek definēts kā dabiskas izcelsmes materiāls, kura galvenie komponenti ir sīkdispersi māla minerāli, kas parasti noteiktā ūdens daudzumā paliek plastiski un pēc apdedzināšanas vai žāvēšanas iegūst akmens cietību. Lai gan māli galvenokārt sastāv no filosilikātiem, māli var būt arī citi materiāli, kas sacietē žāvējot vai apdedzinot un kļūst plastiski ūdens klātbūtnē. Mālos var būt minerālu piemaisījumi, piemēram, kalcīts, kvarcs, laukšpats, dolomīts, oksīdi, hidroksīdi un organiskie savienojumi (Guggenheim un Martin, 1995). Saskaņā ar šo definīciju sintētiskos mālus neuzskata par māliem, lai gan tie var būt smalkgraudaini, sacietē žūstot/apdedzinot un ir plastiski noteiktā ūdens daudzumā (Bergaya un Lagaly 2006; Christidis 2010). Plastiskums attiecas uz materiāla spēju veidot jebkuru formu. Apvienotās nomenklatūras komiteja arī norāda, ka māla plastisko īpašību kvantitatīva noteikšana nav nepieciešama, jo plastiskumu ietekmē daudzi faktori, tostarp ķīmiskais sastāvs un daļiņu agregācija. Turklāt daži neplastiski māli, piemēram, krama māli (to sastāvā vairāk nekā 95% ir kaolinīta), joprojām tiek uzskatīti par "māliem" vēsturiskā lietojuma dēļ (Guggenheim un Martin, 1995; Bergaya un Lagaly 2006). Saskaņā ar Guggenheim un Martin (1995) māla definīcijā netiek ņemta vērā daļiņu izmēra augšējā robeža. Tas ir tāpēc, ka dažādās disciplīnās māli tiek raksturoti ar dažādiem daļiņu izmēriem. Koloīdu zinātnē daļiņu izmēra robeža ir 1 μm, ģeoloģijā un augsnes zinātnēs 2 μm, bet sedimentoloģijā 4 μm (Moore and Reynolds, 1997). Starptautiskā standartizācijas organizācija (ISO) izmanto < 2 μm kā smalkās frakcijas augšējo robežu (Schroeder 2018). Iepriekš minētajā definīcijā "smalki graudains" attiecas tikai uz kristalīta izmēru (Guggenheim un Martin, 1995).

AIPEA un CMS nomenklatūras komitejas definē "māla minerālus" kā "filosilikātu minerālus un minerālus, kas kļūst plastiski mitrā stāvoklī un sacietē pēc žāvēšanas vai apdedzināšanas" (Guggenheim un Martin, 1995). Šī definīcija neietver materiāla izcelsmi (atšķirībā no māla definīcijas), un tāpēc māla minerāli var būt sintētiski,

2. tabula

Atšķirība starp mālu un māla minerālu definīcijām (papildināts pēc Bergaya un Lagaly 2006)

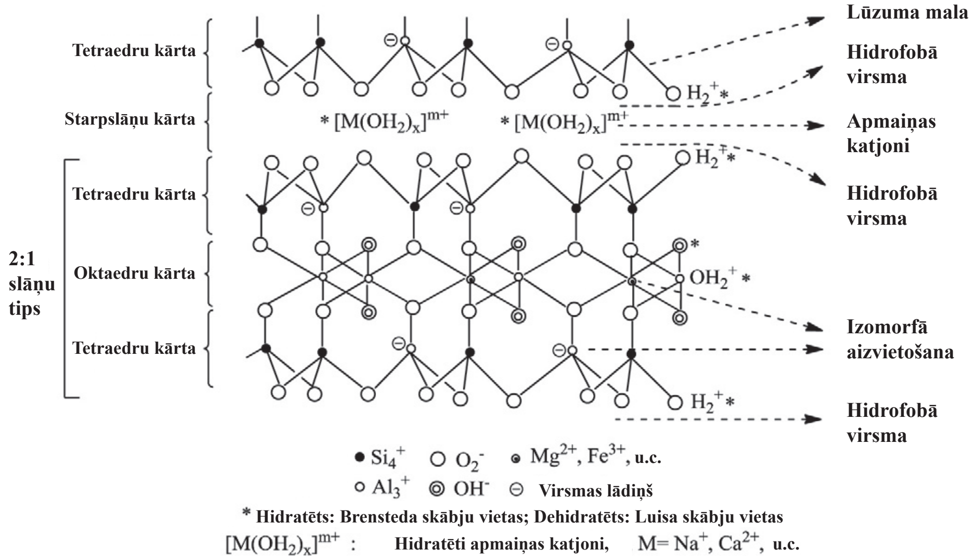
	Māls	Māla minerāli
Izcelsme	Dabiski	Dabiski un sintētiski
Klasifikācija	Dominējošie minerāli ir filosilikāti	Bez filosilikātiem var ietvert arī citus minerālus
Izmērs	Smalkgraudaini (< 1 μm, 2 μm un 4 μm)	Nav izmēra kritērija
Īpašības	Plastiski (izņemot *fint* mālus), sacietē apdedzinot vai žāvējot	Plastiski, sacietē apdedzinot vai žāvējot

piemēram, slāņaini dubulthidroksīdi. Arī minerālu daļiņu lielums definīcijā nav iekļauts kā kritērijs, un tāpēc māla minerāliem var būt jebkurš graudu izmērs (Bergaya un Lagaly 2006; Christidis 2010). Lielākā daļa māla minerālu dabā ir sastopami ar daļiņu izmēru diapazonā, kas ir mazāks par 4 µm (Schroeder 2018). Turklāt saskaņā ar Guggenheim & Martin (1995) minerālus, kas nav filosilikāti, kuri piešķir māliem plastiskumu un sacietē pēc žāvēšanas vai apdedzināšanas, var definēt kā māla minerālus. Galvenās atšķirības starp "mālu" un "māla minerālu" definīcijām ir parādītas 2. tabulā.

1.2. Māla minerālu fizikālās un ķīmiskās īpašības

Konkrēta māla minerāla struktūras un sastāva raksturīgās pazīmes piešķir tiem dažādas fizikālās un ķīmiskās īpašības. Māla minerālus raksturo šādas fizikālās un ķīmiskās īpašības: 1) daļiņu izmērs un forma; 2) īpatnējais virsmas laukums; 3) krāsa; 4) minerālu sastāvs; 5) jonu apmaiņas spēja; 6) deformācija un plūstamība; 7) plastiskums; 8) uzbriešana; 9) virsmas elektriskais lādiņš (Murray, 2007). Vides sektorā svarīgākā mālu īpašība ir katjonu apmaiņas spēja, kas kopā ar raksturīgo nelielo daļiņu izmēru un salīdzinoši lielo īpatnējo virsmu nosaka to efektīvo sorbcijas spēju (Brovkina et al., 2012).

Mālu minerāliem piemīt unikālas īpašības sorbēt katjonus, anjonus un neorganisko vai organisko vielu polārās molekulas (Brovkina et al., 2012). Māla minerālu struktūrā aktīvās sorbcijas vietas rodas, pateicoties 1) "lūzuma" vietām un atklātām virsmas alumīnija un silīcija grupām; 2) izomorfiem aizvietojumiem; 3) apmaiņas katjoniem; 4) hidrofobām silīcija virsmām; 5) apmaiņas katjonu hidratācijas apvalka; 6) hidrofobām vietām uz adsorbētajām organiskajām molekulām (1. attēls) (Zhou un Keeling, 2013).

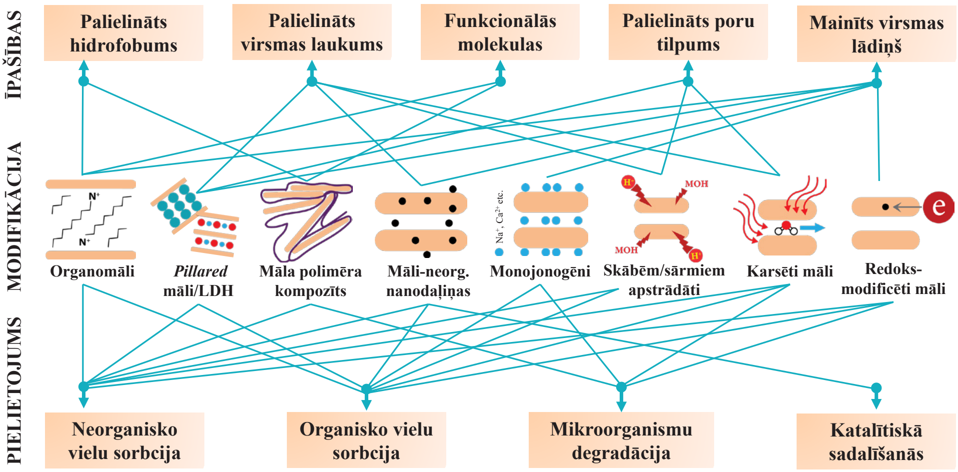


1. attēls. **2 : 1 slāņa māla minerālu shematisks attēlojums, kas parāda aktīvās vietas, kas nodrošina jonu apmaiņas un sorbcijas īpašības** (Zhou un Keeling, 2013)

Anjonu apmaiņas spēja ir saistīta ar kristāla malas lādiņu, kas kļūst pozitīvs, adsorbējot ūdeņraža katjonu (H^+) pie skābā pH, veidojot ūdens molekulu. Šī molekula ir vāji saistīta, tāpēc to var viegli pārvietot un apmainīt ar citām anjonu grupām. Alternatīvi, anjonu grupas var aizstāt OH grupas, kas atrodas kristāla malās (Christidis, 2010). Jo mazāks ir māla minerālu daļiņu izmērs, jo vairāk ir šādu vietu un jo lielāka ir anjonu apmaiņas spēja. Kaolinīta gadījumā "lūzuma" malas virsmas var veidot līdz 15% no kopējās virsmas, savukārt smektītiem tikai 1%. Tādējādi kaolīna grupas minerāliem ir ievērojama anjonu apmaiņas spēja anjonu molekulām, kā, piemēram, fosfātiem (Christidis, 2010). Virsmas lādiņu un "lūzuma" malu vietas uz māla minerāliem var palielināt, iedarbojoties ar skābi (Zhou un Keeling, 2013). Katjonu apmaiņas spēja ir saistīta ar izomorfo aizvietošanu tetraedriskajā un/vai oktaedriskajā tīklā, kas rada lādiņa deficītu. Slāņa lādiņu līdzsvaro starpslāņu telpas katjoni, piemēram, kālija (K^+), nātrija (Na^+), kalcija (Ca^{2+}), magnija (Mg^{2+}) joni, kas ir apmaināmi ar citām molekulām un joniem (Lee un Tiwari, 2012; Zhou un Keeling, 2013). Katjonu apmaiņas spēja ir raksturīga visiem māla minerāliem, bet īpaši svarīga tā ir smektītu grupas minerāliem (Christidis, 2010).

1.3. Māla minerālu modifikācijas metodes un to pielietojums

Māla minerālu fizikālās un ķīmiskās īpašības, to pieejamība, zemās izmaksas, inertums un stabilitāte ir nodrošinājuši daudzus rūpnieciskus pielietojumus (Zhou & Keeling, 2013; Rouquerol et al., 2013). Piemēram, kaolīna grupas minerālus tradicionāli izmanto kā pildvielu un pārklājuma materiālu papīrā, pildvielu krāsās, plastmasā, gumijā, tintē un izmanto keramikā, podniecības, sanitārtehnikas izstrādājumu, izolatoru un ugunsizturīgo materiālu ražošanā. Turklāt smektītu grupas minerālus parasti izmanto kā pretfiltrācijas slāni poligonos, lai izolētu piesārņojumu no apkārtējās vides, un kā saistvielu dzīvnieku barībā, mājdzīvnieku atkritumu absorbentus, lauksaimniecības



2. attēls. **Shematisks māla minerālu modifikācijas attēlojums ar to jauniegūtajām īpašībām un potenciālo lietojumu vidē** (izstrādājusi autore, izmantojot Biswas et al., 2019) insekticīdu nesējus, tos izmanto farmācijas un kosmētikas izstrādājumos (Murray 2000). Tomēr dabā sastopamo māla minerālu pielietojums dažādās progresīvajās tehnoloģijās ir ierobežots to raksturīgo iezīmju dēļ. Piemēram, mālu hidrofilās dabas, mazā starpslāņu attāluma un virsmas augstās enerģijas dēļ tie ir neefektīvi adsorbenti organisko piesārņotāju, tostarp antibiotiku, krāsvielu, pesticīdu un biocīdu, saistīšanai (Ismadji et al., 2015). Tomēr māla virsmas un/vai starpslāņu struktūras modifikācija ir paņēmiens, lai iegūtu specifiskas īpašības, piemēram, hidrofobumu, lādiņa īpašību izmaiņas, palielinātu poru tilpumu, kopējo virsmas laukumu un pieejamās aktīvās vietas, kas savukārt palielina māla minerālu adsorbcijas efektivitāti (2. attēls) (Sarkar et al., 2019).

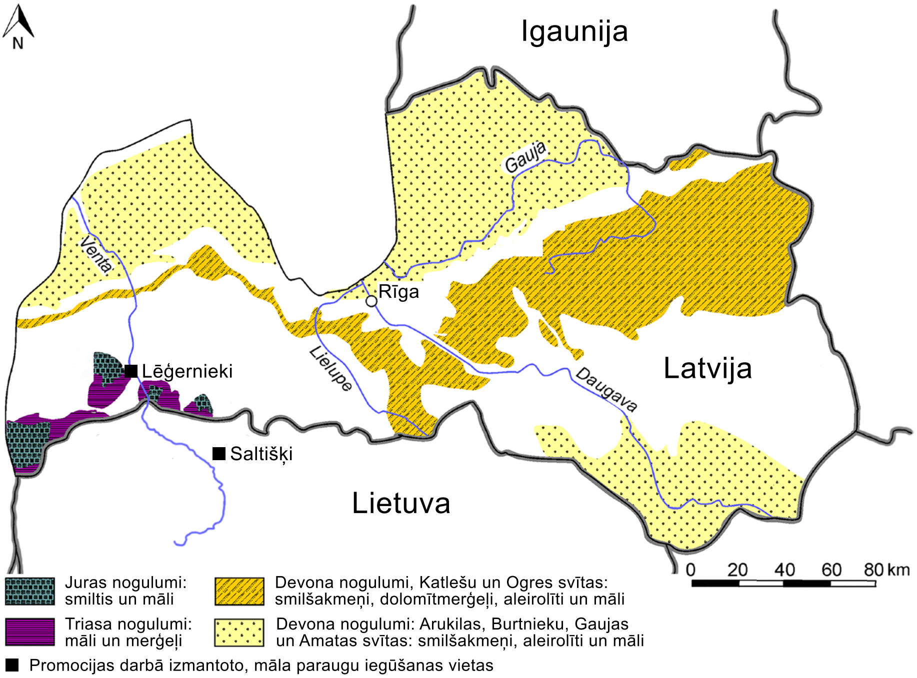
Māla minerālu modifikāciju var veikt, izmantojot dažādas metodes, tāpēc modifikācijas tehnikas un apstrādei izmantoto materiālu izvēle ir nozīmīga, lai sasniegtu vēlamās īpašības paredzētajam mērķim. Paredzētās īpašības var sasniegt ar termisko un skābju/sārmu apstrādi, oksidēšanās-reducēšanās, jonu apmaiņas, organiskām un polimēru interkalācijas reakcijām (2. attēls) (Sarkar et al., 2019).

2. MATERIĀLI UN METODES

2.1. Pētījumā izmantotie mālu un māla minerālu paraugi

Šajā pētījumā tika izvēlēti dabiskas izcelsmes un rūpnieciski ražoti māla paraugi: 1) triasa sistēmas māli, kuros dominē smektīts no Saltišķu atradnes (Saltišķi, Lietuva, koordinātas: N 56°12’55”, E 22°56’50”) – tālāk tiek apzīmēts kā T māli (3. attēls); 2) juras sistēmas māli ar jaukta satura māla minerāliem un organiskajām vielām no Lēģernieku atradnes (Nikrace, Latvija, koordinātas: N 56°32’37”, E 21°59’53”) – tālāk tiek apzīmēts kā J māli (3. attēls); 3) *Montmorillonite K10* rūpnieciski ražots māls ar augstu montmorilonīta saturu, iegādāts no *Sigma-Aldrich* (Vācija) – tālāk tiek apzīmēts kā Mt māli; 4) *Bentonite, sodium form* rūpnieciski ražots māls ar augstu montmorilonīta saturu, iegādāts no *Alfa Aesar* (Vācija) – tālāk apzīmē ar nosaukumu *Bent clay*.

Dabiskās izcelsmes māli pirms modifikācijas tika attīrīti no dažādiem piemaisījumiem, kā, piemēram, karbonātiem, organiskām vielām un kvarca, saskaņā ar metodi, kas aprakstīta Karasa et al. (2012).



3. attēls. **Pētījumā izmantoto dabisko māla paraugu atradnes**
(autores papildināts pēc Stinkule, 2014)

2.2. Māla minerālu modifikācijas metodes

Māla paraugi tika apstrādāti, izmantojot neorganiskos un organiskos modifikatorus. Kā neorganiskie modifikatori tika izvēlēts dzelzs oksihidroksīds (FeOOH) un hidroksilapatīts (Hap), bet par organiskajiem modifikatoriem izvēlēti jonu šķidrumi un virsmaktīvās vielas. Papildus māla paraugi tika apstrādāti ar dabīgiem pigmentiem – antociāniem.

Modifikācijas metodes pamatā ar **dzelzs oksihidroksīdu (FeOOH)** ir māla materiāla impregnēšana ar 0,25 M $FeCl_3{\cdot}6H_2O$ un 3 M NaOH maisījuma nogulsnēm, balstoties pēc paņēmiena, kas aprakstīts Ozola et al. (2019b). Līdzīgi arī, modificējot māla minerālus ar **hidroksilapatītu (Hap)** ($Ca_{10}(PO_4)_6(OH)_2$), tika izmantota nogulsnēšanas metode, iedarbojoties ar 0,5 M $CaCl_2$ un 2 M KH_2PO_4, kur Ca/P ekvimolārā proporcija ir 1,6 (Ozola et al., 2017). Modifikācija ar **virsmaktīvām vielām (VAV)** tika veikta, kā aprakstīts Ozola et al. (2019a). Metodes pamatā ir māla minerālu sastāvā esošo neorganisko jonu apmaiņa ar virsmas aktīvo vielu katjonaktīvām (dodeciltrimetilamonija hlorīds (DTAC); benziltrimetilamonija hlorīds (BTMAC)) vai nejonogēnām (N,N-dimetildodecilamīna N-oksīds (DDAO); 4-metilmorfolīna N-oksīds (NMO)) molekulām. Modifikācija tika veikta, izmantojot dažādas virsmaktīvās vielas daudzuma un māla parauga katjona apmaiņas kapacitātes attiecības: 0,5; 1,0; 2,0 un 3,0. Nepieciešamais virsmaktīvās vielas daudzums pagatavotajos šķīdumos tika aprēķināts pēc šāda vienādojuma:

$$m_{vav} = m_m \times KAK \times 10^{-}3 \times Q_{KAK} \times M, \tag{1}$$

kur m_{VAV} ir nepieciešamais virsmaktīvās vielas daudzums (g), m_m ir izmantotā māla parauga daudzums (g), KAK ir noteiktā katjonu apmaiņas kapacitāte (mmol/g); Q_{KAK} ir nepieciešamā virsmaktīvās vielas un KAK attiecība, M ir virsmaktīvās vielas molmasa (g/mol). Mālu modifikācijas metode ar **jonu šķidrumiem** ir aprakstīta Ozola-Davidāne et al. (2021), un tās pamatā ir māla minerālu sastāvā esošo neorganisko katjonu apmaiņa ar katjoniem, kas atrodas jonu šķidrumu struktūrā. Modifikācijā tika izmantoti imidazolija bāzes jonu šķidrumi ar dažādiem alkilķēdes garumiem: 1-butil-3-metilimidazolija hlorīds ($Bent\_C_4mimCl$), 1-oktil-3-metilimidazolija hlorīds ($Bent\_C_8mimCl$) un 1-dodecil-3-metilimidazolija hlorīds ($Bent\_C_{12}mimCl$). Attiecība starp pievienoto jonu šķidrumu un māla parauga KAK tika izvēlēta 1,0, kas aprēķināta pēc vienādojuma Nr. 1. Mālu modifikācija ar **antociāniem** darbā detalizēti netiek apspriesta, jo šī metode tiek patentēta.

2.3. Sorbcijas eksperimenti

Tika veikti sorbcijas eksperimenti, lai izpētītu neapstrādātu un modificētu mālu kompozītmateriālu sorbcijas spēju, tie tika paredzēti modeļa piesārņotājvielu saistīšanai no ūdens šķīdumiem. Sorbcijas eksperimenti tika pētīti atkarībā no dažādiem vides apstākļiem, piemēram, no sorbāta koncentrācijas, sorbenta daudzuma, pH, temperatūras un kontakta laika. Māla-jonu šķidrumu, māla-virsmaktīvo vielu un māla-FeOOH kompozītmateriālu sorbcijas eksperimenti ir detalizēti aprakstīti attiecīgi publikācijā I, publikācijā II un publikācijā III.

Sorbcijas pētījumos dažādi sorbenta daudzumi tika ievietoti 100 mL stikla traukā un papildināti ar noteiktu daudzumu sorbāta šķīduma dažādās koncentrācijās (3. tabula).

3. tabula

Pārskats par darbā izmantotajiem materiāliem un metodēm

Sorbents	Sorbāts	Sorbcijas apstākļi	Raksturojošās metodes	Publikāciju numurs
Mt/T/J māla – FeOOH	arsēns(V)	Ci = 5–400 mg/L; v = 40 mL; m = 0,5 g; t = 24 h; pH = 2–9; T = 24 °C	XRD, FTIS, SEM, ĪVA pēc BET, TGA, CEC, Fe_2O_3 daudzums	Publikācija III
	sudrabs(I), alumīnijs(III)	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		n/a

Mt/T/J māla – Hap	lantāns(III), neodīms(III), cērijs(III)	Ci = 5–600 mg/L;
		v = 100 mL;
		m = 0,1 g; t = 24 h;
		pH = 6; T = 24 °C
			XRD, FTIS, SEM, ĪVA pēc BET, TGA	Publikācija VII

	sudrabs(I), alumīnijs(III)	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		n/a
Mt/T/J māla – DDAO NMO BTMAC DTAC	*p*-nitrofenols	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, FTIS, SEM, ĪVA pēc BET, TGA	Publikācija II
Bt/T māla– C_4mimCl C_8mimCl C_{12}mimCl CmmimDMP C_4mmimDMP C_8mmimDMP C_{12}mmimDMP	Kongo sarkanais	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, FTIS, ĪVA pēc, TGA	Publikācija I
Mt māla – antociāni	Antociāniem bagāts ekstrakts no ogu izspiedņēm	Patents (apstiprinājuma procesā)	Informācija nav iekļauta promocijas darbā	Patents (apstiprinājuma procesā)

Iegūtais maisījums tika nepārtraukti maisīts daudzfunkcionālajā orbitālajā kratītājā Biosan PSU-20i (Rīga, Latvija) istabas temperatūrā 24 stundas. Pēc kratīšanas maisījumus centrifugēja 12 minūtes ar ātrumu 3000 apgr./min un pēc tam filtrēja. Lai izpētītu pH ietekmi uz sorbcijas kapacitāti, sorbāta šķīduma pH tika noregulēts diapazonā no 2 līdz 12, pievienojot 0,1 M HCl vai NaOH. Sorbcijas kinētikas pētījumos šķīdumi tika maisīti 10–60 minūtes ar 10 minūšu intervālu un 120–360 minūtes ar 60 minūšu intervālu. Iegūto rezultātu standartnovirzes tika noteiktas, pamatojoties uz 3 paralēliem atkārtojumiem.

Māla-virsmaktīvās vielas, māla-FeOOH, māla-jonu šķidruma un māla-Hap kompozītmateriālu gadījumā tika izvēlētas attiecīgās modeļpiesārņotājvielas: *p*-nitrofenols, arsēns, Kongo sarkanais un retzemju elementi (La, Ce un Nd). *p*-nitrofenola (PNF) un Kongo sarkanā (KS) gadījumā centrifugāti tika analizēti, izmantojot UV-Vis spektrofotometru (Shimadzu UV 1800, Kioto, Japāna) attiecīgi pie 318 nm un 500 nm. As(V) koncentrācija filtrātā tika analizēta, izmantojot PerkinElmer AAnalyst 200 ar liesmas izsmidzināšanu (FAAS – *Flame Atomic Absorption Spectrometry*).

La(III), Ce(III) un Nd(III) koncentrācijas filtrātā tika mērītas ar iCAP7000 savienotās plazmas-optiskās emisijas spektroskopu (ICP-OES) (*Thermo Scientific*). Modeļa piesārņotājvielu daudzums, kas sorbēts uz māla kompozītmateriāla, tika aprēķināts, izmantojot šādu vienādojumu:

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

kur q_e ir modeļa piesārņotājvielas sorbētais daudzums uz sorbenta (mg/g), C_i un C_e ir attiecīgi sorbāta sākotnējā un līdzsvara koncentrācija (mg/L), v ir šķīduma tilpums (mL), un m ir izmantotā sorbenta masa (g). Antociānu koncentrācijas noteikšana tika veikta, izmantojot spektrofotometrisko pH diferenciālo metodi (Lee et al., 2005). Metode ir balstīta uz antociānu molekulu spēju mainīt krāsu pie dažādiem pH.

Tika aprēķinātas Lengmīra un Freindliha izotermas, lai aprakstītu saistību starp sorbētās vielas daudzumu un tās līdzsvara koncentrāciju. Lagergrena linearizētie pseido-pirmās un pseido-otrās pakāpes kinētikas modeļi tika izmantoti, lai aprakstītu saistību starp sorbcijas laiku un sorbcijas kapacitāti.

2.4. Mālu kompozītmateriālu raksturošanas metodes

Mālu kompozītmateriālu paraugu fizikāli ķīmiskās īpašības tika raksturotas ar dažādām multiparametru metodēm: 1) īpatnējās virsmas laukums un poru izmērs tika mērīts, izmantojot *Brunauer*, *Emmett* un *Teller* (BET) metodi; 2) paraugu minerālo sastāvu un strukturālās izmaiņas tika identificētas ar rentgenstaru difraktometrijas (XRD) metodi; 3) jaunas funkcionālās grupas māla minerālu sastāvā tika noteiktas ar Furjē transformācijas infrasarkano spektroskopiju (FTIS); 4) virsmas morfoloģijas izmaiņas – ar skenējošo elektronmikroskopiju (SEM) un 5) masas zuduma izmaiņas – ar termogravimetrijas (TGA) metodi.

3. REZULTĀTI UN DISKUSIJA

3.1. Māla kompozītmateriālu izstrāde un raksturojums

3.1.1. Neapstrādāti māli un māla minerāli, to modifikācijas koncepts

Pētījumā izmantoti dabiskas izcelsmes māla paraugi no Latvijas un Lietuvas atradnēm, kā arī rūpnieciski ražoti mineraloģiski tīri paraugi (skat. 2.1. nodaļu). Izmantoto māla paraugu raksturīgie parametri ir apkopoti 4. tabulā. Paraugi tika izvēlēti, ņemot vērā perspektīvu izstrādāt jaunus Latvijā nozīmīgus māla resursu pielietojumus, kā arī pārbaudīt izstrādāto metožu koncepciju uz mineraloģiski labi raksturotiem māla paraugiem.

Lai izstrādātu jaunas māla materiālu pielietošanas iespējas, tika veikta izvēlēto mālu modifikācija ar mērķi palielināt sorbcijas spēju attiecībā uz izvēlētajām vielām, ņemot vērā perspektīvas izstrādāt jaunus pielietojumus vides tehnoloģijās un bioekonomikā. Māla kompozītmateriālu izstrādes koncepcija balstās uz diviem principiem (4. attēls):

1. Māla impregnēšana ar citu materiālu (dzelzs oksihidroksīdu vai hidroksilapatītu), kas nodrošina jaunu sorbcijas centru izveidi. Izvēlēto modifikatoru sorbcijas spējas ir plaši pētītas (Ansone-Bērtiņa 2015; Ozola et al., 2017; Ozola-Davidāne et al., 2019a), un māla sorbcijas profila kombinācija ar modifikatoriem ļauj sasniegt jaunas sorbcijas iespējas un tādējādi palielināt pielietojuma potenciālu.
2. Māla minerālu struktūras modificēšana, lai uzlabotu un mainītu mālu sorbcijas spēju, kas orientēta uz modifikatora interkalāciju māla minerālu starpslāņu telpā. Šajā pētījumā ir ierosināta mālu modifikācija ar jaunu (līdz šim mālu modifikācijai neizmantotu) virsmaktīvo vielu grupām un jonu šķidrumiem. Rezultātā jaunizveidotie materiāli kļūst hidrofobi, ar palielinātu sorbcijas spēju attīrīšanā no organiskām vielām.

3.1.2. Māla-dzelzs oksihidroksīda kompozītmateriālu raksturojums

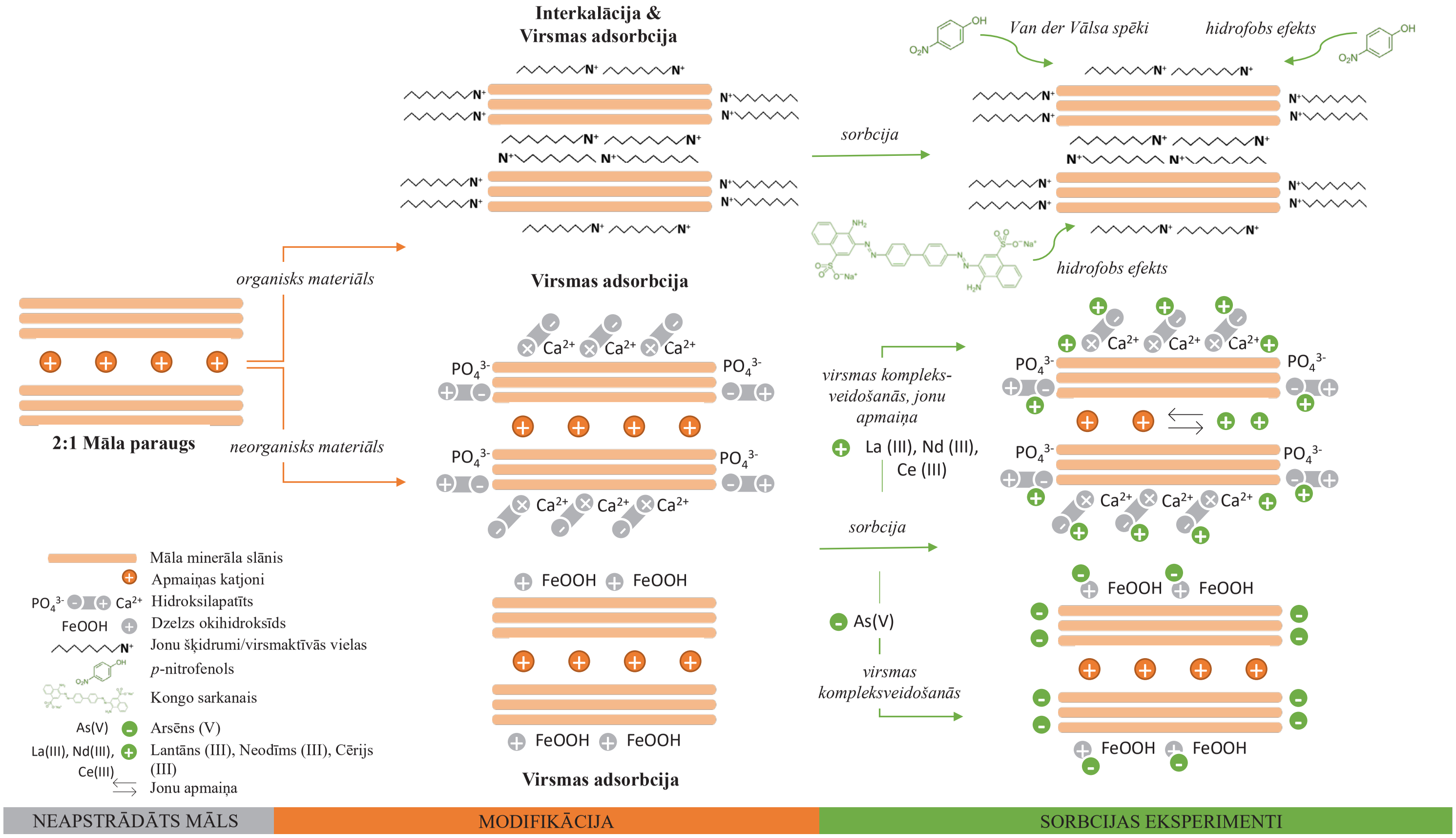
Mālu modifikācija ar dzelzs oksihidroksīdu (FeOOH) tika veikta pēc Ozola et al., 2019a. Metodes pamatā bija Mt, T un J mālu impregnēšana ar dzelzs savienojumiem, lai izveidotu sorbcijas vietas negatīvi lādētām piesārņotājvielām, kā, piemēram, arsēnam (As(V)), kura dominējošā forma ir $HAsO_4^{2-}$, kad šķīduma pH

4. tabula

Promocijas darbā izvēlēto māla paraugu raksturojums

Māla paraugs	Dominējošā māla minerālu grupa	KAK* (mmol/g)	d(001) (Å)	Starpslāņu telpa (nm)	ĪVL ar BET metodi (m^2/g)
Bt māls	Smektīts	0,98 ± 0,03	12,63	0,30	45,21
Mt māls	Smektīts	0,50 ± 0,03	13,40	0,38	252,03
T māls	Smektīts, ilīts- smektīts, ilīts	0,33 ± 0,03	12,08	0,25	57,29
J māls	Smektīts; ilīts; kaolinīts; hlorīts	0,25 ± 0,02	n/a	n/a	n/a

*KAK tika noteikts pēc metilēnzilā testa



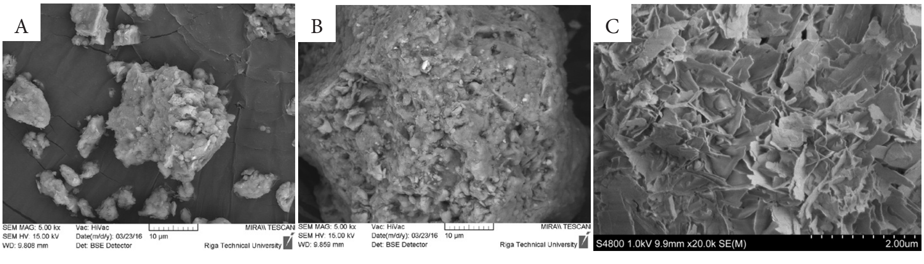
4. attēls. **Izmantoto modifikācijas metožu shematisks attēlojums un iespējamie modeļu piesārņotāju sorbcijas mehānismi uz izstrādātajiem sorbentiem** ir 3–9 (Ansone-Bērtiņa 2015). **SEM attēli** parādīja, ka māla-FeOOH kompozītmateriālu virsmas morfoloģija ir mainījusies salīdzinājumā ar neapstrādātiem māla paraugiem (4. attēls).

Visiem kompozītmateriāliem vairs nebija redzama raksturīgā smektīta tipa minerālkristālu forma, jo virsma bija pārklāta ar dzelzs savienojumiem. **XRD** rentgendifraktogrammas uzrāda ievērojamu intensitātes samazināšanos un smektīta bazālā refleksa (15–15,5 Å apgabals) izlīdzināšanos māla paraugos, kas modificēti ar FeOOH. Tāpat tika konstatēts, ka difraktogrammas neuzrāda jaunas fāzes modificētajos materiālos, salīdzinot ar neapstrādātiem māliem. Tas atbilst sagaidāmajiem rezultātiem, jo paredzams, ka FeOOH fāze būs amorfa. Turklāt modificētajiem māliem tika novērots palielināts "fona troksnis", lai arī tas nav viennozīmīgs, un tas liecina par amorfās fāzes pieaugumu. Turklāt difraktogrammas liecināja par hematīta (Fe_2O_3) klātbūtni T un T-FeOOH paraugos, kas varētu pozitīvi veicināt As(V) sorbciju. Pamatojoties uz **FTIS** datiem, Mt-FeOOH kompozītam nebija jaunu absorbcijas maksimumu. Tomēr modificēto T un J mālu FTIS spektri uzrādīja jaunu absorbcijas maksimumu rašanos pie ~1400 cm^{-1}, kas liecina par Fe-O funkcionālās grupas klātbūtni maghemītam (γ-Fe_2O_3) (Khorshidi un Azadmehr, 2017).

Ar FeOOH modificēto mālu paraugu **TG analīze** parādīja svara zudumu, kas novērots 500 °C un 800 °C temperatūras diapazonā un norāda uz maghemīta (γ-Fe_2O_3) fāzes daļēju pārvēršanos par hematītu (α-Fe_2O_3), kas atrodas kompozītmateriālos (Wu et al., 2016). Mt māla, Mt-FeOOH, T māla, T-FeOOH, J māla, J-FeOOH kopējais svara zudums, ko attiecina uz termiskās dehidroksilēšanas reakcijām un γ uz α fāzes pāreju, bija attiecīgi 3,91%, 6,31%, 11,22% , 11,90%, 3,89%, 7,55%. Šie rezultāti atbilst XRD un FTIS datiem. Turklāt **ĪVL vērtības** ievērojami palielinājās pēc māla materiālu modifikācijas, netieši norādot, ka māla-FeOOH kompozītmateriālu sorbcijas spēja būs augstāka nekā salīdzinājumā ar nemodificētiem māla paraugiem.

3.1.3. Māla-hidroksilapatīta kompozītmateriālu raksturojums

Mālu modifikācija ar sintētisko hidroksilapatītu (Hap) tika veikta, kā aprakstīts Ozola et al., 2017. Modifikācijas metodes pamatā māla paraugi tika impregnēti ar Hap, lai palielinātu sorbcijas kapacitāti retzemju elementiem, kā, piemēram, lantānam(III), neodīmam(III) un cērijam(III). **SEM attēli** parādīja, ka pēc modifikācijas ar Hap mālu virsmas morfoloģija ir mainījusies – pilnībā pārklāta ar hidroksilapatīta kristāliem (5. attēls). Pēc modifikācijas ar Hap kompozītmateriālu **ĪVL** ir nedaudz samazinājies, piemēram, Mt-Hap gadījumā no 252,03 m^2/g līdz 121,53 m^2/g. Kompozītmateriālu



5. attēls. **SEM attēli (5000× palielinājumā) ar neapstrādātiem T māliem (A), T māliem modificētiem ar dzelzs oksihidroksīdu (B) un hidroksilapatītu (C).**

virsmas laukuma samazināšanās ir saistīta ar hidroksilapatīta daļiņu klātbūtni uz māla daļiņām (El-Nagar et al., 2020). **XRD dati** parādīja, ka mālu modifikācijas procesos ar hidroksilapatītu tiek pilnībā izmainīts minerālais sastāvs. Hlorīta, kalcīta, ilīta/smektīta, laukšpata un citu minerālu fāžu raksturīgo refleksu intensitāte būtiski samazinājās vai izzuda pavisam. Rentgendifraktogrammā parādās jauns pīķis pie ~26° un ~32° 2θ, liecinot par hidroksilapatīta klātbūtni modificētajos paraugos. **FTIS spektri** jaunizveidotajam kompozītmateriālam parādīja jaunas funkcionālās grupas pie 1412 cm^{-1} un 1450 cm^{-1}, liecinot par karbonātjonu klātbūtni CO_3^{2-}, un pie 600 cm^{-1}, liecinot par fosfātu jonu PO_4^{3-} klātbūtni (Shaltout et al., 2011). **TGA** rezultāti parādīja, ka pēc modifikācijas 610 °C rodas jauns sadalīšanās apgabals, kas norāda uz oglekļa dioksīda izdalīšanos no apatīta. Kopumā FTIS rezultāti atbilst termiskās analīzes datiem un apstiprina hidroksilapatīta klātbūtni kompozītmateriālos.

3.1.4. Māla-virsmaktīvo vielu kompozītmateriālu raksturojums

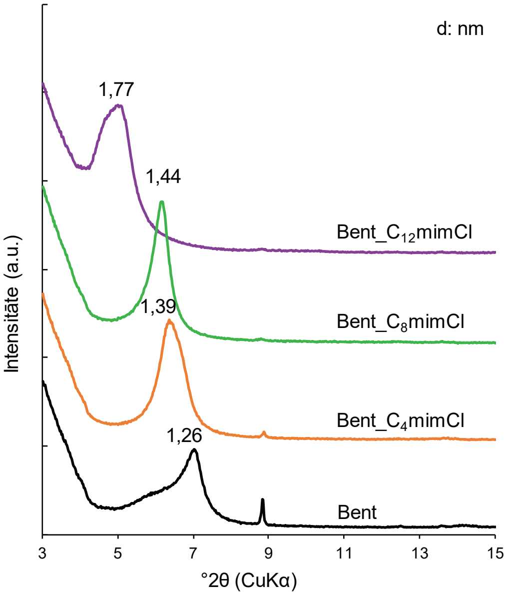
Mālu modifikācija ar katjonaktīvām un vai nejonogēnām virsmaktīvām vielām tika veikta atbilstoši, kā aprakstīts Ozola et al., 2019a. Metodes pamatā ir māla minerālu struktūrā esošo nātrija jonu apmaiņa ar virsmaktīvās vielas joniem. Tādējādi māla virsma kļūst hidrofoba un spēj saistīt organiskās piesārņotājvielas, kā, piemēram, *p*-nitrofenolu (PNF). **XRD** rentgendifraktogramma parādīja, ka pēc modifikācijas māla minerālu starpslāņa telpa ir būtiski palielinājusies. Lielākais starpslāņu attāluma pieaugums tika konstatēts ar virsmaktīvo vielu DDAO (0,46 nm), bet mazākas izmaiņas tika novērotas ar NMO (0,04 nm). Šīs izmaiņas var izskaidrot ar virsmaktīvās vielas alkilķēdes garumu jeb n_c, oglekļa atomu skaitu (He et al., 2014). Organomālu **ĪVL** bija atkarīgs no pievienotās virsmaktīvās vielas daudzuma attiecības pret mālu KAK. SSA samazinājās šādā secībā:
Mt_Na > Mt_BTMAC_0,5 > Mt_BTMAC_1 > Mt_BTMAC_2 > Mt_BTMAC_3.

ĪVL samazināšanās pēc modifikācijas ir saistīta ar to, ka virsmaktīvās vielas veido monoslāni uz māla minerāla ārējās virsmas, veidojot "kāršu namiņa struktūru" un aizņem poras starp māla daļiņām (Zhang et al., 2015). **SEM attēli** parādīja, ka pēc modifikācijas ar virsmaktīvām vielām smektīta tipa minerālam raksturīgā morfoloģija paliek neskarta. Pēc mālu modifikācijas ar virsmaktīvām vielām **FTIS** dati uzrādīja jaunus signālus pie 2930 cm^{-1} un 2854 cm^{-1}. Šajā reģionā ir raksturīga metilgrupas asimetriskā un simetriskā C-H saišu izstiepšanās. **TGA analīze** parādīja, ka pēc montmorilonīta modifikācijas parādījās jauns sadalīšanās apgabals no 200 °C līdz 500 °C, kas saistīts ar virsmaktīvo vielu molekulu sadalīšanos. Līdzīgi rezultāti tika iegūti arī citos organomālu pētījumos (Taleb et al., 2018; Andrunik and Bajda, 2019).

3.1.5. Māla-jonu šķidrumu kompozītmateriālu raksturojums

Mālu modifikācija ar jonu šķidrumiem tika veikta, kā aprakstīts Ozola-Davidāne et al., 2021. Metodes pamatā bentonīta starpslāņu telpā tika interkalēti imidazolija bāzes jonu šķidrumi ar dažādiem alkilķēdes garumiem, izmantojot jonu apmaiņas reakciju. Modifikācijas rezultātā kompozītmateriāls iegūst hidrofobas īpašības un spēj saistīt organiskās piesārņotājvielas, kā, piemēram, Kongo sarkano krāsvielu. Pēc bentonīta modifikācijas ar jonu šķidrumiem **FTIS** dati uzrādīja jaunus signālus pie 2927 cm^{-1} un 2847 cm^{-1}, kas raksturīgi metilgrupas asimetriskām un simetriskām C-H saišu svārstībām (Stuart, 2004). Šo saišu klātbūtne diapazonā no 3000 cm^{-1} līdz 2840 cm^{-1} liecina, ka jonu šķidrumu katjoni ne tikai aizņem māla virsmu, bet ir arī veiksmīgi interkalēti bentonīta struktūrā (Sun et al., 2017). **XRD** rentgendifraktogramma atklāja, ka pēc bentonīta modifikācijas ar jonu šķidrumiem d_{001} maksimums nobīdījies uz zemākām leņķa vērtībām. Starpslāņu telpas attālums bija tieši saistīts ar imidazolija katjona alkilķēdes garumu – jo garāka bija alkilķēde, jo lielāka starpslāņu telpas izplešanās (6. attēls). Līdzīgi rezultāti ir atrodami arī citos pētījumos (Nasser et al., 2016; Sun et al., 2017), un tas apstiprina veiksmīgu jonu šķidrumu interkalāciju bentonīta starpslāņa telpā. **TGA** dati atklāja, ka pēc modifikācijas ar jonu šķidrumiem parādās jauns sadalīšanās apgabals intervālā no 480 °C līdz 580 °C, kas norāda uz jonu šķidrumu sadalīšanos no kompozītmateriāla virsmas un starpslāņu telpas (Litefti et al., 2019).

Māla-jonu šķidruma kompozītmateriālu **ĪVL** vērtības samazinājās, palielinoties izmantotā jonu šķidruma alkilķēdes garumam. ĪVL pakāpeniski samazinās no 45,21 m^2/g uz 29,83 m^2/g, 18,80 m^2/g, 6,89 m^2/g pēc modifikācijas attiecīgi ar C$_4$mimCl, C$_8$mimCl, C$_{12}$mimCl. Iegūtās bentonīta-jonu šķidrumu kompozītmateriālu tekstūras īpašības liecina, ka jonu šķidrumi ir ne tikai nonākuši māla starpslāņa telpā, bet arī adsorbējušies uz ārējās virsmas (Park et al., 2013).



Paraugs	d$_{(001)}$ (nm)	Starpslāņu telpas attālums (nm)	Starpslāņu telpas palielināšanās (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

6. attēls. **XRD difraktogramma un starpslāņu attālums modificētam mālam ar imidazolija bāzes jonu šķidrumiem ar dažāda garuma alkilķēdēm**

3.2. Neorganisko un organisko jonu sorbcijas pētījumi

3.2.1. Arsēna(V) sorbcijas pētījumi

Negatīvi lādēti arsēna(V) joni tika izvēlēti kā modeļa piesārņotājviela, lai izpētītu sorbcijas efektivitāti no ūdens šķīdumiem ar neapstrādātiem māliem un modificētiem ar dzelzs oksihidroksīdu (FeOOH).

Sorbenta veids. Māla materiālu modificēšana ar dzelzs oksihidroksīdu uzlaboja pētīto sorbentu saistīšanas spēju attiecībā pret As(V) vairāk nekā sešas reizes. Vislielākā sorbcijas kapacitāte tika noteikta Mt-FeOOH, kam sekoja J-FeOOH, T-FeOOH un neapstrādāts Mt māls. Mt-FeOOH, J-FeOOH un T-FeOOH sorbcijas kapacitāte sasniedza attiecīgi līdz 15,62, 11,84 un 11,40 mg/g, un tas nozīmē, ka šie sorbenti sākotnēji spēj saistīt vairāk nekā 99% As(V), ja As(V) koncentrācija ir 50 mg/L. Fe-modificēto mālu sorbcijas kapacitāte ir salīdzinoši augsta, salīdzinot ar citiem literatūrā aprakstītajiem adsorbentiem (Mohan un Pittman, 2007). **pH ietekme.** Vislielākā As(V) sorbcija uz modificētajiem māliem bija pie sākotnējā pH 2, un tā bija 16,22 ± 0,91, 16,22 ± 0,91 un 14,56 ± 0,82 mg/g attiecīgi šādiem paraugiem Mt-FeOOH, J-FeOOH un T-FeOOH. FeOOH modificēto mālu maksimālā sorbcijas spēja pie pH 2–6 ir izskaidrojama ar As(V) dominējošās formas un sorbenta virsmas lādiņa izmaiņām. Sorbcijas process var notikt, mijiedarbojoties negatīvi lādētām As(V) formām $H_2AsO_4^-$ un pozitīvi lādētām $Fe(OH)_2^+$ virsmas grupām, kā rezultātā veidojas virsmas kompleksi (Li et al., 2021). **Sorbcijas izotermas.** Iegūtās korelācijas koeficienta (R^2) vērtības (>0,89) liecināja, ka gandrīz visiem sorbentiem (izņemot T mālu un Mt mālu, kas modificēts ar FeOOH) gan Lengmīra, gan Freindliha izotermas var adekvāti aprakstīt sorbcijas datus. Abu izotermu modeļu piemērotība pētāmajām sistēmām liecina, ka pētītajos eksperimentālajos apstākļos pastāv gan vienslāņa, gan daudzslāņu sorbcija. Tādējādi As(V) sorbcija uz sorbentiem ir sarežģīts process, kas ietver vairāk nekā vienu mehānismu (Freundlich 1906; Langmuir 1918; Febrianto et al., 2009).

3.2.2. Lantāna(III), neodīma(III), cērija(III) sorbcijas pētījumi

Pozitīvi lādēti lantāna(III), neodīma(III) un cērija(III) joni tika izvēlēti kā retzemju elementu modeļvielas, lai izpētītu saistīšanas efektivitāti no ūdens šķīduma ar neapstrādātu Mt mālu un Mt mālu, kas modificēts ar hidroksilapatītu (Hap).

Sorbenta veids. Sorbcijas kapacitāte palielinājās vairāk nekā divas reizes pēc montmorilonīta modifikācijas ar hidroksilapatītu, un augstākā sorbcijas spēja bija 284 mg/g La(III). Modifikācija ar Hap palielināja sorbcijas vietas pozitīvi lādētiem elementiem. Pamatojoties uz iepriekšējiem pētījumiem, La(III), Ce(III) un Nd(III) saistīšanas mehānismi var ietvert katjonu apmaiņu ar kalcija joniem un virsmas kompleksēšanas mehānismu, ko veicina virsmas fosfātu anjonu grupas (Ramakrishnan et al., 2016). **Sorbcijas izotermas.** Iegūtās korelācijas koeficienta vērtības liecināja, ka neapstrādātam Mt māla un Mt-hidroksilapatīta kompozītam Lengmīra izotermas modelis ir vispiemērotākais vienādojums sorbcijas raksturošanai. Tas norāda, ka pētītajiem sorbentiem La(III), Nd(III), Ce(III) sorbcija ir vienslāņa rakstura (Langmuir, 1918; Febrianto et al., 2009).

3.2.3. p-nitrofenola sorbcijas pētījumi

p-nitrofenols (PNF) tika izvēlēts kā organiskās piesārņotājvielas modeļviela, lai izpētītu saistīšanas efektivitāti no ūdens šķīduma ar neapstrādātiem un modificētiem māliem ar nejonogēnām (DDAO, NMO) un katjonaktīvām virsmaktīvām vielām (BTMAC, DTAC) dažādās virsmaktīvās vielas/CEC attiecībās.

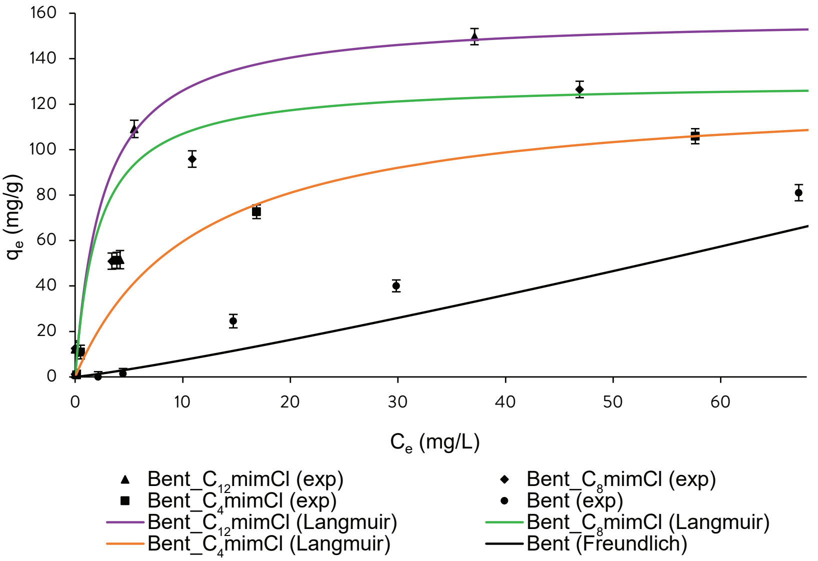
Virsmaktīvās vielas slodzes ietekme. Iegūtie rezultāti atklāja, ka PNF saistīšanas spēja uz neapstrādāta Mt māla bija niecīga, bet pēc Mt māla modifikācijas ar BTMAC sorbcijas kapacitāte būtiski palielinājās pie virsmaktīvās vielas/CEC attiecības 2. Tomēr jaunizstrādāto materiālu PNF sorbcijas spēja pie VAV/CEC attiecībām 0,5, 1,0 un 3,0 bija salīdzinoši zema. Ja virsmaktīvās vielas slodze pārsniedz māla KAK, virsmaktīvās vielas aizņem gan māla starpslāņu telpu, gan virsmu. Tādējādi PNF sorbcija notiek ne tikai hidrofobas mijiedarbības, bet arī elektrostatiskās mijiedarbības rezultātā (Park et al., 2013). **Sorbenta veids.** Lielākā PNF sorbcijas spēja tika novērota uz Mt_DDAO_2 (0,36 mg/g), kad PNF koncentrācija bija 25 mg/L. XRD rezultāti (sk. 3.1.4. nodaļu) liecināja, ka palielināto starpslāņu telpu var saistīt ar PNF sorbcijas efektivitāti (Park et al., 2013). **Kontakta laika ietekme.** PNF sorbcijas spēja uz Mt māliem un T māliem, kas modificēti ar dimetildodecilamīna N-oksīdu ar VAV/CEC attiecību 2,0 (Mt_DDAO_2 un T_DDAO_2), sasniedza maksimumu 60 minūšu laikā, pēc tam būtiskas izmaiņas netika novērotas. To daļēji var izskaidrot ar samazinātu pieejamo brīvo sorbcijas vietu skaitu un palielinātu kontakta laiku (Zhang et al., 2015). **pH ietekme.** Visaugstākā saistīšanas efektivitāte tika iegūta skābā vidē, no pH 2 līdz 6. Kad pH pārsniedza 6, sorbcijas efektivitāte ievērojami samazinājās, pateicoties māla virsmas lādiņa maiņai un PNF protonēšanai (Park et al., 2013). **Sorbcijas izotermas.** Korelācijas koeficienta vērtības bija > 0,89, kas norāda, ka gan Lengmīra, gan Freindliha izotermas var adekvāti aprakstīt sorbcijas datus (Alkaram et al., 2009). Tomēr Mt mālu gadījumā, kas modificēts ar benziltrimetilamonija hlorīdu (Mt_BTMAC_2), R^2 ir mazāks par 0,89, un tas nozīmē, ka sorbciju nevar adekvāti aprakstīt ar šīm izotermām. Abu izotermu modeļu piemērotība pētāmajām sistēmām liecina, ka pētītajos eksperimentālajos apstākļos pastāv gan vienslāņa, gan daudzslāņu sorbcija. Tādējādi PNF sorbcija uz šīm virsmām ir sarežģīta, iesaistot vairāk nekā vienu mehānismu (Freundlich 1906; Langmuir 1918; Febrianto et al., 2009).

3.2.4. Kongo sarkanā sorbcijas pētījumi

Krāsviela Kongo sarkanais (KS) tika izvēlēta kā organiskā piesārņotājvielas modeļviela, lai izpētītu saistīšanas efektivitāti ūdens šķīdumos ar neapstrādātu un modificētu Bt mālu ar imidazolija jonu šķidrumiem, kam ir dažāda garuma alkilķēdes.

Sorbenta veids. Sorbcijas kapacitāte būtiski palielinājās pēc Bent mālu modifikācijas, un lielākā sorbcijas spēja bija 150 mg/g ar 1-dodecil-3-metilimidazolija hlorīdu (Bent_C_{12}mimCl) modificētiem Bent māliem, kad Kongo sarkanā (KS) koncentrācija bija 100 mg/L. Saskaņā ar sorbcijas datiem un XRD rezultātiem (skatīt 3.1.5. nodaļu) KS saistīšanas efektivitāte ir atkarīga no modificēto Bent paraugu starpslāņa telpas lieluma – jo lielāka starpslāņu telpa, jo augstāka sorbcijas kapacitāte (7. attēls).

Kontakta laika ietekme. Sākotnējā posmā KS saistīšana notiek salīdzinoši ātri; izmantojot 10 mg sorbentu, pirmajās 30 minūtēs tika sorbēti aptuveni 50% krāsvielu molekulu. Kongo sarkanā sorbcijas līdzsvara laiks uz neapstrādātiem Bent māliem, kas modificēti ar 1-dodecil-3-metilimidazolija hlorīdu (Bent_C_{12}mimCl), bija attiecīgi 60 minūtes un 240 minūtes. **Sorbcijas kinētika.** Iegūtās korelācijas koeficienta vērtības liecināja, ka neapstrādātiem Bent māliem, modificētiem ar 1-dodecil-3-metilimidazolija hlorīdu (Bent_C_{12}mimCl), Lagergrena linearizētais pseido-otrās pakāpes kinētiskais modelis ir vispiemērotākais vienādojums, lai aprakstītu sorbcijas mehānismu starp sorbentu un sorbātu.

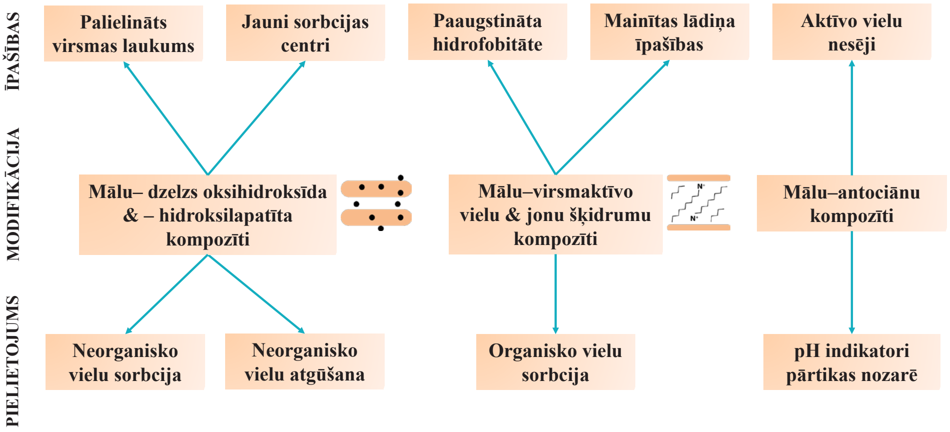


7. attēls. **Izejas koncentrācijas ietekme uz Kongo sarkanā saistīšanu ar neapstrādātu Bent mālu, modificētu ar imidazolija jonu šķidrumiem, kam ir dažāda garuma alkilķēdes (eksperimenta apstākļi: Ci = 0,5–50 mg/L, pH = 5,5, kontakta laiks = 24 h, T = 24 °C)**

No tā izriet, ka sorbcijas kinētikas procesu regulē hemosorbcijas mehānisms (Alshammari et al., 2020). **pH ietekme.** Maksimālā līdzsvara sorbcijas kapacitāte 98 mg/g, kas atbilst 100% saistīšanas efektivitātei, tika sasniegta pie pH 2. Pie pH 4 gan saistīšanas efektivitāte, gan līdzsvara sorbcijas kapacitāte samazinājās attiecīgi līdz 70% un 76 mg/g. Intervālā no pH 5 līdz pH 10 saistīšanas efektivitāte nedaudz palielinājās un bija vidēji 80%. KS saistīšanas samazinājums, palielinoties pH, ir saistīts ar KS sulfonātu grupu disociāciju, kas producē krāsvielu anjonus (Yang et al., 2021). **Sorbcijas izotermas.** Iegūtās korelācijas koeficienta vērtības liecina, ka neapstrādātam Bent mālam Freindliha izotermas modelis ir vispiemērotākais vienādojums sorbcijas uzvedības raksturošanai. Savukārt Bent-jonu šķidrumu kompozītmateriālu gadījumā visatbilstošākais ir Lengmīra izotermas modelis. Tas liecina, ka neapstrādātiem Bent māliem KS sorbcija ir heterogēna, savukārt modificētiem māliem KS sorbcija ir vienslāņa (Freundlich, 1906; Langmuir, 1918; Alkaram et al., 2009).

3.3. Jaunizstrādāto materiālu potenciālie pielietojumi un nākotnes perspektīvas

Sorbenti ir materiālu grupa ar augstu pielietojuma potenciālu vides problēmu risināšanā (piesārņoto vietu sanācija), inženierbūvniecībā (dzeramā ūdens attīrīšana), aprites ekonomikā (vērtīgo vielu reģenerācija), bioekonomikā (blakusproduktu izmantošana augstas pievienotās vērtības materiālu radīšanai) un daudzās citās jomās. Tajā pašā laikā sorbentu materiāli tiek ražoti no naftas pārstrādes produktiem (sintētiskie jonu apmaiņas sveķi, poliestera, polipropilēna un poliuretāna un citi materiāli), un, neskatoties uz

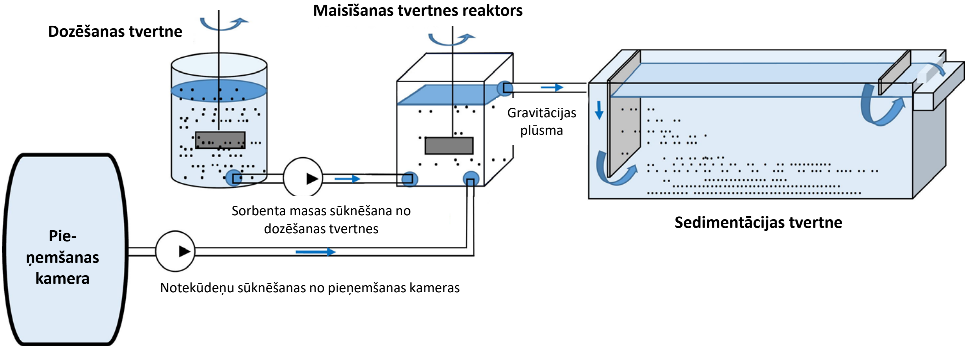


8. attēls. **Promocijas darbā iegūtie māla kompozītmateriāli, to iegūtās īpašības un vides pielietojuma perspektīvas**

to izcilo veiktspēju, to izmantošana nav uzskatāma par ilgtspējīgu (Murray un Bugdayli 2021). Turklāt Eiropas zaļā kursa ietvaros (piemēram, dokumentā "Ķīmisko vielu stratēģija ilgtspējībai") tiek uzsvērts, cik svarīgi ir izstrādāt videi draudzīgas tehnoloģijas un palielināt drošu un ilgtspējīgu materiālu izmantošanu, kas nekaitē cilvēkiem un videi (European Commission 2020). Šī pētījuma rezultāti parāda, ka mālus var veiksmīgi izmantot, lai aizstātu sintētiskos sorbentus. Māli ir dabisks, plaši pieejams un lēts materiāls, taču izstrādātie modificētie māla materiāli paplašina iespējas iegūt sorbentus ar nepieciešamajām īpašībām, lai risinātu konkrēto problēmu.

Šajā pētījumā tika veikta māla minerālu mērķtiecīga modifikācija, lai mainītu to fizikālās un ķīmiskās īpašības un izstrādātu inovatīvus materiālus videi draudzīgām tehnoloģijām. Detalizēts izveidoto mālu kompozītu raksturojums liecināja par izmaiņām starpslāņu telpā, īpatnējā virsmā, poru tilpumā, daļiņu morfoloģijā, lādiņa īpašībās un arī par jauniem sorbcijas centriem (sk. 3.1. un 3.2. nodaļu). Tādējādi modificēto mālu materiālus šajā pētījumā var izmantot kā efektīvus sorbentus: 1) vides atveseļošanā, piemēram, no ūdens un notekūdeņiem atdalot neorganiskos un organiskos jonus; 2) aprites ekonomikā, reģenerējot no atkritumiem vērtīgus metālus; 3) bioekonomikā, izmantojot lauksaimniecības blakusproduktus, lai izstrādātu materiālus ar augstu pievienoto vērtību, piemēram, pH jutīgus indikatorus pārtikas svaiguma kontrolei (8. attēls).

Pētījumā izstrādātajiem materiāliem var rast dažādas lietojuma iespējas. Pamatojoties uz diskusiju un iegūtajiem rezultātiem, kas aprakstīti iepriekšējās nodaļās, mālus, kas modificēti ar jonu šķidrumiem, virsmaktīvām vielām, dzelzs oksihidroksīdu un hidroksilapatītu, var veiksmīgi izmantot cietu vielu-šķidrumu sorbcijas sistēmās, piemēram, fiksētos slāņa reaktoros vai sērijveida reaktoros. Galvenā mālu sorbentu izmantošana ietver, bet neaprobežojas ar šādām ūdens attīrīšanas sistēmām: 1) notekūdeņu attīrīšanas iekārtās jaunu piesārņotāju saistīšanai; 2) rūpniecisko notekūdeņu priekšattīrīšanas iekārtās; 3) izmantošana konstruētās mitrāju sistēmās; 4) *in situ* filtru sistēmās piesārņojošo vielu saistīšanai no ūdens plūsmām. Piemēram, Heiderscheidt et al. (2020) ir ierosinājis inovatīvu attīrīšanas sistēmu minerālu un biomasas bāzes sorbentu izmantošanai rūpniecisko notekūdeņu priekšattīrīšanas iekārtās. Pētījumā tika izveidots nepārtrauktas plūsmas nepārtrauktas maisīšanas tvertnes reaktors, kam sekoja sedimentācijas iekārta sorbenta/ūdens atdalīšanai (9. attēls). Dozēšanas tvertnē tiek sagatavota sorbenta suspensija, pēc tam nepieciešamā suspensijas koncentrācija tiek sūknēta uz notekūdeņu attīrīšanas tvertni ar maisīšanas režīmu. Tad suspensija, kas satur notekūdeņus un dozēto sorbentu, tiek pārnesta ar gravitācijas spēku no maisīšanas tvertnes reaktora uz sedimentācijas bloku, lai izņemtu cieto materiālu no attīrīta ūdens. Šis attīrīšanas iekārtas piemērs atrisina vienu no galvenajiem izaicinājumiem mālu sorbentu integrācijā NAI – efektīva cieto/šķidruma atdalīšanu pēc notekūdeņu attīrīšanas procesa.



9. attēls. **Nepārtrauktas plūsmas nepārtrauktas maisīšanas tvertnes reaktora sistēmas un sedimentācijas tvertnes vizualizācija minerāla sorbentu izmantošanai NAI sistēmās** (Heiderscheidt et al., 2020)

A

B

Mālu-antociānu kompozīts	**Uzglabāšanas laiks 24 °C**	**Uzglabāšanas laiks 8 °C**	**Organo-leptiskais novērtējums (punktos)***
🟥	0 h	0. diena	5
🟪	24 h – 36 h	7.–8. diena	3
🟦	> 48h	virs 8. dienām	<2

10. attēls. **(A) Vistas filejas paraugs, kas iepakots ar māla-antociānu kompozīta sensoru; (B) māla-antociānu kompozīta krāsas izmaiņas atkarībā no uzglabāšanas laika un temperatūras gaisa atmosfērā.**

*Organoleptiskie parametri tiek novērtēti punktos, kur 1 ir neatbilstoša kvalitāte un 5 ir laba kvalitāte

Māla-antociānu kompozītmateriāli ir piemēroti inovatīvai izmantošanai pārtikas rūpniecībā kā svaiguma indikatori, kas nosaka pārtikas produktu kvalitāti. Promocijas darba ietvaros tika veikti svaigu vistas fileju bojāšanās testi, lai novērtētu māla-antociānu kompozītmateriālu sensoru darbību viedajos pārtikas iepakojumos (10. A attēls).

Eksperimentu rezultāti parādīja, ka sensora krāsa maina krāsu no sarkanas uz zilu: kad organoleptiskie parametri ir neatbilstoši un gaļas produkta konsistence, garša, smarža un izskata izmaiņas norāda uz zemu produkta kvalitāti (10. B attēls); pirms bakteriālais piesārņojums pārsniedz Komisijas Regulā par pārtikas produktu mikrobioloģiskajiem kritērijiem Nr. 2073/2005 noteiktās robežvērtības.

Eiropas Savienībā ik gadu ES mājsaimniecībās tiek izšķiesti 8,8 miljoni tonnu pārtikas, jo patērētājiem ir grūtības nolasīt datumu etiķetes (European Commission, 2018). Māla un antociānu kompozīti atrisina problēmu, datumu etiķetēm papildus piedāvājot svaiguma sensorus, kas ir iekļauti standarta pārtikas iepakojumā. Sensora krāsas maiņas vienkāršība samazinātu pārtikas atkritumus, no kuriem iespējams izvairīties. Turpmākajos pētījumos perspektīvākos māla kompozītmateriālus plānots pārbaudīt ne tikai laboratorijas eksperimentos, bet arī ražošanas līmenī. Papildus tiek plānotas jaunas modifikācijas metodes un pielietojuma iespēju izpēte, piemēram, siltumnīcefekta gāzu, t. i., oglekļa dioksīda, sorbcijā; māla-polifenola kompozītmateriālu izmantošanā viedo zāļvielu nesējos ar imūnmodulējošām īpašībām vai magnētisko mālu izmantošanu notekūdeņu attīrīšanā.

SECINĀJUMI

Izstrādātās mālu modifikācijas metodes sniedz iespējas mērķtiecīgi mainīt mālu īpašības, integrējot to struktūrā jaunas funkcionālās grupas, kas spēj mainīt māla fizikālķīmiskās īpašības, un tādējādi rodas iespēja attīstīt jaunas pielietojuma iespējas:

- **Māla-dzelzs oksihidroksīda materiālu** raksturošanas metodes (SEM, XRD, ĪVL pēc BET, FTIS, TG, KAK, Fe_2O_3 saturs) norādīja uz māla daļiņu morfoloģijas izmaiņām, palielinātu virsmas laukumu, jaunām Fe-O funkcionālām grupām, maghemīta klātbūtni (γ-Fe_2O_3) un izmaiņām citos parametros, un tas liecina par veiksmīgu māla modifikāciju ar dzelzs oksihidroksīdu.
- **Māla-hidroksilapatīta materiālu** raksturošanas metodes (SEM, XRD, ĪVL pēc BET, FTIS un TG) norādīja uz hidroksilapatīta izgulsnētu kristālu klātbūtni, jaunām CO_3^{2-} grupām pēc IS, būtiskām izmaiņām minerālu sastāvā, sadalīšanās reģionos, kas saistīts ar oglekļa dioksīda izdalīšanos no karbonizēta apatīta, un izmaiņām citos parametros, un tas liecina par veiksmīgu māla modifikāciju ar hidroksilapatītu.
- **Māla-virsmaktīvo materiālu** raksturošanas metodes (SEM, XRD, ĪVL pēc BET, FTIS un TG) uzrādīja jaunas CH_2 grupas pēc IS, starpslāņu telpas paplašināšanos, ĪVL un poru izmēra samazināšanos, izmaiņas lielākas daļiņu aglomerācijas, hidrofobumu un citos parametros, un tas norāda uz veiksmīgu māla modifikāciju ar nejonām un katjonām virsmaktīvām vielām.
- **Māla-jonu šķidrumu materiālu** raksturošanas metodes (XRD, ĪVL pēc BET, FTIS un TG) uzrādīja jaunas CH_2 grupas pēc IS, starpslāņu telpas paplašināšanos, poru tilpuma palielināšanos, ĪVL un poru izmēra samazināšanos, hidrofobumu un izmaiņas citos parametros, un tas norāda uz veiksmīgu māla modifikāciju ar jonu šķidrumiem ar dažāda garuma alkilķēdēm.

Šajā pētījumā iegūtie modificētie māli demonstrē augstu veiktspēju un potenciālu vides problēmu risināšanā. Proti, specifisku vielu klātbūtne rada nevēlamu ietekmi vidē, un modificētos mālus var izmantot izvēlēto vielu grupu saistīšanai:

- **Nemetālu, piemēram, As(V) sorbcijas,** pētījumi ar māla-dzelzs oksihidroksīda sorbentiem dažādos vides apstākļos atklāja, ka augstāko As(V) sorbcijas kapacitāti var sasniegt, modificējot montmorilonīta sorbentu (Mt-FeOOH). Sorbcijas kapacitāte palielinās skābā vidē, veidojot virsmas kompleksu, un Lengmīra vai Freindliha sorbcijas modeļi apraksta sorbciju kā vienslāņa un daudzslāņu. Tādējādi sorbcijas pētījumi liecina par efektīvu māla-dzelzs oksihidroksīda sorbentu modifikāciju, lai no ūdens šķīdumiem izņemtu negatīvi lādētus neorganiskos piesārņotājus.
- **Retzemju elementu, piemēram, La(III), CeIII), Nd(III), sorbcijas** pētījumi ar māla-hidroksilapatīta sorbentiem dažādos vides apstākļos norādīja, ka augstāko sorbcijas kapacitāti La(III), CeIII), Nd(III) var panākt, modificējot montmorilonīta sorbentu (Mt-Hap), un Lengmīra modelis apraksta sorbciju kā vienslāņa. Tādējādi sorbcijas pētījumi liecina par efektīvu māla-hidroksilapatīta sorbenta modifikāciju, lai no ūdens šķīdumiem izņemtu pozitīvi lādētus neorganiskos piesārņotājus.

- **Fenolu, piemēram, *p*-nitrofenola (PNF) sorbcijas** pētījumi ar māla- virsmaktīvo vielu sorbentiem dažādos vides apstākļos atklāja, ka vislielāko PNF izņemšanu var panākt, modificējot montmorilonītu ar dimetildodecilamīna N-oksīdu (DDAO), kur virsmaktīvās vielas/CEC attiecība ir 2 (Mt-DDAO_2). Sorbcijas kapacitāte palielinās skābā vidē, pateicoties hidrofobai mijiedarbībai un Van der Vālsa spēkam, Lengmīra vai Freindliha modeļi apraksta sorbciju kā vienslāņa un daudzslāņu. Tādējādi sorbcijas pētījumi liecina par efektīvu mālu-virsmaktīvo vielu sorbentu modifikāciju, lai no ūdens šķīdumiem izņemtu organiskos (neitrālas molekulas) piesārņotājus.
- **Organisko krāsvielu, piemēram, Kongo sarkanā (KS), sorbcijas** pētījumi ar mālu-jonu šķidrumu sorbentiem dažādos vides apstākļos atklāja, ka vislielāko KS sorbcijas kapacitāti var sasniegt, modificējot bentonītu ar 1-dodecil-3-metilimidazolija hlorīdu (Bent_C_{12}mimCl), kam bija garākā alkilķēde starp pētītajiem materiāliem. Sorbcijas kapacitāte palielinās skābā vidē, pateicoties hidrofobām mijiedarbībām, Lengmīra vai Freindliha modeļi apraksta sorbciju kā vienslāņa un daudzslāņu, savukārt Lagergrena pseido-otrās kārtas kinētika liecina, ka sorbcijas procesu regulē hemosorbcijas mehānisms. Tādējādi sorbcijas pētījumi liecina par efektīvu māla-jonu šķidrumu sorbentu modifikāciju, lai no ūdens šķīdumiem izņemtu negatīvi lādētus organiskos piesārņotājus.

Mālus, kas modificēti ar jonu šķidrumiem, virsmaktīvām vielām, dzelzs oksihidroksīdu un hidroksilapatītu, var veiksmīgi izmantot cietu vielu-šķidrumu sorbcijas sistēmās, lai izņemtu piesārņotājus vai atgūtu vērtīgus elementus no atkritumu plūsmām. Savukārt māla-antociānu kompozītmateriālus var izmantot pārtikas rūpniecībā kā svaiguma indikatorus, kas nodrošina pārtikas kvalitāti produktiem, kas ātri bojājas.

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