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SAPROPEL FOR THE DEVELOPMENT OF BIOCOMPOSITE MATERIALS: PROPERTIES AND APPLICATION POSSIBILITIES

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ABSTRACT

The aim of the doctoral thesis "SAPROPEL FOR THE DEVELOPMENT OF BIOCOMPOSITE MATERIALS: PROPERTIES AND APPLICATION POSSIBILITIES" is to study properties of sapropel and possibilities to use it for development of biocomposites for applications in agriculture, construction industries and other fields as well as to test properties of obtained materials in respect to their application possibilities. Samples of composite materials were created by using different types of sapropel as binder and birch wood grinding dust, birch wood fibre, hemp shives and fibre aerosil, mahagony sawdust as fillers. Birch wood veneer and beech wood planks, peat was used for testing sapropel adhesive properties. In the theoretical part of thesis is offered an overview of scientific literature about sapropel, possibilities of utilization, characteristics and consistence of environmentally friendly construction materials. The created composite materials were analyzed at the results section. Measuring of mechanical strength, thermal conductivity, microbial stability, biodegradation, ageing of composite materials, compressive and flexural strength of composite materials, sound insulation properties, comparison of auto-ignition were carried out and analyzed. Thesis convincingly demonstrates that using local resources such as sapropel and by-products of the production process, such as birch wood sanding dust, birch wood fibers, hemp shives and wood chips, it is possible to develop environmentally friendly composite materials in construction and agriculture, adapting them to the needs of use. Biological stability of natural sapropel containing biocomposites is one of key parameters for their application potential and should include detailed evaluation of composites in respect to major groups of microorganisms of concern. The mechanical and thermal properties of sapropel-based composites were similar to those of synthetic as well as mineral materials, suggesting that sapropel composites could have similar use in the construction industry: as a self-bearing wall thermal insulation material that works together with the structural timber frame.

The thesis consists of 210 pages with 14 illustrations and 16 tables.

Key words: sapropel, binder, composite material, microbial stability, biodegradation

TABLE OF CONTENTS

ABBREVIATIONS AND GLOSSARY

A	*Alternaria alternata*
AL	ALINA additive
AO	ALINA organoclay additive coating
B	Biocide additive
C	*Cladosporium herbarum*
CBS	Pilvelu cyanobacteria sapropel
CH	Ageing in climate chamber
CS	Padelis carbonatic sapropel.
E	Evaluation/Intensity of growth
EC	Electric conductivity
F	Fungi mixture
FDA	Fluorescein diacetate acetate
FHL	Formulated hydraulic lime
FS	Flax shives
GAS	Veveru green algae sapropel
HL	Hydraulic lime
HS	Hemp shives
Inoc.	Inoculation
K	Control sample
K	Control without additive
LH	Lime binder coating
LHC	Lime-hemp composite
LOI	Loss on ignition
MH	Magnesium oxychloride coating
MHC	Magnesium-hemp composite
MOC	Magnesium oxychloride cement
MPC	Magnesium phosphate cement
mV	Redox potential
OD	Optical density
pH	Potential of hydrogen
RH	Relative humidity
S	Sapropel
SIR	C-CO_2 reacted with NaOH, g C-CO_2/h gdw
SLHC	Sapropel-lime-hemp composite
SWD	Sapropel-wood sanding dust
SWF	Sapropel-wood fibre
WC	Wood fibre cement board
WD	Wood sanding dust
WW	Wood wool/wood fiber

INTRODUCTION

The contemporary economy worldwide is based mainly on fossil material use (Ingrao et al., 2018), and this approach significantly contributes to the depletion of resources and environmental problems, especially climate change. Bioeconomy (biotechonomy) can be considered as an alternative to fossil material-based economy. It implies using biomass or biotechnology to produce goods, services or energy (Lewandowski, 2018). Taking into account global environmental and climate problems as well as the decrease and depletion of global resources, a need to reduce the use of synthetic chemicals and to develop a bioeconomy is necessary. Expanded use of bio-based materials can be considered as an action tool within the sustainable development strategies in European Union (Altozano, 2012) and in Latvia (Latvijas Republikas Zemkopības Ministrija, 2017). Thus, it is crucial to search for applications of natural materials as a replacement of synthetic ones (Fava et al., 2015).

Organic-rich lake sediments such as sapropel, gyttja are believed to be prospective materials for diverse applications (Balčiūnas et al., 2016; Stankevica, 2020). Sapropel is regarded as a waste product of lake reclamation (an action actual for eutrophic lakes) and could be required to remove sediment bulk mass to maintain the lake ecosystem by not allowing overgrowth. Thus, sapropel processing and use are sustainable from the perspective of circular economy with the additional benefit of developing sapropel-based products required in the market. In Latvia, the majority of lakes are eutrophic, with significant impacts of anthropogenic eutrophication and the total volume of sapropel resources is ~2 billion m^3. Sapropel reserves in Latvia's lakes reach 700–800 million m^3, while sapropel reserves in bogs reach 1.5 billion m^3 (Segliņš, 2014). Sapropel can be considered a renewable resource since lake eutrophication, being a natural process, is continuous. Thus, the development of new possibilities to facilitate sapropel application can support the reclamation of lakes, as well as can significantly contribute to the development of bioeconomy.

Sapropel properties limit its direct application that is usually tended to agricultural applications. Together with a limited level of research and often outdated application studies, it results in a lack of interest from industries involved in the development of new products. One of the remarkable properties of sapropel is its ability upon processing and drying to act as adhesive and/or binder for other materials (Balčiūnas et al., 2016; Gružāns, 1958, 1960; Klavins and Obuka, 2018). Thus, sapropel can be used to develop composites based on the combination of properties of different groups of materials and to develop new materials with new characteristics. New composite materials is a general trend of material development nowadays. Commonly, composites are synthetic material based, e. g. mineral wool, stone wool, glass wool, while unique properties of sapropel support allow introducing a new group of composite materials formed by a matrix and a reinforcement of fibers – biocomposites (Mohanty et al., 2000). Nevertheless, sapropel has not been used for the production of biocomposites, but this direction of research can is believed to be highly prospective since natural material-based binders for biocomposites are limited.

One of the main challenges of working with sapropel is that its properties limit its direct application to the development of sapropel based composites includes options to use waste biomass as fillers. Such approach provides possibilities to find new applications of waste materials, such as hemp shives, wood sanding dust and wood chips. Another challenge in developing biocomposites is proper testing of their properties (Bulota et al., 2011; Jawaid et al., 2019; Mngomezulu et al., 2014). Biocomposite testing traditionally concentrated on testing functional properties (mechanical strength, durability of use etc.), but the biological stability tests often are neglected as the testing methodologies are not elaborated, and their functioning has not been much studied. However, as biocomposites might be subjected to biological degradation, the biological stability studies are of utmost significance for estimation of their more comprehensive application.

The aim of the doctoral thesis is to study properties of sapropel and possibilities to use it for development of biocomposites for applications in agriculture, construction industries and other fields as well as to test properties of obtained materials in respect to their application possibilities.

The worktasks of the thesis includes:

1. Study of sapropel properties, relevant for development of biocomposite materials
2. Develop principles for biocomposite material production using sapropel
3. Prepare new, application oriented sapropel based biocomposites
4. Develop biocomposite material testing methods as well as analyse and evaluate sapropel composite material application possibilities

Hypothesis

Elaboration and aprobation of new testing methodologies are essential, to develop application oriented, sapropel based biocomposites, which includes detailed studies of elaborated material biostability in addition to functional property estimation.

Scientific and applied significance

1. Development of new approach for lake recultivation waste product – sapropel use for production of natural material based biocomposites and demonstration of the approach efficiency.
2. Creation of design concepts of biomaterial based biocomposite material using sapropel.
3. Preparation of sapropel based biocomposites for new, market oriented applications in building material industry and design, as well as in other fields, thus supporting use of local, natural based material use.
4. Elaboration of sapropel based biocomposite analytical characterization and testing methodology, to prove their biostability, functional properties and application potential.

Approbation of the results

The results of the doctoral Thesis are published in 9 scientific articles, including 8 articles in SCOPUS; Web of Science and discussed in 5 international as well 6 local scientific conferences.

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Author's contribution

The author has obtained and studied sapropel based composite materials made from hemp shive, wood sanding dust, wood fibre used as filler materials and organic-rich freshwater sapropel used as binder. Samples of 4 freshwater sapropel in Latvia were used. During the research used sapropel samples were from Lake Padelis, Lake Veveru and Lake Pilvelis, Lake Pikstere.

Preparation and analysis of sapropel samples were done at the Faculty of Geography and Earth Sciences (University of Latvia).

The author has contributed to direct work with sapropel based biocomposite materials preparation research performing following activities: mixing and curing materials (done both at the University of Latvia and Riga Technical University with a help from Māris Šinka), mechanical strength tests (done by Māris Šinka and Nikolajs Toropovs in Riga Technical University and Ilmārs Preikšs in Latvian University of Agriculture), thermal conductivity tests (done by Māris Šinka and Nikolajs Toropovs in Riga Technical University), microbial stability tests (done by author at University of Latvia with a help of Vizma Nikolajeva, who provided access to equipment needed for the study and helped with analysis of results), biodegradation tests (done by author at University of Latvia with a help from Olga Mutere, who provided access to equipment needed for the study and helped with analysis of results), ageing of composite materials (done by Ilmārs Preikšs in Latvian University of Agriculture and author in University of Latvia), compressive and flexural strength tests of composite materials (done by staff in Forest and Wood Products Research and development Institute), sound insulation properties tests (done by author in Latvian University of Agriculture with a help from Raitis Brencis), comparison of self-ignition tests (done by author at University of Latvia). For sapropel properties is done analysis of moisture, organic matter, ash, carbonate and mineral matter. The author has also performed as well as summarization, estimation, and analysis of all research results, assessment of the relationship between different parameters and properties.

1. LITERATURE REVIEW

1.1. Sapropel: formation conditions and composition

There are 2256 lakes larger than 3 ha in Latvia with a total area of 1001 km^2 and covering 1.5% of the territory of Latvia (Nikodemus et al., 2018). In many of these lakes sapropel can be found – lake sediment containing more than 15% organic matter (Kurzo et al., 2004), which is a mixture of plant and animal organic matter decay residues mixed with mineral particles (Kaķītis, 1999).

Sapropel is a partially renewable resource (Segliņš and Brangulis, 1996) formed under differing conditions. Complex formation conditions reflects problems of terminology as recently is discussed in thesis work (Stankevica, 2020). Sapropel is a loose and fine-grained sediment rich in organic matter in inland waters (Emeis, 2009). Sapropel has a low content of inorganic biogenic components and a mixture of mineral nature (Stankeviča and Kļaviņš, 2014). Sapropel organic matter mainly consists of residues of aquatic plants and aquatic animals – phytoplankton and zooplankton (Kurzo et al., 2004), which reproduce in large quantities in stagnant or poorly flowing overgrown water basins (Lācis, 2003). Sapropel consists of diatoms, green algae and cyanobacteria, as well as foraminifera, radiolaria, dinoflagellates, various species of crustaceans, sponges and bacteria. Benthos organisms, infusors and molluscs also play a role in the development of sapropel (Bambergs, 1993).

In its natural state, sapropel is a loose organomineral sediment that is a clot-like mass with varying shades and colloidal structure (Bambergs, 1993; Vimba, 1956). Extremely intensive sapropel formation occurs in the temperate climate zone (Stankeviča and Kļaviņš, 2014; Штин, 2005), where masses of dead aquatic organisms (plankton, benthos, higher plants) settle at the bottom of the lake at the end of the vegetation period. These residues are optionally anaerobically transformed into complex biochemical, mechanical, microbiological and physico-chemical transformation processes over time into organic rich lake sediments – sapropel (Bogush et al., 2013).

In the composition of sapropel, the amount of minerals can fluctuate over a wide range, up to 85% (Kaķītis, 1999). In the territory of Latvia, sapropel minerals are composed of sand, clay, calcium carbonate and other compounds, which are introduced into the lake by runoff from the catchment or accumulate in the lake, or from dead animals and plants (Gružāns, 1960; Kuršs and Stinkule, 1997; Lācis, 2003).

The composition, properties and thickness of sediments are determined by the type of lake, the geographical conditions of the region, the anthropogenic impact, the characteristics and size of the catchment area (Stankeviča and Kļaviņš, 2014). The main reason for the formation of the sapropel is the interruption of lake substances and energy flows, which are common in eutrophic lakes.

Water sediment accumulates in water bodies by layers. Each subsequent layer covers the layer that had accumulated last year (Stankeviča and Kļaviņš, 2014). Sapropel's layer thickness of deposited sediment during the year depends on the lake's flow and intensity of biological process. Formation of the sapropel layer began in the deepest parts of the lake and during the year is approximately 0.1 mm in small run-off lakes and up to 6.64 mm in lakes with good flow (Kaķītis, 1999; Штин, 2005).

There are two types of sapropel deposits: terrestrial, which are located in bogs under peat layer and in lakes (under water) (Kaķītis, 1999). According to the results of Latvian lakes research, sapropel reserves in Latvia's lakes reach 700–800 million m^3, while sapropel reserves in bogs reach 1.5 billion m^3. Total sapropel resources in Latvia can be estimated at 2 billion m^3 (Segliņš, 2014) however the estimation of the accumulated resources should be re-evaluated considering results of recent studies (Stankevica, 2020).

The sapropel sediments are unevenly distributed in the territory of Latvia, and their amount mainly depends on the area's lake content (Stankevica 2020). Sapropel with high organic matter content (up to 90%) is more common in south-eastern Latvia, including the Latgale Upland (Stankeviča and Kļaviņš, 2014).

In recent years, people have started to pay much more attention to ecosystem services when calculating monetary values of nature, with the aim of using natural resources in an environmentally friendly and efficient way. The abundance, availability and extensive use of sapropel stocks make it an important natural resource, the extraction and use of which solves the necessary recultivation measures of overgrown and swampy lakes (Bakšiene and Janušiene, 2005). Although overgrowth of lakes is a natural process, it is facilitated by the use of inappropriate fertilizers, the construction of agricultural and livestock farms in the immediate surroundings of the lakes, and the disruption of natural water exchange caused by overgrowth of drains and small rivers (Kaķītis, 1999; Skromanis et al., 1989). The recultivation of the lakes is carried out in a complex way, mechanically cleaning and deepening the lake. These processes deplete the lake of sediment and remove overgrowth along the shores of the lake (Bakšiene and Janušiene, 2005; Kaķītis, 1999).

However, the composition and properties of a sapropel that determine its rational use depend on many factors during its formation. To systematize the use of these sediments, researchers have developed sapropel classifications, which have been developed based on research directions and objectives. The widely used classification of sapropel is the classification types developed by A. Fomin and E. Tomin in 1964, based on the analysis of the biological composition of sapropel (Штин, 2005). Belarusian scientists led by G. Evdokimov in the 1970s, developed the classification of sapropel, taking into account the genesis of sapropel and industrial requirements (Евдокимова et al., 1980). The classification created is based on the quantitative indicators of the seven indicators of chemical composition of sediment and divides the sapropel into four types. After the breakdown of mineral and organic matter, the sapropel is divided into low-ash (ash content less than 30%) and ash (ash 31-85%). There are four types of organic sapropel, depending on their amount of humic substances. Ash-rich sapropel is divided into three types, depending on the mineral composition ratio: silica-containing, mixed and carbonate-sapropel.

Recent updating of the sapropel classification system provided (Stankevica, 2020) considering character of the sediments, common form sedimentation conditions and geochemical conditions, common for Latvia specifically and for the Northern Europe in general (Table 1.1.).

Table 1.1

Sapropel Classification System adapted for Latvia (Stankevica, 2020)

Class	Order	Type	Symbol	Diagnostic marks					Possibilities of use
				Ash, %	g/kg DM		Microfossil and granulometric composition, %		
					Ca	Fe			
Biogenic	Organogenic (O)	Peaty		<30	<60	<140	vascular plants	>35	HS products, growth stimulators, binder, fertilizers
		Zoogenic					animals	>15	Therapeutic mud, fertilizers, source of biologically active substances, raw for chemical processing
		Algae					total algae	>45	
		Cyanobacteria					cyanobacteria	>35	Binder, drilling fluids, therapeutic mud, fertilizers
		Green algae					green algae	>35	
	Diatomic (D)	Diatomic		<65	<60	<140	diatoms	>35	Growth stimulators, therapeutic mud, fertilizers
Silicate	Organogenic silicate (OS)	Organogenic sandy		30–65	<60	<140	organic remains sand	40 >30	Fertilizers, therapeutic mud, drilling fluids, raw for chemical processing
		Organogenic silty					organic remains silt	40 >30	
		Organogenic clayey					organic remains clay	40 >30	
		Diatomic sandy					diatoms sand	<20 >30	Therapeutic mud, raw for chemical processing
		Diatomic silty					diatoms silt	<20 >30	
		Diatomic clayey					diatoms clay	<20 >30	
	Silicate	Sandy		65–85	<60	<285	sand	30–50	Soil improvers
		Silty					silt	30–50	
		Clayey					clay	30–50	

Carbonate	Carbonate (C)	Organogenic carbonate		<30	60–140	<140	organic remains calcite	40 <20	Fertilizers, feed additives, raw for chemical processing
		Sandy carbonate		30–65	60–140	<140	calcite sand	<20 30–50	Fertilizers, soil lime
		Silty carbonate					calcite silt	<20 30–50	
		Clayey carbonate					calcite clay	<20 30–50	
		Carbonate sandy		65–85	60–140	<140	calcite sand	<20 >50	Soil improvers
		Carbonate silty					calcite silt	<20 >50	
		Carbonate clayey					calcite clay	<20 >50	
		Carbonate					calcite	>20	Soil lime, therapeutic mud, feed additives
Mixed	Ferruginous (F)	Organogenic limonite		<65	<60	140–285	limonite	5–10	Fertilizers
		Carbonate limonite		<65	60–140	140–285	limonite	5–10	Soil lime, therapeutic mud
		Limonitic carbonate		<85	>140	140–285	limonite	5–10	Soil lime
		Limonite		<85	<140	>285	limonite	>10	Not applicable
	Sulphur (Su)	Sulphide		<85	<140	<140	sulphide	>10	
	Mixed (M)	Organogenic silicate carbonate		<30	60–140	<140	silicate calcite sulphide	<10	Fertilizers, binder, therapeutic mud
		Silicate carbonate limonite		<30	60–140	140–285	sulphide	<10	Drilling fluids, binder, therapeutic mud
		Organogenic silicate limonite		<30	<140	140–285	sulphide	<10	Therapeutic mud
		Organogenic carbonate sulphide		<30	60–140	<140	sulphide	>10	Therapeutic mud

One of the most important properties of moist sapropel is its colloidal structure, which determines the ability of the organic colloidal particles of sapropel to absorb large amounts of water, resulting in a high moisture capacity of 70-97% (Vimba, 1956) and low filtration rate (Liužinas et al., 2005). The relative humidity of sapropel is related to its organic content – the higher the organic content, the higher the moisture content (Stankevica, 2020). Organic sapropel contains more water because its organic part corresponds to gel that binds water molecularly (Kaķītis, 1999). Naturally, the structure of the moist sapropel is viscous, gelatinous or clotted, plastic and with high sorption capacity (Skromanis et al., 1989; Vucāns, 1989). When the moisture content of sapropel drops to 60%, its colloids collapse (Bambergs, 1993). At low temperatures the sapropel loses its bond and its mass becomes loose and friable. This property makes it possible to obtain a sapropel fertilizer that is easy to apply in soil (Vucāns, 1989).

Sapropel dries slowly and returns water with difficulty – it evaporates slowly (Liužinas et al., 2005). When dried, it becomes hydrophobic (Vimba, 1956). Sapropel has an average dry matter content of 5–20% with a mass density of 1040–1080 kg/m^3 (Kaķītis, 1999). The air-dry sapropel has a glossy cut surface and the colloids therein, after solidification, reach the level of a horn's solidness (Bambergs, 1993; Kaķītis, 1999). As moisture decreases, the specific mass of the sapropel increases and the density increases (Skromanis et al., 1989).

Sapropel organic matter is of both autochthonous and allochthonous origin. The allochthonous components of sapropel contains shoreline erosion material, consisting of mineral particles, as well as inorganic substances of biogenic origin and animal and plant residues, surrounding the lake flowing from the catchment area of the lake with rainwater, rivers, air currents (Leonova et al., 2011; Liužinas et al., 2005).

Depending on the composition of the sapropel, it can have different colors: dark brown (with oily sheen), brownish, light and dark grey, greenish, yellow, light pink, etc. The color of sapropel is determined by minerals and organic substances: the admixture of sand gives a grey color, lime – white, clay – yellow. The green color in the sapropel is determined by the chlorophyll contained in the green algae, while the diatoms pink (Bambergs, 1993; Vucāns, 1989; Кордэ, 1960). In the lakes studied in Latvia, the organic matter content of sapropel dry matter is higher than 60% in about 80% of cases (Vucāns, 1989).

According to the composition of sapropel, the dry matter can be divided into three groups of substances: minerals (non-indigenous origin), organic matter complex (plant and animal residues), inorganic components of biogenic origin (Stankeviča and Kļaviņš, 2014). Sapropel organic matter is one of its most important properties. Their content in the sapropel dry matter ranges from 15% to 90% and more (Liužinas et al., 2005; Stankeviča and Kļaviņš, 2014; Кордэ, 1960; Курзо, 2005). Elemental composition of sapropel organic matter: carbon 50.8–59.2%, oxygen 27.9–35.2%, hydrogen 6.7–7.4%, nitrogen 4.7–5.4%, sulfur 0.6–1.4% (Vimba, 1956; Бракш, 1971).

Depending on the conditions and composition of the sapropel, the organic part of the sapropel may contain different groups of organic substances: humic substances 5.1–61.9%, hemicellulose 9.8–52.5%, cellulose 0.4–6.0%, amino acids 9.8–17.8%, bitumens 6.8–15.2% (Бракш, 1971; Евдокимова et al., 1980; Штин, 2005). Further subdivided bitumen and humic substances: group A bitumen 3.4–10.7%, group B bitumen 2.1–6.6%, humic acid 11.0–37.6%, fulvic acid 2.1–2.5%, insoluble residue 5.1–22.6%. Kaķītis emphasized that sapropel bitumens contain waxes, solid hydrocarbons, resins, fats and various acids (Kaķītis, 1999), however these suggestions are not supported with experimental studies. The other non-organic constituents of the sapropel dry matter are called ash and can have a very different composition: SiO_2 3.2–72.4%, CaO 2.5–33.5%, MgO 0.4–2.3%, P_2O_5 0.14–0.27%, Fe_2O_3 1.1–2.6%, Al_2O_3 0.8–3.9% (Бракш, 1971; Евдокимова et al., 1980; Штин, 2005). Sapropel also includes various trace elements: Si, Al, Fe, Ca, Be, Sr, Mg, Ti, Na, K, V, Cr, Mi, Ag, Mo, Ga, Pb, As, Sn, P, S, Na, Sc, Ni, As, Rb, Y, V, I, Zr, Nb, Mo, Cd, Cs, Ba, La, Ce, Hf, Th (Leonova et al., 2011; Lukashev et al., 1991)1990. The amount of macro and micro elements in sapropel dry matter (mg/kg) in lakes of Latvia is Mn 145.3–456.1, Cu 4.7–14.6, Co 1.2–8.0, B 4.3–17.2, Zn 3.6–16.6 (Bambergs, 1993; Бракш, 1971).

In sapropel also 11 vitamins are found: carotene, folic acid, B1 (thiamine), B2 (riboflavin), B3, B4, B5 (pantothenic acid), B6 (pyridoxine), B9 (folic acid), B12 (cyanocobalamin), C (ascorbic acid), D, P and E (tocopherol). This determines the potential of sapropel in veterinary and medical applications as a source of polyvitamins (Kalēja, 1959; Mikulionienė and Balezentienė, 2012).

Sapropel organic matter contains elevated nitrogen concentrations of up to 6% (Skromanis et al., 1989; Vucāns, 1989). Sapropel with the highest amount of nitrogen in aquatic animals contains 4.4–4.8% nitrogen on average, sapropel rich in algae residues 3.0–4.4%, nitrogen content in peaty sapropel, which is made up of peat-forming plants and other vascular plants, can reach 2.6–3.5% (Stankeviča and Kļaviņš, 2014).

Sapropel contains 15 amino acids: glycine, aspartic acid, glutamic acid, alanine, lysine, proline, histidine, tyrosine, serine, arginine, phenylalanine, threonine, valine, leucine and cystine (Lukashev et al., 1991; Mikulionienė and Balezentienė, 2012).

In this study, adhesion and hydrophobic capacity is a most important property of organic rich lake sediment (Brakšs et al., 1960; Gružāns, 1960; Штин, 2005). The adhesion capacity of sapropel is determined by the residues of the animals and plants it contains. Green algae casings are composed mainly of cellulose, which poorly decomposes over time, so organic sapropel, which is composed of green algae, is rich in cellulose, poor in ash-containing minerals and low in humus content, produced mainly from peat plants (Stankeviča and Kļaviņš, 2014). It should be noted that the adhesive properties of sapropel are also conferred by nitrogenous substances, including free amino acids. In addition, the sapropel composition is influenced by the structure and amount of the humic acid molecules, i.e., by increasing the proportion of humic acids in the composition, the branching of the molecules of the peripheral part increases. This promotes the formation of strong bonds between molecules and especially between macromolecules during material creation. Molecules in humic substances remain more elastic, comprising solid particles of the molded composite material, which are capable of providing durability and high strength of the material (Курзо, 2005). It is therefore rational to use sapropel with the above properties as an adhesive and binder in the production of various ecological building and finishing materials.

Summary. Sapropel as natural, renewable resource have complex composition, significant variability in one site (lake or bog) as reflected in the sapropel classification system, have many unique properties supporting its application potential. Organic sapropel contains numerous organic compounds formed during decay of living organic materials and secondary biosynthesis in sedimentary phase as well as mineral matter of allochthonous origin.

1.2. Sapropel application possibilities

Sapropel can be found in significant quantities and thus of importance is to study its application possibilities. Sapropel can be considered as a renewable and natural material and for example, in case of lake recultivation, involving removal of sediments it can be considered as a waste material and thus available for use as low-cost product. Sapropel, like peat, has a wide range of possible uses, which vary with the composition, properties and availability of the sapropel resource. It can be used in various sectors of the economy (Figure 1.1), such as agriculture, medicine, veterinary, construction industry, etc.

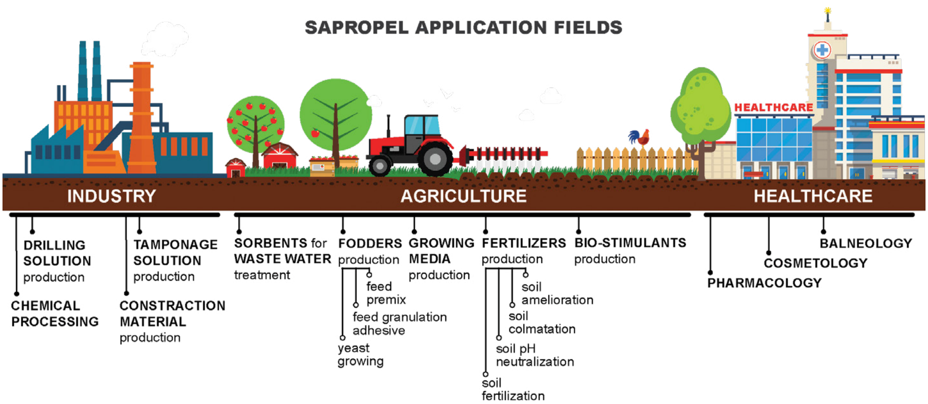

Figure 1.1. **Application options of sapropel in the fields of national economics** (Stankeviča 2020)

When question arises, where to use sapropel in any of the previously mentioned sectors of the economy (Figure 1.1), it must meet certain requirements. The most important diagnostic features that determine the uses of sapropel are listed in the industrially genetic classification of sapropel (Stankeviča et al., 2017) (Table 1.1).

From the point of view of use, organic sapropel is accepted as the most valuable type of sapropel, however, this does not mean that this type is versatile and produces equally good results in all areas of use of sapropel (Brakšs et al., 1960; Gružāns, 1960; Штин, 2005).

1.2.1. Use of sapropel in agriculture

Agricultural applications of sapropel have been most widely studied. Sapropel properties influence its application potential in agriculture: 1) sapropel can support development and optimisation of soil structure, 2) sapropel can enrich soil with organic matter, especially with humic substances, 3) sapropel is a source of nutrients and can ensure slow release of nutrients 4) biologically active substances in sapropel can support plant growth (sapropel can act as biostimulant). In Latvia, the use of sapropel in field fertilization has been studied at the Latvian Academy of Agriculture since 1954. As an organic fertilizer, sapropel can be used both fresh and as a compost or substrate. It is important to note that freshly obtained, non-aerated sapropel contains zinc, aluminum, non-oxidized iron compounds and bituminous substances that may inhibit its conversion into plant nutrients during the first year of use and reduce soil microorganism activity (Kaķītis, 1999). Although the sapropel is highly effective in the first year of application, it is mixed with manure or sludge.

Sapropel and manure compost are organic fertilizers that can bind ammonia. For the formation of granular complex organic fertilizers, the rational use of sapropel is with organic matter content more than 50% and the addition of macro- and microelements is necessary (Skromanis et al., 1989; Vucāns, 1989; Курзо, 2005). If sapropel is composted 6 to 8 months before application, its effectiveness increases. This prevents the formation of unpleasant odors and pollution of the environment (Grigalis, 1987). During composting, it is important to ensure that the moisture content of the compostable material does not exceed 55–65%. If it is higher, anaerobic and compost-inhibiting conditions begin to form in the compost (Kaķītis, 1999).

To increase nutrient stability and reduce leaching of mineral fertilizers, they can be granulated with organic sapropel. This reduces the deposition of fertilizers during storage and improves their physico-chemical properties as well as slow release of nutrients. The moisture content of the fertilizer granules during storage should be 10–25%. Under these conditions, the sapropel increases adhesion properties and the granules has shape holding ability (Курзо, 2005). Sapropel applications in agricultural tests demonstrates reasonably high efficiency, for example, the average yield increase using sapropel for soil improvement provided by A. Kaķītis (1999) is: 1) by 10 to 15% for cereals; 2) rolling crops 15–20%; 3) for vegetables 20–30%.

B. Kurzo's research shows that acid-alkali hydrolysates of sapropel (liquid sapropel humic fertilizers) are better than peat liquid humic fertilizers because of their higher biological activity. In these studies, barley seed germination using liquid sapropel humic fertilizers compared to controls is 114.2–118.9% and seed germination increases from 13.4 to 18.9%. Significantly high biological activity is found in plant growth promoters derived from peaty sapropel (Table 1.1) containing up to 70% humic acid in organic matter (Kurzo et al., 2004).

Carbonatic sapropel can be used in agriculture as a liming material to replace dolomite flour and lime. Studies in the use of sapropel in horticulture have shown that it accelerates plant development and flowering time. It is promoted by humic acids, trace elements and other biologically active substances in the sapropel. It is recommended that organic sapropel can be used for the production of balanced organic fertilizers for growing and replanting greenhouses in agriculture (Skromanis et al., 1989).

An interesting and progressive idea is to use the heat generated on the farm during the composting process. These studies were conducted at the Swedish Institute of Agricultural Mechanization in Sweden. The results show that the temperature of the compost pile can reach up to 70 °C as a result of the action of microorganisms. Researchers recommend placing a heat transfer circuit in the compost heap that removes excess heat energy, thereby keeping microorganism activity processes at the highest possible level. The heat dissipated heats the water in a special tank to 58 °C, keeping the compost temperature 60–62 °C. The amount of heat produced by this technology is equivalent to 25 tons of liquid fuel per year. Similarly, composting processes for sapropel – reed and sapropel – straw can be used. Compost heaps are placed in greenhouses, providing air exchange in the compost, with the possibility for farms to use the heat and carbon dioxide generated by the composting process. The substrate obtained from composting is used for growing seedlings (Kaķītis, 1999).

Summary. Several studies done mostly in Northern Europe, Russia, and Belarus demonstrates good potential of sapropel application in agriculture. Considering sapropel composition, biological activity aspects most prospective could be sapropel applications in biological agriculture. However just these aspects have not received duly attention as well as economic feasibility of sapropel use.

1.2.2. Use of sapropel in animal husbandry

Considering properties of sapropel, there is good potential to develop sapropel applications in animal husbandry to support the efficiency of livestock farming, the efficient use of bird and animal feed. Argument in respect to use of sapropel are related to its biogenic nature and evident need to reduce of synthetic products. To achieve this, highly effective biologically active substances such as sodium and hydrohumate are used, which promote oxidation in the body, increase metabolism and protein accumulation in the blood serum, improve vitamin synthesis, and increase red blood cell production in the bone marrow.

One of the uses of sapropel is a dietary supplement in animal husbandry that would increase the live weight of animals without the use of chemical preparations. Organic sapropel, which is natural and safe for poultry, is usually used for this purpose. When enriched with natural vitamins and micronutrients, sapropel can be used in animal husbandry (livestock farming) as a vitamin and micronutrient supplement. The addition of 1.0 to 1.5% of sapropel to the daily ration of cattle increases their live weight and milk yield by 12–15% (Курзо, 2005; Штин, 2005).

Studies in which piglets were fed an organic sapropel preparation from birth showed that such preparations prevent animals from developing rickets, dyspepsia and anemia (Штин, 2005). These diseases include metritis (inflammation of the urogenital tract), mastitis (inflammation of the mammary gland), bursitis (inflammation of the mucous membrane), tendovaginitis (inflammation of the tendon of the vagina), phlegmon (Штин, 2005). These examples demonstrate that organic sapropel has high therapeutic efficacy in animal husbandry for the treatment of surgical, gynecological and other diseases in animals. With the use of sapropel, cattle are treated for external, internal skin inflammatory diseases, gynecological and chronic diseases.

S. Mikulioniene and L. Balezentiene (2012) studied the use of sapropel in animal feed additives (changes in animal body weight and digestive tract development, meat quality), concluded that organic selenium in sapropel has antioxidant properties and prevents stress-induced malnutrition. Biologically active substances such as vitamins, enzymes, amino acids, antibiotics, estrogens, carbohydrates, lipids and humic substances contribute to the physiological role of sapropel in poultry feed additives. The humic substances in the sapropel improve the function and microbiological balance of the intestinal tract of animals. In contrast, copper and zinc in the sapropel promote animal growth, immune function and maintain the antioxidant regulatory effects on iron (Mikulionienė and Balezentienė, 2012).

Sapropel is also added to bird droppings as an additional element to promote their rational use (Grigalis, 1987; Lukashev et al., 1991)a rather wide range of element concentrations permits the selection of lakes and deposits with the most valuable proproties for these uses. The agrochemical effectiveness of sapropels is determined by the content of N, P, K, a number of trace elements, the silty fraction, the amount of biologically active substances, and the level of exchange acidity. It is also important to know the content of harmful components, e.g. pesticides, benzopyrine, a number of heavy metals (such as Pb, Hg and Cd and to enhance the activation and quality of microbiological processes (Штин, 2005).

Summary. Several studies have demonstrated good application potential of sapropel in animal husbandry and other related fields, however the level of knowledge is too low, and the information sometimes is not enough convincing and scattered.

1.2.3. Use of sapropel in healthcare

Sapropel application potential in healthcare is backed up with a long history of balneology based on use of peloids or medical mud for external applications and baths as well as other preparations and materials. As peloids are described organic-mineral complexes with high concentrations of organic matter and others that are used in therapeutic procedures (Badalov and Krikorova, 2012). Main factors affecting efficiency of sapropel use in balneology includes known presence of numerous biologically active substances such as hormones, sterols, amino acids and vitamins (Szajdak and Maryganova, 2007). Sapropel is used in balneotherapy and cosmetology (Badalov and Krikorova, 2012) as extracted from their source (lake or bog) and in combination with physical factors (sapropel moisture, heat holding capacity) psychological aspects (relaxing atmosphere) its application convincingly demonstrates biostimulating effects, activate metabolism and immune system (Anderson, 1996). Sapropel applications in several studies have demonstrated high efficiency to treat bone and muscle disorders, joint and spine diseases, myositis, ulcers as well as positive impact on nervous system disorders (Bellometti et al., 1996, 2000). Of importance is the sapropel capacity to reduce inflammatory processes as well as skin diseases especially chronic eczema and several forms of dermatitis (Carabelli et al., 1998).

Organic and mineral compounds in sapropel determine its effectiveness in treating a variety of diseases such as musculoskeletal disorders, peripheral and nervous system diseases, gastrointestinal disorders. Studies on the metabolic activity of sapropel have shown that the healing properties of sapropel are determined by its organic components, including humic substances (Курзо, 2005). Sapropel is used in the treatment of chronic gastritis, mastitis, duodenal and ulcer diseases, furunculus, ENT and skin (dermatitis, eczema, and burns) as well as in the treatment of hepatobiliary disease prior to exacerbation (Штин, 2005).

During World War I, sapropel was used as an antiseptic to treat soldiers' wounds (Bajārs and Brakšs, 1950). The effect of sapropel on epithelial cell development was demonstrated in its ability to accelerate skin regeneration. This was determined by phenols in the sapropel, which have antioxidant properties that determine the ability of the sapropel to promote wound healing (Vysokogorskii et al., 2009). Conversely, the adsorption property of sapropel accelerates the drying of fresh wounds, while antibiotics stimulate the stopping of inflammatory processes (Штин, 2005). Sapropel does not cause rapid haemodynamic changes in the body that help to treat musculoskeletal disorders (Курзо, 2005).

In the 1950s, a Latvian scientist G. Liepiņa studied the effect of medicinal mud compacts on peripheral leukocytic picture and changes in blood pressure. She concluded that basophilic leukocytes have a tendency to decrease during sulfur water bath and mud compacts. However, the circulatory reactions caused by the sludge compress are general and mainly depend on the functional state of the organism (Liepiņa, 1948, 1953).

Organic sapropel type has plasticity and viscosity, homogeneous structure, high heat capacity. It contains various macronutrients, free amino acids, enzymes, vitamins that determine the use of sapropel in mud baths as curative mud (Курзо, 2005).

Studies have shown that green algae sapropel helps treat stomach diseases, while peat sapropel helps peripheral nervous system diseases. Sapropel has an effect on the entire body during treatment, affecting the nervous system, blood circulation, body temperature (Курзо, 2005) and blood pressure without stress because the effects of mud are gentle, slow and mild (Liepiņa, 1953).

Warm sapropel applications can be used to treat phlegmons, which is a diffuse inflammation of adipose tissue that results in pus. Sapropel warm applications stimulate phagocyte activity, which results in intense tissue regeneration (Штин, 2005). Sapropel has a high calorific value that determines the long-term warming of deep tissues, thereby normalizing blood pressure, and contributes to the treatment of skin and female genital inflammation and joint pain relief (Курзо, 2005). Since 1999, research by F. Puntus has raised the issue of the use of organic sapropel in cosmetics (Курзо, 2005). Sapropel hard soap containing sapropel and glycerol, beeswax, coconut oil, olive oil and NaOH sodium hydroxide is patented in the United States in 2011. Researcher's studies have shown that glycerol interacts with sapropel to promote the treatment of various skin conditions in soap. As a result of this synergy, soap is not only moisturizing but also stops or prevents symptoms of eczema, dermatitis, psoriasis, acne and skin allergy, and prevents skin cracking (Bevan et al., 2011).

Recent study has demonstrated that Latvian freshwater sapropel can be used as raw material for obtaining sapropel extract and use it in the preparation of pharmaceuticals (Pavlovska et al., 2020).

Summary. Comprehensive research on the use of sapropel in the field of healthcare products is one of the most promising and sustainable directions on the basis of natural and ecologically pure raw materials.

1.2.4. Use of sapropel in energy production

One of the alternatives to the use of sapropel is its use in the production of briquettes and pellets for heating residential and household buildings (Kozlovska-Kędziora and Petraitis, 2011; J Kozlovska and Petraitis, 2012; Курзо, 2005; Штин, 2005). The use of sapropel briquettes saves other energy resources because the burning process of sapropel briquettes is longer than that of conventional briquettes (Kozlovska-Kędziora and Petraitis, 2011; Justyna Kozlovska, 2012). In the production of these briquettes, sapropel can be mixed with straw, sawdust or peat (Штин, 2005). Studies have shown that the concentration of contamination during the burning process of sapropel briquettes does not exceed regulatory limits. Briquettes of this type can reduce pollution and ensure a smooth use of the energy source (Justyna Kozlovska, 2012). The use of sawdust-sapropel briquettes results in lower CO_2 emissions and improved combustion (Штин, 2005).

The proposal of Russian scientists was to completely replace coal fuel with sapropel for the production of agloporite. Agloporite (thermal insulation material) is a porous, lightweight material from which lightweight cement can be made. Complete or at least partial replacement of high-grade coal with sapropel would reduce the cost price of agloporite (Штин, 2005). By mixing sapropel ash with cement, it is possible to reduce cement overproduction in concrete production (Штин, 2005). For the production of activated carbon, organic sapropel can be used as a feedstock for hydrocarbons. Such coal has low mineral content and high absorption capacity (Курзо, 2005). Mineralized types of sapropel containing elevated levels of silicates and carbonates are useful for the synthesis of porous materials (Штин, 2005).

In 1991, Russian researchers analyzed the possibilities of using sapropel for enrichment in high-shale oil shale with the aim of increasing the yield of gas and resin to improve shale composition (Kurzo et al., 2004). Organic sapropel was used in the oil shale treatment to increase the yield of resin and gas in the optimum amount of 10%, reaching a resin release rate of up to 54% (Штин, 2005).

Summary. There is some experience in application of sapropel in the energy production industry, however from perspective of: 1) application efficiency, especially in case of higher amounts of mineral substances; 2) needs to reduce greenhouse gas emissions and especially considering the EU Green Deal, there are serious doubts that this direction of the sapropel application will have future.

1.2.5. Use of sapropel in chemical industry

A lot of research has been done into the use of sapropel in the chemical industry. Due to its chemical composition, availability, relatively low cost and ecological safety, sapropel is one of the most suitable raw materials for drilling solutions, which reduce friction and are required for geological exploration wells (Штин, 2005). Sapropel contains high molecular weight substances: humic substances, natural biopolymers, cellulose, carbohydrates, lignin, hemicellulose and bitumens, its solution dispersion rheological properties and inhibitory activity properties on metallic surface corrosion determine the use of sapropel working fluids in drilling plant hydro systems, and diatomaceous dispersions (Курзо, 2005; Штин, 2005).

For the production of façade bricks, a sapropel with high alkaline content and low value can be used as an additive. The alkalis contained in sapropel and its reducing medium increase the proportion of the glass phase in the ceramic products (Kaķītis, 1999; Stankeviča and Kļaviņš, 2014; Штин, 2005). The use of sapropel as an additive to clay products during firing improves the porosity and agglomeration of the ceramic. Scientists of Kaunas University of Technology have investigated the use of both carbonate and organic sapropel in ceramic products and concluded that adding 7 to 10% sapropel does not change product strength and water permeability, but the product dries faster, the deformation process does not compress and flexural properties as well as thermal conductivity improves (Kasperiunaitė et al., 2009).

From sapropel it is possible to obtain liquid fuels, oils, carboxylic acids, bitumen, high molecular weight, ammonium compounds, as well as “softening” agents for rubber production and other products (Bajārs and Brakšs, 1950; Штин, 2005). It is thus possible, by chemical processing, to obtain hydrolyzates from the sapropel containing the sugars necessary for the cultivation of yeasts (Brakšs un Miļins, 1960; (Bajārs and Brakšs, 1950). These hydrolysates can be used as concentrates for feed supplements for livestock. The resulting sapropel hexose hydrolysates can be used in the alcohol extraction industry (Brakšs and Miļins, 1960). Low-yield sapropel can be used as a binder in the manufacture of drainage pipes, expanded clay and porous ceramic stones (Курзо, 2005).

Theoretically, sapropel can be used in the metallurgical industry – formable liquids. Sapropel used for this purpose must have low hygroscopicity and high mechanical properties (Штин, 2005).

The chemo-technological applications of sapropel have been studied at the Institute of Chemistry of the Latvian Academy of Sciences. It is recognized that sapropel with a profitability of 20–35% is best suited for this purpose (Штин, 2005), since semi-coking sapropel with such high organic matter content can yield a lot of tar, semi-coke, gas and tar water. Tar is considered to be the most valuable sapropel semi-coking product, as sapropel tar can be used for electrical insulating mass, liquid fuel, phenol, paraffin pyridine-based products, and semi-coke can serve as an energy fuel. In addition, tar water contains ammonia, phenols, methyl alcohol and acetone (Bajārs and Brakšs, 1950). In the research of scientist N. Brakšs, 27–35% of viscous oil (according to viscosity corresponds to the type of light shaft oils) and 13–17% of paraffin are obtained from sapropel (Bajārs and Brakšs, 1950).

Summary. Sapropel as a rich source of organic substances can find different applications and can be subjected to chemical transformations thus supporting productions of many substances for chemical industry, however accordingly to contemporary trends of use of biomaterials, much more work should be done, to develop pilot scale/ real applications as many other biomass kinds (at first wood and food waste etc) are more prospective.

1.3. Use of sapropel for development of biocomposites

For many applications growing attention gain composite materials and especially biocomposites. Biocomposites are composite materials formed by a matrix (resin, glue etc) and a reinforcement of fibrous material. Environmental concern and cost of synthetic fibres have led the foundation of using natural fibre as reinforcement in polymeric or mineral composites where the matrix phase is formed by renewable or nonrenewable resources. Composite materials find new and exciting applications in different areas, but the dominant ones are building and construction material industries.

The use of sapropel in the building industry for production of construction materials have been studied. In Latvia research on development of such materials started in 1957 under the leadership of A. Kalniņš in The Latvian Institute of Forestry Problems. N. Brakšs and N. Miļins have found that alkali-treated organic sapropel (with a particle size more than 50 μm) and hydrolyzed sapropel have good hydrophobic and adhesive properties. As a result, sapropel have a high potential for bonding particle board and thermal insulation materials. This is also proved by the technical and physical mechanical characteristics of the sapropel, which correspond to the characteristics of the thermal insulation materials; density 150–300 kg/m^3, thermal conductivity of air-dry mass (25 °C) 0.048–0.075 W/m*K, resistance limit 0.4–3.0 MPa, water absorption 9–20% (Brakšs and Miļins, 1960).

There are studies about technical tests of sapropel concrete (Brakšs et al., 1960; Gružāns, 1960), sapropel-hemp shives (Pleiksnis et al., 2016; Pleikšnis and Dovgiallo, 2015) and sapropel-wood chips (Obuka et al., 2014) composites. One of the latest study has been done by G. Balčiunas, who have studied sapropel-hemp-paper production waste (PPW) composite materials properties (Balčiūnas et al., 2016). In these studies, the researchers concluded that the use of sapropel as a binder with different materials is such that technical quality can be included in the category of thermal insulation materials for finished products. According to the literature, sapropel can be used as binder for various wood waste, unused waste from the paper and cardboard industry, flax processing (Курзо, 2005), degraded peat and similar raw materials (Gružāns, 1958, 1960) containing composites. Sapropel is a good substitute for protein-based glues, for example, albumin and possibilities to replace proteins would be a significant benefit of sapropel application.

Sapropel with an organic content of more than 85% and nitrogen more than 3.3% can be used for the production of sapropel binder (Курзо, 2005). Organic and carbonate sapropel can be used to replace binders for cement and other building materials, resulting in sapropel concrete, where gravel and a byproduct of wood processing as a filler are used. Sand and slaked lime can also be added for strength (Brakšs et al., 1960; Gružāns, 1960).

Thermal insulation materials are classified as efficient building materials, which allows significantly reduce the cost of construction (Штин, 2005). The adhesive properties of sapropel can be used in the production of building materials, both cold-pressed and hot-pressed composites are stable at elevated temperatures and pressures (Brakšs and Miļins, 1960).

One of the properties of sapropel is its ability to bind large amounts of water. When producing heat-insulating materials, it is important to keep the material to a minimum shrinkage. Inventors and researchers of sapropel concrete recommend the use of sapropel with moisture up to 60% and filler materials with moisture below 20% to reduce shrinkage. The sapropel concrete produced with such raw materials does not show a high shrinkage rate and reduces the energy and time spent in the drying process (Gružāns, 1960).

The thermal insulation material should be as light as possible as it will better prevent heat flow, thus avoiding heat loss indoors. In composite materials using lightweight aggregates (low density), sapropel concrete has a density of approximately 313 kg/m^3 (Brakšs et al., 1960).

In comparison with wood, sapropel concrete has a high fire safety: its burning process stops and does not continue at temperatures below 380 °C. This means that sapropel concrete can be used in construction not only as a heat insulation material, but also as a cover for non-load bearing walls and partitions: freezer walls, ceilings, residential and industrial buildings, appliances and piping (up to 100 °C) (Gružāns, 1958).

Although several studies were carried out in the 1960s and 70s demonstrating the potential of using sapropel for the use and production of such building materials, the study of practical use was not continued. As issues arise, the use of local and natural resources in this area of research in the production of environmentally friendly building materials becomes more relevant today (Klavins and Obuka, 2018; Obuka et al., 2015; Obuka et al., 2019; Obuka et al., 2014, 2016, 2017)

It is important to talk about other building materials produced from biomaterials and organic binders, but first of all some general studies about building industry impact to environment will be discussed.

One of the most important tasks producing the building materials in the future, is to lower energy use at all stages of their lifecycles, from construction to end of use (Asdrubali et al., 2015).The construction industry consumes 60% of all lithospheric raw materials consumed and has high energy consumption (Zabalza Bribián et al., 2011). Building industry consumes about 40% of the worldwide global energy and 25% of the global water resources and 40% of the worldwide resources. As well as it is estimated that building industry is responsible for 1/3 of greenhouse gas emissions (Asdrubali et al., 2015). Developing sustainable, environmentally friendly thermal insulation materials of buildings is one of the most applicable ways to save energy by reducing heat or cold losses through casings. Nevertheless, many traditional building materials do not have favourable thermal insulation properties. In this way, many parts of buildings, such as exterior walls, floors, roofs, exterior doors, use various types of additional thermal insulation materials, such as solid boards (panels), hard bucks, particles, sandwiches, coils (L. F. Liu et al., 2017). It should be emphasized that it is vital to examine the processes which affect carbon emissions and energy consumption and over a building's life-cycle – and this includes examining the potential of new ecological building materials (Binici et al., 2014). To promote the reduction of material and energy consumption, increased use of renewable and semi-renewable natural resources is needed. This would ensure sustainable building construction based on balancing environmental, economic and social issues. The ecological benefits of such construction are: reduced CO_2 and sulfur emissions, reduced solid waste, conservation and saving of air, water and other natural resources, preservation of ecosystems and biodiversity (Kreijger, 1987; Štrausa et al., 2011).

Generally, thermal insulation materials can be classified into four categories depending on the raw materials: (1) From rocks and slag, such as rock wool, glass wool, expanded clay perlite, glass beads, vermiculite, cinder, ceramic products, etc, (2) Petrochemical and coal chemical intermediates such as polystyrene, polyurethane, polyethylene, (3) From plants, including agricultural waste, forestry waste and industrial fiber waste such as straw, rice husks, waste paper, wood chips, cotton, maize crops, (4) Of metals, such as metal reflective films, hard metal visors, radiant plates, whose use is still limited because they can only be used on roofs and are much more expensive than other thermal insulation materials (Liu et al., 2017).

The basis of environmentally friendly construction is the following principles: (1) Environmentally friendly materials shall be used in the finishing materials and basic constructions, (2) Construction materials must be recycled after use, (3) Recycling of building materials should result in new raw materials, (4) Materials should provide energy saving potential, (5) Local resources must be used to develop materials.

It is essential for materials used in construction that they do not emit harmful chemical compounds and are long-lasting (Isnin et al., 2013; Kreijger, 1987). The materials must be aesthetically and visually appealing and meet all design requirements. Ecological construction should be based on building materials that are not harmful to human health and the environment. Its production must be decentralized with low energy consumption. The material must be reusable or recyclable (Kruše et al., 1995; Zabalza Bribián et al., 2011).

The choice of eco-friendly building materials is the basis for a healthy living environment, so the building materials that make up the room must meet the following requirements: (1) The building materials must be "breathable" to ensure the exchange of fresh and used air in the building, (2) Building materials and finishing materials must be composed of natural raw materials and have a comfortable surface temperature and natural scent (Zabalza Bribián et al., 2011).

Modern research shows that 10 to 25% of the energy used in the entire life cycle of a home depends on the materials used in the construction of the building. On the other hand, in low-energy homes with annual energy consumption ranging from 15 to 50 kWh/m^2, the energy consumption depending on the materials used in the construction can reach 50%. The issue of plus-energy homes, which produce more energy than they can use through renewable energy sources (solar and wind), is becoming more and more important in the world (Dylewski and Adamczyk, 2012). The construction of these houses is also based on the principles of ecological construction and natural materials.

Avoiding the use of toxic protective equipment and the use of toxic binders in materials is essential to energy-efficient and ecological construction so that they do not cause ecological damage or danger to the environment (Kruše et al., 1995). Long-term economy and rational construction are possible through the use of natural building materials and the development of environmentally friendly materials, as well as by reducing the use of transport in the production process, which reduces the energy and pollution consumed in the production of the material (Asdrubali et al., 2015).

It is necessary to use technically efficient thermal insulation materials to reduce heat loss of the building envelope (Štrausa et al., 2011). Their main task is to reduce the building from heat loss and excessive warming. The best insulation material is air at rest. When using thermal insulation materials, it is important to protect them from moisture, as moisture increases the thermal conductivity of materials and reduces mechanical strength (Gorenko, 2002).

According to the principle of operation, thermal insulation materials are classified into three large groups – convective (mainly porous with a minimum convention index), reflective or reflexive (high surface reflectivity), vacuum ("airless" principle – no convection heat transfer) (Štrausa et al., 2011).

On the other hand, chemical insulation materials can be divided into organic and inorganic materials. Organic insulation materials are made from peat, wood by-products (sawdust, wood fibre), sheep wool, straw, hemp, flax, cellulose and cork (Korjakins et al., 2013; Kymäläinen and Sjöberg, 2008). The most common organic insulation materials are fibrolite, particle board and fiber board, but also inorganic and organic materials such as cell glass, perlite, vermiculite, polyurethane, polystyrene, mineral wool (rock wool, glass wool, slag wool) and so on (Gorenko, 2002) can be used. Natural fiber insulation material is widely used worldwide because of its ability to repel moisture above hydrophobic properties of inorganic materials (Kymäläinen and Sjöberg, 2008).

The quality characteristics and criteria of the function of the insulation materials are determined by the regulations of law. Internationally developed standards for them are based on environmental protection requirements and material life cycle. In Germany, for example, the European quality label "Natureplus" has been developed, which regulates building material standards that meet the technical characteristics of thermal insulation materials for the development of environmentally friendly materials. This quality label is awarded to thermal insulation materials such as hemp, flax, cork, sheep wool, and other natural raw materials (Kymäläinen and Sjöberg, 2008; Obuka et al., 2014). Among industrialized countries, for example, in the Netherlands, legislation requires that 80% of building materials that become debris after demolition of buildings be recycled into new structures or road construction (Berge, 2009).

As the aim of the dissertation is to develop composite materials, that one of the uses of which is thermal insulation, it is important to look at specific examples of thermal insulation materials made from renewable natural resources.

Studies of Riga Technical University on hemp shives as a filler and hydraulic lime as a binder showed that the thermal conductivity and compressive properties of these materials are consistent with thermal insulation materials (Sinka et al., 2014). Alongside research on the use of hemp in building materials, the use of hemp fibers and stems in architectural and interior elements is being explored (Bolgzde and Ulme, 2010). The potential of using peat in the production of thermal insulation materials in peat – particleboard thermal insulation composite materials was also investigated. Although the developed product meets the requirements of thermal insulation materials, the research is not continued (Korjakins et al., 2013).

Research on wood composite materials has developed thermal insulation materials from woodworking byproducts (wood chips) and expanded polystyrene, which were glued with organic glue (Agoua et al., 2013). A study has been carried out on the feasibility of developing lightweight concrete blocks from wood fiber residues, rice hull ash and limestone powder waste for cement replacement (Aigbomian and Fan, 2013; Torkaman et al., 2014).

Summary. Sapropel as a rich source of organic substances can find different applications for development of building materials, especially in thermal insulation materials. Although several studies were carried out in the 1960s and 70s demonstrating the potential of using sapropel for the use and production of such building materials, the study of practical use was not continued. However accordingly to contemporary trends of use of biomaterials, much more work should be done in development on new environmentally friendly materials. Development of pilot scale/real applications in building materials as many other biomass kinds can be used as filler materials, for example wood, energy agriculture, livestock farming, food byproducts from industry are more prospective to use in creating new sustainable materials.

2. MATERIALS AND METHODS

The methods that were used in detail are described in papers included in the current thesis.

2.1. Sapropel samples used in the study

In the thesis organic rich freshwater sapropel were used. Sapropel sediments were sampled from four lakes in Latvia – Padelis 56°14′9,83″ N 27°21′1,88″ E, Pilvelu 56°28′33,23″ N 27°7′45,64″ E, Veveru 56°15′53,6″ N 27°04′14″ E located in Rezekne district, Latgale region. Piksteres lake 56°27′01.8″ N 25°34′13.8″E – located in Jekabpils District, Selonia Region. Bulk sampling using Ekman dredge were used – usually in one sampling more than 10 L from each site were sampled. Obtained material represents organic rich, recent upper sediment layers. Thus, the studied sapropel samples can be considered as renewable material, representing material to be removed from lake during it recultivation.

2.2. Characterisation of sapropel samples

Loss on ignition. To estimate moisture, carbonate matter content and organic matter of sediments loss on ignition (LOI) method was used (Heiri et al., 1993). Moisture of sapropel was determined after drying at 105 °C, following organic matter estimation at 550 °C for 4 h. The content of mineral substances was determined after heating at 900 °C for 2 h.

Biological composition. The biological composition of samples was determined with a light microscope, counting and expressing as a percentage of organic matter content by groups in all identified groups of organic residues. Sapropel type, class, grade and application possibilities were identified using sapropel type classification (Stankeviča and Kļaviņš, 2014).

pH and electric conductivity (EC). Measurements were done for 100 mL supernatants made of 5g air-dried sample with HANNA pH 213 pH-meter (Pansu and Gautheyrou, 2006) and HANNA HI 9932 conductivity meter (Pansu and Gautheyrou, 2006). Bulk density for non-homogenised and homogenised sapropel were calculated and expressed as sample mass in grams divided with sample volume in cubic centimetres (Grossman and Reinsch, 2002).

2.3. Fillers of composites and their characterization

Hemp shives ("Bialobrezeskie") were taken from "Zalers" Ltd. Hemp shive mixture includes 1.7% fibre and 2.2% dust by weight, the rest is shives with different sizes – 3.7% are in length 10-20 mm, 92.0% – 0.63–10 mm, 0.5% are longer than 20 mm. Their bulk density is 108.36 kg/m^3, moisture content 11.75% and thermal conductivity is 0.058 W/m*K.

Birch wood sanding dust (wood dust) and fiber (wood fibers) were selected as fillers for production of composite materials. Birch wood sanding dust and fibre are industrial by-products from JSC "Latvijas finieris" – a plywood manufacturing company. Birch wood fibre is up to 15 mm long with the diameter up to 0.1 mm. In producing of composites, an additional thickening additive filler was used – colloidal silica product "Aerosil". It is a filler that creates a smooth mixture, often in combination with other fillers. For a reference of biodegradation tests a biocomposite materials with the same filler (hemp shives) were used. Block peat (Ltd "Laflora") was also used for composite materials biodegradation studies as a control material.

For the study of "Sapropel as an adhesive: assessment of essential properties" birch wood veneer with a thickness of 1.5 mm and moisture content of 6% was used for the preparation of plywood. Samples for determination of tensile shear strength: beech wood planks with a thickness of 5 mm and moisture content of 6% and with density 700–750 kg m^3 were used for the preparation of composite material samples for the tests. Peat samples: dried natural peat was used for tests with the moisture content of 16.4% and with density 90–250 kg m^3.

To study properties of peat-wood chips, sapropel-wood chip thermal insulation boards, to develop peat-wood chip composite materials, Baložu peat field peat with humidity of 73% was used. The wood chips used in the work were 0–1.5 cm long pine wood chips.

2.4. Binders used for preparation of composites

In addition to sapropel also commercially available binders were used. Binders used for preparation of composites for microbial stability tests was magnesium oxychloride cement (MOC) which requires highly reactive magnesium oxide. The caustic magnesium oxide, supplied by the Austrian company RHI AG Ltd, CCM RKMH-F, was with MgO content at least 73% and low calcination temperature (750–800 °C). The hydraulic lime (HL) and formulated hydraulic lime (FHL) were used. As well as magnesium phosphate cement (MPC) were used, which consists of 55% (by mass) dead-burned magnesium oxide M76 burned at 1700 °C (Integra Ltd, Slovakia) and 45% mono-potassium phosphate 0-52-35 (N-P-K proportion) with P_2O_5 content at least 52.1% (Praton SA Ltd). For biodegradation tests were used additional binders – dolomitic lime consisting of 100% DL60 lime (Dolomite) and hydraulic lime consisting of 60% DL60 lime and 40% calcinated kaolin clay (Clay).

To study properties of peat-wood chips, sapropel-wood chip thermal insulation boards peat as a binder were used.

2.5. Composite material preparation and curing

To develop composite materials as a binder or adhesive raw sapropel was used for the microbial stability tests (Obuka et al., 2017, 2021). For reference in some cases also inorganic binders were added. Mixtures of the samples are listed in Table 2.1. Mixing of the sapropel-filler mass was done manually until homogeneous and smooth mixture was reached by state where filler was fully covered with sapropel. Sapropel were mechanically treated by mixing together with electrical hand mixer until smooth and homogeneous material was formed. The mixing of the samples was done manually. Mixtures of the LHC, SLHC and MHC have two different target densities – 300 and 500 kg/m^3 in order to test variation of properties at different densities. To mix the LHC (1,2) samples and SLHC (1,2) samples, at first shives were mixed with lime and then water (for LHC) or sapropel (for SLHC) were added. The shives:water or sapropel ratio is 1:2.5 (LHC or SLHC 1-2) and 1:5 (LHC or SLHC 3-4). Added water or sapropel:lime ratio in composite materials were 1:1. The SWD and SWF were made by mixing sapropel-filler mass. It was done manually until homogeneous mixture has been obtained at the stage where filler was fully covered with binder. Sapropel was mechanically treated by mixing together with electrical hand mixer until homogeneous material has formed. ALINA LIFE^{TM} organoclay coating was added to the mass and treated by mixing until smooth mass has formed. Metal mold (dimension of 30 × 30 cm) with adjustable height was used for composite material curing. The mixture of raw materials was put in mold. Sapropel-filler samples were cured at the temperature of 80 °C for 72 hours.

For the MHC samples, at first shives were premixed with water, for hemp shives not to deprive MOC binder of the water because of its high hygroscopic nature. The shives:water ratio was 1:1.25. MgO was added in dry form, mixed with wet shives, afterwards $MgCl_2$ brine was added and blended together, $MgO:MgCl_2$ ratio was 1:0.67.

After mixing the samples were laid in molds hand compressing every ⅓ of the height. Samples were demolded after 2 days and afterwards were cured for 28 days in laboratory conditions (40 ± 10 %RH and 20 ± 2 °C) until testing.

Table 2.1

Composition of the mixtures used for development of composite material samples (mass proportion)

Type	Filler type	Filler	Water for filler	S*	HL**	MgO brine	$MgCl_2$ brine 1:1	Water for binder
SLHC(1)	hemp shives	1	–	2.5	2.5	–	–	–
SLHC(2)	hemp shives	1	–	5	5	–	–	–
LHC(1)	hemp shives	1	–	2.5	2.5	–	–	–
LHC(2)	hemp shives	1	–	5	5	–	–	–
MHC(1)	hemp shives	1	1.25	–	–	0.9	0.6	–
MHC(2)	hemp shives	1	1.25	–	–	2	1.33	–
SWF	wood fibre	1	–	6	–	–	–	–
SWD	wood dust	1	–	6	–	–	–	–

* – sapropel
** hydraulic lime

For the study of "Sapropel as an adhesive: assessment of essential properties" for the composite material preparation and curing the sapropel samples were mixed completely just before the preparation of three-layer plywood of dimensions 4 × 250 × 250 mm. Glue spreading level for Lake Veveru sapropel was 276–290 g m^2 and 264–288 g m^2 for Lake Pilvelis sapropel. The plywood was pressed under the pressure of 2.0 MPa for 24 hours, at 100 °C for first 16 hours. The samples were stored for one day at temperature 20 ± 3 °C with 65 ± 5% relative humidity until reaching equilibrium moisture content. Subsequently, the plywood panel was cut into shear specimens with the dimension of 4 × 50 × 150 mm to determine its bending strength and 4 × 25 × 200 mm to define shear strength.

To prepare sapropel composites with insulation properties the activated peat mass with binder properties was obtained by mechanical treatment of peat in the thermal bullet planetary mill RETSCH PM 400. The activated peat mass was prepared using 300 g of peat and placed in a grinding vessel with 8 grinding balls and grinding for 30 minutes at 300 rpm. Sapropel was not mechanically heat-treated before obtaining thermal insulation materials but was immediately mixed with the chips. The mixing of sapropel and wood chips (raw material weight ratio 1:3) was performed manually until a uniform mass was obtained. The resulting mass was then placed in a mold (30 × 30 cm with height adjustment) and sealed at 0.03 MPa for 3 hours to provide a denser structure of the composite material, increase its mechanical strength, reduce shrinkage of the final product, as well as shrinkage crack formation. Sapropel-peat composite plates were dried at 25 °C for 24 h and at 105 °C for 24 h.

For the developed composite materials raw sapropel was used as a binder (adhesive) in a study- Sapropel as a Binder: Properties and Application Possibilities for Composite Materials. Mixing of sapropel-filler mass was done manually until homogeneous and smooth mixture was reached at the stage where filler was fully covered with sapropel. Sapropel was mechanically treated by mixing together with electrical hand mixer until smooth and homogeneous material was formed. Metal mould with dimension of 30 × 30 cm and with adjustable height was used for composite material production. The mixture of raw materials was laid in by layers in mold for more dense composite material structure, higher mechanical strength and for minimizing final product shrinkage. Sapropel-filler samples were cured at the temperature of 80–105 °C for 36–72 hours.

2.6. Sample preparation with antimicrobial additives for microbial stability tests

Together 3 experiments were done in microbial stability tests. ALINA Ltd. Product ALINA LIFE^{TM} organoclay coating was added to materials in 4% concentration of dry mass in SWD (sapropel – birch wood sanding dust) or SWF (sapropel – wood fibre). In addition, organoclay additive was added to materials in 4% concentration of added lime or MOC in case of SLHC, LHC, MHC composite materials as a coating. Among the material samples were three that were coated with ALINA LIFE^{TM}, three that were coated with lime and three without any coating.

For the first stage of the experiment in part two ACTICIDE FD, a combination of (chloromethylisothiazolinone, also known as 5-chloro-2-methyl-2H-isothiazol-3-one) and MIT (methylisothiazolinone also 2-methyl-2H-isothiazol-3-one) were used for additional biological protection tests. It was added to the composite materials in the amount of 1% of the total mass. It is effective against *Aspergillus* spp., *Cladosporium* spp., *Penicillium funiculosum* and others (Thor, 2020).

In the second stage of the experiment in part two, the biocide BACTERICIDE was used as an active substance containing quaternary ammonium compounds. It was added to the composite materials in the amount of 1% of total mass. In the both the experiments, ALINA Ltd. product ALINA LIFE™ organoclay coating was used for additional biological protection tests.

2.7. Ageing of composite materials for microbial stability tests

For the microbial stability tests ageing of obtained composite materials in climate chamber was done by exposing the samples to 30 freeze-thaw cycles, with temperature amplitude of –20 °C (3 hours) to +20 °C (1 hour), which corresponds to EN 12390-9 (Anonymous, 2006). Climate chamber ageing test comprised of thirty cycles in two weeks. After the test samples were inspected visually no cracked or crumbled material was detected. In total 197 material samples were tested.

2.8. Thermal conductivity test of composite materials

Before the thermal conductivity test, the density of the samples was calculated by weighting the samples and measuring the dimensions. The thermal conductivity was measured using LaserComp FOX 600 heat-flow measurer. Samples are tested following the guidelines of the standard LVS EN 12667.

Test settings was 0 °C upper and 20 °C lower plate. Automatic determination of sample thickness was chosen for this study.

In the study of peat-wood chips, sapropel-wood chip thermal insulation boards thermal conductivity was determined for dry (0%) and wet plates (15%), as well as after the study of the effects of freezing thawing (5, 10, 25 cycles), obtaining a relationship between the thermal conductivity coefficient and the degree of moisture of the product. Freezing-thawing effects were studied in a climate chamber (Environmental Chamber JHT Series, Model No. YHT-100 z / 07-394B).

2.9. Compressive and flexural strength tests of composite materials

For testing compressive and flexural strength, the samples were specially prepared (sawed in necessary dimensions). For compressive strength a stress at 10% deformation was recorded, for compressive crosswise and flexural – until failure. For sapropel-hemp shives a layer of gypsum was spread over the interfaces to ensure even pressure application. Mechanical tests were performed on ZWICK Z100 universal testing machine.

Static bending strength (parallel and perpendicular to grain direction), shear strength test according EN 314-1 (requirements) (Anonymous, 2005) and EN 314-2 (Anonymous, 2000b) standards were tested. The sapropel samples were mixed completely just before the preparation of three-layer plywood of dimensions 4 × 250 × 250 mm. Glue spreading level for Lake Veveru sapropel was 276–290 g m^2 and 264–288 g m^2 for Lake Pilvelis sapropel. The plywood was pressed under the pressure of 2.0 MPa for 24 hours, at 100 °C for first 16 hours. The samples were stored for one day at temperature 20 ± 3 °C with 65 ± 5% relative humidity until reaching equilibrium moisture content. Subsequently, the plywood panel was cut into shear specimens with the dimension of 4 × 50 × 150 mm to determine its bending strength and 4 × 25 × 200 mm to define shear strength.

Adhesive strength of sapropel durability according to their operating performance conformity to EN 205 standard (Anonymous, 2002) was measured. The sapropel samples were mixed completely just before the preparation of beech blanks fabrication of dimensions 10 × 75 × 600 mm. Glue spreading for Lake Veveru sapropel and Lake Pilvelis sapropel was 290–310 g m^2. In addition to understand the sapropel properties used as a glue, comparing to glue that already exists in market, the samples made with PVA – Polyvinyl acetate glue were used. The planks were pressed at 100 °C under the pressure of 1.0 MPa for 24 hours. The samples were stored for one day at 20 ± 3 °C with 65 ± 5% relative humidity until reaching equilibrium moisture content. Subsequently, the plywood panel was cut into shear specimens with the dimension of 10 × 20 × 150 mm to determine tension shear strength.

Dried natural peat and sapropel as a glue were tested for tensile strength perpendicular to grain direction according to standard EN 319 (Anonymous, 2000a). The sapropel samples were mixed completely just before the preparation of the samples of dimensions 32 × 50 × 50 mm. Glue spreading level was 1600 g m^2 for Lake Veveru and Lake Pilvelis sapropel. The dried peat-sapropel samples were pressed under the pressure of 0.1 MPa for 48 hours. The samples were stored for one day at 20 ± 3 °C with 65 ± 5% relative humidity until reaching equilibrium moisture content. The material samples made from dried natural peat and sapropel were tested for tensile strength perpendicular to grain direction.

After cooling test specimens at ambient conditions, they were measured for the previously mentioned methods using Zwick Z100 universal testing machine. The data in this research were processed by routine statistical analysis and displayed by the standard deviation.

2.10. Sound insulation properties

In the study of properties of peat-wood chips, sapropel-wood chip thermal insulation boards – the materials were also tested for sound insulation. The equipment standard has the number LVS EN ISO 10534-2:2002 (Anonymous, 1998). The 4-microphone method is used in an acoustic tube -impedance/transmission loss measurement tubes – type 4206 and the four-microphone method with PULSE acoustic material testing software – Type 7758 were used.

The device works on the principle that a sample is placed in the middle between the 2 gypsum boards, but at the end of the pipe there is a sponge that absorbs sound so that it does not echo. The diameter of the sample that was placed in the acoustic tube is 98–99 mm, but the thickness is 45–50 mm.

2.11. Auto-ignition test

In the study of properties of peat-wood chips, sapropel-wood chip thermal insulation boards simple combustion tests were performed to judge the combustion characteristics of the composite materials. The temperature at which the samples start to ignite spontaneously was determined. SNF muffle furnace was used for combustion experiments. Samples (peat – wood chips, sapropel – wood chips, wood chips) were placed in porcelain crucibles and placed in a muffle, setting a steady increase in T °C to 500 °C. Three samples of each material were placed in the muffle, repeating the heating procedure three times (Obuka et al., 2014).

2.12. Evaluation of the biodegradability of the tested materials

In order to compare the potential biodegradability of the composite materials tested, an experimental scheme was developed: soil microbial enzyme activity and respiration were used as the main indicators (Zibilske, 1994). Considering the need for microorganisms to adapt to the substrate, a 7-day incubation period was included in the process requiring appropriate physicochemical conditions, growth factors (macro- and microelements, nutrients, vitamins). To accelerate the biodegradation process, the composite materials were placed in the soil amended with nutrients (molasses and a source of vitamins (plant extract)), as well as a consortium of soil-derived microorganisms with a high hydrolytic activity (Muter, 2015). Altogether 10 composite materials were evaluated.

Incubation of 0.25 mg specimen for evaluation of the biodegradability of the tested materials was performed in the sealed 100 mL vessels containing 10 g soil at 37 ± 2 °C for 7 days. The composition of the substrate added to the specimens was the following: 10 g clay loam soil, 2 mL mineral broth, 100 μL 30% molasses, 200 μL cabbage leaf extract, 100 μL inoculum (2.0×10^{10} CFU/mL) and 50 mL sterile distilled water (Muter, 2015). The composition of mineral broth was the following, g/L: $MgSO_4$ – 0.2, $CaCl_2$ – 0.02, KH_2PO_4 – 1.0, K_2HPO_4 – 1.0, NH_4NO_3 – 1.0, $FeCl_3$ – 0.05). Specimens were prepared in three replicates. Soil moisture was 60% of the maximum water capacity. The physicochemical characteristics of clay loam soil are summarized in Table 2.2.

2.13. Respiration intensity of microorganisms

The microbial respiration was tested according to (Rowell, 2014; Zibilske, 1994; Гавиленко et al., 1975) with some modifications. The glass with 5 mL 0.05 M NaOH was placed in the sealed 100 mL vessel as described in 2.12. The respiration was estimated by back-titration of the unreacted NaOH using 0.05 HCl (adding 1% phenolphthalein indicator to the NaOH prior to titration). Two measurements of respiration have been made for each vessel with a sample, i.e., at the beginning of incubation and after 7-day of incubation period. Respiration assay was performed at 23 °C for 24h in the dark. The respiration assay used in this study, was attributed to the substrate induced respiration (SIR), because carbon sources were added to the soil with specimen. However, the standard principles of SIR measurement (e.g., incubation for 4h) were not considered because of specific tasks of this study. In particular, bioaugmentation and a 7 day incubation was performed for stimulation of the biodegradation process.

An intensity of the SIR was calculated as follows. First, the volume of a NaOH solution used for reaction with CO_2 in the vessel with soil and specimen, was calculated by Equation (1):

$$X = \frac{(A-B)\times 1.1}{m\times h} \qquad (1)$$

where,
X – volume of the 0.05M NaOH solution used for reaction with CO_2, mL;
A – titrated, control sample, mL;
B – titrated, test sample, mL;
1.1 – coefficient (the ratio of the actual molarity to the theoretical molarity of the NaOH and HCl solutions);
m – sample weight, g dry weight;
h – trial time, hours.

Second, the amount of CO_2 reacted with NaOH during incubation, was calculated by Equation (2):

$$SIR = \frac{0.05\times X\times 12}{1000\times 2} \qquad (2)$$

where,
SIR – amount of C-CO_2 reacted with NaOH, g C-CO_2/h gdw;
0.05 – molarity of NaOH solution, M;
X – volume of the 0.05M NaOH solution used for reaction with CO_2, mL;
1000 – coefficient for calculating the number of NaOH moles in the volume used for titration (X);
12 – mass of carbon in the CO_2 molecule, g;
2 – coefficient for calculating the number of CO_2 moles reacted with NaOH (one molecule CO_2 reacts with two molecules NaOH).

2.14. Enzyme activity of microorganisms: fluorescein diacetate hydrolysis

After 7-day incubation period, as described in 2.12., the fluorescein diacetate (FDA) hydrolytic activity of microorganisms was tested. 100 μL specimen was transferred to 1 mL tube containing 400 μL reaction mixture (4 mg FDA, 2 mL acetone, 48 mL 0.06M phosphate buffer, pH 7.6). The mixture was incubated for 60 min at + 37 ± 2 °C (Chen et al., 2005; Margesin and Schinner, 2005)compost and sludge in laboratory-scale biofilters (8 l reactor volume. After incubation, 500 μL acetone was added to the specimens to stop the hydrolysis reaction. The optical density was measured at 490 nm using a microplate reader Infinite f50 (TECAN, Switzerland). Calibration curve was prepared using the thermally hydrolysed FDA.

The soil characteristics of the clay loam used in the experiment was determined (Table 2.2.) using standard soil analysis methods (Carter and Gregorich, 2008).

Table 2.2.

Characteristics of the soil used

Parameter	Values	Parameter	Values
N, %	0.20	Electrical conductivity, mS/cm	0.162
C, %	2.06	Water capacity, %	149.47
P, µg/g	15.6	Mg, mg/kg	218.5
pH (1M KCl)	6.72	K, mg/kg	146.5

The Na, Mg, K, Ca content of the specimens was determined using a PerkinElmer AAnalyst 200 atomic absorption spectrometer. A non-electrode discharge lamp (Perkin Elmer) was used as a source, Na measurements were made at 589 nm wavelength, Mg at 285.2 nm, K measurements at 766.5 nm and Ca at 422.7 nm using flame atomization. N_2O, acetylene was used as the oxidizing gas. ANOVA (Anova: Single factor analysis) was used for statistical data processing.

2.15. Microbiological stability tests

Together 3 experiments were done in microbiological stability tests.

2.15.1. Artificial inoculation with fungi/microbiological stability test part 1

Comparison of microbiological resistance of sapropel-based composite materials, LHC and MHC was carried out. Artificial infection with fungi *Alternaria alternata* MSCL 280 and *Cladosporium herbarum* MSCL 258 was used in microbial stability tests before and after experimental accelerated ageing of materials in climate camera. Fungi were grown in Petri dishes with Malt extract agar for 7 days at room temperature and afterwards fungal spores and mycelial fragments were scraped off the agar surface and vortexed to make a suspension with optical density OD_{545} 0.16. Triplicate samples of each building material were inoculated with fungal suspension. Each sample was watered (inoculated) with 3–5 ml of the suspension. The samples were prepared in 70 × 70 × 70 mm cube moulds, wood wool (WW) was cut with a similar surface area.

Inoculated samples were kept under the same conditions (20 ± 2 °C) and watered with sterile distilled water every second or third day to keep moist. Fungal growth on the materials was examined visually every 3–4 days. When the growth was observed the fungi were identified microscopically at least to the generic level. Intensity of fungal growth was assessed according to the scale (Stefanowski et al., 2017) (Table 2.3.):

0 – No growth can be seen under the microscope.
1 – Visible growth up to 50% coverage.
3 – Visible growth, 50–80% coverage.
4 – Visible growth, practically the entire sample surface area (80%) covered, the surface of the sample can be seen only in few parts.
5 – Whole surface of the sample (100%) covered.

Table 2.3

Evaluation of fungi growth on materials (average values)

Evaluation/Intensity of growth	Colour, percent
1–2	0% < 50%
2–3	50% ≤ 80%
3–4	80 < 99%
4–5	100%

2.15.2. Artificial inoculation with fungi/microbiological stability test part 2

Two experiments were conducted to determine the microbiological stability in this part 2. In both experiment stages, material samples were artificially inoculated with six fungal strains:

1. *Aspergillus versicolor* MSCL 1346;
2. *Penicillium chrysogenum* MSCL 281;
3. *Alternaria alternata* MSCL 280;
4. *Cladosporium herbarum* MSCL 258;
5. *Chaetomium* sp. MSCL 851;
6. *Trichoderma asperellum* MSCL 309.

Aspergillus versicolor and *Penicillium chrysogenum* belong to primary colonisers, *Alternaria alternata* and *Cladosporium herbarum* to secondary, and *Chaetomium* sp. and *Trichoderma asperellum* to tertiary colonisers. Primary colonisers can develop at a relative humidity <80%, secondary at 80%–90%, and tertiary at a relative humidity >90% (Stefanowski et al., 2017).

For the experiments the fungi were grown in Petri dishes and a suspension of mycelial fragments and spores were prepared from each fungus in sterile (autoclaved at 121 °C for 15 min) distilled water to obtain OD_{545} 0.16. All six suspensions were mixed in equal amounts. Analysed samples of materials were inoculated with 3 ml or 5 ml (depending on the size of the sample) of the mixed fungal suspension. Samples were prepared in 40 mm diameter and 10 mm high cylindrical forms, with wood fibre cement board (WF) and WW cut with similar surface area.

When fungal growth was observed the fungi were identified by macroscopic and microscopic (Leica DM 2000, Leica Microsystems) features at least to the generic level. Intensity of fungal growth was assessed according to the scale seen in Table 2.4.

according to the ASTM C1338-96 *Standard test method for determining the fungi resistance of insulation materials and facings* (Klamer et al., 2004):

Table 2.4

Evaluation of fungal growth on materials (average values)

Evaluation/ Intensity of growth	Characteristics	Colour scale
0	No growth detected microscopically	
1	Microscopically detected growth	
2	Microscopically detected growth covering the whole surface	
3	Macroscopic (visible to naked eye) growth present	
4	Macroscopic growth covering >80% surface	

After visual evaluation, 1.0 ± 0.5 g material samples were removed from the composite material where fungal overgrowth was observed. Samples were divided into smaller fractions with a knife, scissors or tweezers, then placed in plastic tubes. They were then poured into 1 ml of sterile (autoclaved at 121 °C for 15 min) distilled water, then shaken vigorously for 5 min. The sample suspension (0.1 mL) was then plated on Malt Extract Agar medium (Oxoid) and the samples incubated at room temperature (20 ± 2 °C) for 5–7 days. Fungal genera were determined by microscopic and macroscopic methods (Klamer et al., 2004).

In the first stage of the experiment in test part two, the analysed material samples were incubated in two humidity modes – RH 75% and 99% – and at 20 °C. 75% RH were found as typical operating conditions of biocomposite building materials measured during in-situ tests (Sinka et al., 2018)hence various directives have been adopted, such as the European directive 2012/27/EU on energy efficiency, i.e. ensuring from 2019 the construction of the near-zero energy buildings (nZEB, 99% RH represent elevated moisture that can occur during drying or improper building maintenance. Moisture levels and temperature was monitored with digital sensors. To ensure 75% RH a sodium chloride salt solution was kept in the chamber with the samples. To ensure 99% RH samples were kept in separate sealed boxes with sensors inside and 3 ml of sterile water poured on the samples, once the RH lowered. Visual evaluation of composite materials was performed after 4 months of incubation.

In the second stage of the experiment in test part two, samples were kept only at relative humidity 99% and temperature 20 ± 2 °C, the visual assessment was performed after 45 days. To ensure 99% RH samples were twice a week poured with 3 ml of sterile water, thus maintaining a humid environment that simulates rain condition.

2.16. Sapropel, peat, biochar granules for the agricultural purposes

2.16.1. Sapropel, peaty sapropel, sapropel – peat granules

The granules were made in the Building Materials Laboratory of Riga Technical University. During the development of sapropel – peat, the sapropel granule binder was machined – blended to a homogeneous mass before incorporation. In the study, tests were performed to determine the physical-mechanical properties of sapropel granules for 3 types of granules (pure sapropel, peaty sapropel, sapropel-peat granules). Burial density was determined using the standard LVS EN 1097-3 (Anonymous, 1999), water absorption using the standard LVS EN 1097-6 (Anonymous, 2013), testing and pellet compressive strength testing using the standard EN 1606 (Anonymous, 2007), environmental acidity reaction and electrical conductivity.

2.16.2. Biochar-sapropel granules

For the studies of biochar-sapropel granules for agriculture as filler materials were used: biochar, which is created as a side product from cogeneration process, by pyrolyzing wood of deciduous trees at 600 °C. Two kinds of biochar were used: biochar (B), deciduous tree biochar (LB.)

For the study of the biochar-sapropel granules for agriculture composite materials were created by manually mixing wet sapropel and biochar until homogenous consistency was reached. Different ratios of biochar and sapropel were used (1:3, 1:4, 1:6, 1:8 and 1:10) to determine best option. The mass was further divided in two samples and each part was put in prepared metal forms. One sample was air dried (relative air humidity 14–20%), while the other was oven dried in 80 °C temperature. Air dried sample was weighted every hour for first 3 hours and once more after 24 hours of creation moment. Oven dried sample was weighted every 15 minutes.

2.16.3. Biochar – sapropel granules granulation

Granules were made in collaboration with Riga Technical University faculty of material sciences and applied chemistry. Two types of granules were made. One was made using extrusion and the other using rotation of the material. Extruded granules are made by mixing homogenized sapropel with biochar powder (sieved through 1.5 mm sieve) with CLATRONIC KM3350 mixer at 50Hz rotation speed. The obtained mass is then extruded through 9 mm nozzles and cut every 2 seconds creating granules of approximately 9 mm length.

Granules created using rotation are formed by centrifugal force. Biochar and sapropel mass are rotated in a cylinder until granules are formed. Biochar powder is added as needed during this process to prevent granules from sticking together. Both types of granules were oven dried for 2 days at 50 °C temperature.

2.16.4. Specific surface area

Analysis of specific surface area was carried out in collaboration with Riga Technical university scientists. Specific surface area was measured using Quantachrome

QuadraWin – Data Acquisition and Reduction for QuadraSorb SI, version 5.11 2000-12. (USA) QUADRASORB SI Kr with Standart Autosorb degasser device.

2.16.5. Water absorption

Water absorption capacity was determined in collaboration with Riga Technical university scientists. Water absorption capacity of granules was determined according to ГОСТ 26713-85 standard. Measurements were done in 7 repetitions and calculated as average (minimum and maximum were removed from calculation). Temperature of measurements was 105 °C.

2.16.6. Mechanical strength

Mechanical strength was determined in collaboration with Riga Technical university scientists. Mechanical strength was measured according to ГОСТ 8269.0-97 (Anonymous, 1997) standard with ZWICK Z100 ROELL. Total volume used for testing was 2 L of granules. Measurements were done in three repetitions.

3. RESULTS AND DISCUSSION

3.1. Sapropel properties

In the thesis organic rich freshwater sapropel were used as most prospective for the development of composites. Sapropel sediments were sampled from four lakes in Latvia – Padelis, Pilvelu, Veveru located in Rezekne district, Latgale region. Piksteres lake is located in Jekabpils District, Latgale Region, Latvia. The sapropel from these lakes has been studied previously and can be considered as prospective for development of composite materials. Characteristics of the sapropel samples are listed in Table 3.1.

Table 3.1

Characteristics of the sapropel samples

Lake	Moisture, %	Organic matter, %	Carbonates, %	Density, g/cm^3
Padelis	85.97	15.27	35.57	1.24
Pilvelu	94.99	84.51	1.26	1.10
Veveru	97.66	86.25	1.18	1.08
Piksteres	96.45	82.67	17.33	1.028

Sapropel samples differ from one another within moisture (%), organic matter (%) and carbonates (%) amount. Colour of Lake Padelis sapropel is pale gray-pink and density is 1.24 g/cm^3. Lake Pilvelis sapropel sample is dark greenish brown with homogeneous and jelly-like structure and density – 1.10 g/cm^3. Lake Veveru sapropel colour is black and density – 1.08 g/cm^3. Lake Piksteres sapropel sample is greenish brown and density is 1.028 g/cm^3. Removal of sapropel sediments from lakes (dredging) during lake recultivation helps to improve the quality of freshwater resources and lake ecosystems. Thus, the use of sapropel obtained during lake recultivation is a sustainable, environmentally friendly and efficient approach as it supports recovery of environmental quality of lake ecosystems and might promote creation of innovative, high value-added products that are non-toxic, environmentally friendly.

Summary. Used sapropel samples represent sapropel types prospective for use as binding materials.

3.2. Development of sapropel composite materials

Sapropel can be used as a binder for by-products of the wood, flax and hemp processing and paper and cardboard industries to produce insulation and finishing boards. Sapropel has also been used to replace cement binder in the development of sapropel concrete, a composite material used in construction, with sapropel as the binder and sawdust and gravel as a filler material (Brakšs et al., 1960; Gružāns, 1960). Studies on the potential of sapropel as a binder have been carried out in Latvia, Lithuania and

Belarus. Opportunities for the development of sapropel-straw (Kasperiunaite and Navickas, 2010), sapropel-hemp shives (Pleikšnis and Dovgiallo, 2015) and sapropel-lime-hemp-paper processing by-products (Balčiūnas et al., 2016) have been studied. Technical tests show that the use of sapropel as a binder in combination with various by-products to create new materials allows the finished product to be included in the category of thermal insulation materials in terms of technical quality. Considering results of previous studied dedicated to development of sapropel containing materials the concepts of elaboration of new materials were proposed.

As prospective components to design sapropel based composites can be considered natural fibers and at first – hemp. To reveal potential of sapropel-lime binder in hemp concrete composites it has been suggested to use sapropel-lime, magnesium oxide-chloride, and lime binders. The obtained compositions were compared with each other and with data available in the literature. Hemp shives, wood fiber and birch wood sanding dust have been used as filler for composite materials as well. These fillers are agricultural and wood processing industry by-products that need to find reusability.

The use of hemp-lime composite has a positive impact on the environment associated with CO_2 emissions. Both components are absorbing by CO_2 – lime during hardening (carbonation) and hemp – during growth (Ip and Miller, 2012; Pretot et al., 2014). Sapropel, in its formation, also contains CO_2 in the form of organic substances, thus being equivalent to hemp-lime materials. Thus, these composites can be considered as climate-neutral materials.

Studies on the potential of sapropel as a binder have been carried out in Latvia, Lithuania and Belarus. By-products of the processing of sapropel concrete (Brakšs et al., 1960; Gružāns, 1960), sapropel-straw (Kasperiunaitė et al., 2009), sapropel-hemp shives (Pleikšnis and Dovgiallo, 2015) and lime-hemp-paper (Balčiūnas et al., 2016) technical features is studied. It was concluded that by using sapropel as a binder in combination with various materials, it is possible to include the finished product in the category of heat insulating materials in terms of technically qualitative performance. Sapropel with an organic content of more than 85% and nitrogen more than 3.3% is used for the production of sapropel binder (Курзо, 2005).

Research of Riga Technical University on the material of hemp shives as filler and hydraulic lime as binder found that the thermal conductivity and compressive properties of these materials are consistent with the thermal insulation materials (Sinka et al., 2014).

The aim of the study was to find out the potential of composite materials using sapropel and lime as binder and hemp shives, wood fiber and birch wood as a filler and to determine their optimum properties. The composite materials were prepared in the Department of Composite Materials and Structures of Riga Technical University. Density, thermal conductivity, and compressive strength were determined for the specimens produced. The compressive strength of the various composite materials in the tests is shown in the Table 3.2, and it shows that the obtained materials can be used as thermal insulation materials, because their strength meets the requirements of the regulatory framework.

Samples were prepared using mechanical mixing until homogeneous composition were obtained and the sequence of the addition of components were mixed.

Table 3.2

Characteristics of composite building materials

Designation	Composition	Characteristics	
Sapropel-lime-hemp composite SLHC 1-2	Sapropel Lime Hemp shives	Raw material ratio (filler:binder:binder)	1:2.5:2.5
		Density kg/m^3	306.88; 296.31
		Thermal conductivity, W/m·K	–
		Mechanical strenght, MPa	0.25
Sapropel-lime-hemp composite SLHC 3-4	Sapropel Lime Hemp shives	Raw material ratio (filler:binder:binder)	1:5:5
		Density kg/m^3	533.58; 540.59
		Thermal conductivity, W/m·K	0.089
		Mechanical strenght, MPa	0.77
Lime-hemp composite LHC 1-2	Lime Hemp shives	Raw material ratio (filler:binder:binder)	1:2.5:2.5
		Density kg/m^3	294.09; 302.40
		Thermal conductivity, W/m·K	–
		Mechanical strenght, MPa	0.29
Lime-hemp composite LHC 3-4	Lime Hemp shives	Raw material ratio (filler:binder:binder)	1:5:5
		Density kg/m^3	498.32; 562.93
		Thermal conductivity, W/m·K	0.099
		Mechanical strenght, MPa	0.90
Lime-hemp composite LHC	Lime Hemp shives	Raw material ratio (filler:binder:binder)	1:5:5
		Density kg/m^3	408.10
		Thermal conductivity, W/m·K	0.086
		Mechanical strenght, MPa	0.61
Sapropel-wood fiber composite SWF	Sapropel Wood fiber	Raw material ratio (filler:binder)	1:6
		Density kg/m^3	319
		Thermal conductivity, W/m·K	0.19
		Mechanical strenght, MPa	0.060
Sapropel-birch wood sanding composite SWD	Sapropel Wood sanding dust	Raw material ratio (filler:binder)	1:6
		Density kg/m^3	470
		Thermal conductivity, W/m·K	0.061
		Mechanical strenght, MPa	0.67
Magnesium-hemp composite MHC 1	Magnesium chloride Hemp shives	Raw material ratio (filler:binder:binder:binder)	1:1.25:0.9:1.33
		Density kg/m^3	302.3
		Thermal conductivity, W/m·K	0.076
		Mechanical strenght, MPa	0.25
Magnesium-hemp composite MHC 2	Magnesium chloride Hemp shives	Raw material ratio (filler:binder:binder:binder)	1:1.25:2:0.6
		Density kg/m^3	504.4
		Thermal conductivity, W/m·K	0.111
		Mechanical strenght, MPa	1.12

Obtained results show that the thermal conductivity of lime-hemp composite material (density 408.10 kg/m^3) is on average low – 0.086 W/m·K. Similar values are obtained for sapropel-lime-hemp material – 0.089 W/m·K. The results obtained are satisfactory, similar to those used in practice in the world for hemp shives, and with the current regulation, the wall insulated with such materials should be approximately 400 mm thick to reach regulatory values (Sinka et al., 2014).

The research direction is promising because the material has great potential to reduce global CO_2 emissions, both directly from production, as the main components are CO_2 neutral or negative, and indirectly providing better thermal performance of buildings, thus reducing the amount of fuel needed. The study should be continued by developing new solutions to improve the properties of sapropel-lime composites.

In the study on sapropel and peat as a binder for wood chips (Obuka et al., 2014), the study also determined the mechanical strength of the materials. The activated peat mass with binder properties was obtained by mechanical treatment of peat in the thermal bullet planetary mill. The activated peat mass was prepared using 300 g of peat and placed in a grinding vessel with 8 grinding balls and grinding for 30 minutes at 300 rpm. Sapropel was not mechanically heat-treated before obtaining thermal insulation materials but was immediately mixed with the chips. The mixing of sapropel and wood chips (raw material weight ratio 1: 3) was performed manually until a uniform mass was obtained. The resulting mass was then placed in a mold (30 × 30 cm with height adjustment) and sealed at 0.03 MPa for 3 hours to provide a denser structure of the composite material, increase its mechanical strength, reduce shrinkage of the final product, as well as shrinkage crack formation. Sapropel-peat composite plates were dried at 25 °C for 24 h and at 105 °C for 24 h.

Depending on the amount of moisture, the compressive resistance of the board's changes. The compression resistance of sapropel-wood chips is 0.06 MPa and that of peat-wood chips is 0.13 MPa. In contrast, the bending resistance shows that the resistance of sapropel-wood chips is 0.02 MPa and that of peat-wood chips – 0.3 MPa. The results of compression and bending resistance show that the composite materials have sufficient strength to form adhesive joints and perform assembly work.

In a study "Sapropel as a Binder: Properties and Application Possibilities for Composite Material", the obtained results show that composite materials with filler of birch wood sanding dust and binder of green algae sapropel exhibit higher values in compression deformation perpendicular and parallel to the direction of specimen formation. The compressive results of perpendicular deformations range from 0.67 to 0.76 MPa. The result in linear deformations is 0.72 and 0.67 MPa, respectively. The results obtained from the compression resistance show that the materials are durable enough to be used in assembly work and to form adhesive joints.

Summary. Developed new materials are durable enough to be used in assembly work and to form adhesive joints. This study has demonstrated good application potential of sapropel as a binder. From natural materials and local resources, such as sapropel, and industrial by-products, such as birch wood sanding dust, fibre and hemp shives, sawdust it is possible to develop environmentally friendly composite materials for construction for various needs of utilisation. The particle granulometric composition, surface area and other characteristics of the filler have an effect on the binding with sapropel as a binder.

3.3. Thermal conductivity of composite materials

In a study on composite materials of sapropel as binder, a thermal conductivity test was performed by changing the types of sapropel and different filler materials (Obuka et al., 2015). Three types of sapropel from Lake Veveru (green algae) and Pilvelu (cyanobacterial algae) and a carbonate sapropel from Lake Padelis (carboniferous) were used. Fillers used were hemp fibers and shives, wood fiber, birch wood sanding dust. These fillers are a by-product of agriculture and woodworking industry that can be reused. For the developed composite materials raw sapropel was used as a binder (adhesive). Mixing of sapropel-filler mass was done manually until homogeneous and smooth mixture was reached – filler fully covered with sapropel. Sapropel was mechanically treated by mixing together with electrical hand mixer until smooth and homogeneous material was formed. Metal mould with dimension of 30 × 30 cm and with adjustable height was used for composite material production. The mixture of raw materials was laid in by layers in mold for more dense composite material structure, higher mechanical strength and for minimizing final product shrinkage. Sapropel-filler samples were cured at the temperature of 80–105 °C for 36–72 hours. The results obtained from the tests are shown in Table 3.3.

Based on the obtained results, it can be concluded that the material which contains wood fibers and sapropel of green algae from the Lake Veveru shows the best results. The results show that these composite materials have similar characteristics and thus similar applications and potentials. The composite materials produced have low thermal conductivity due to their mixed, fine-porous structure and have a homogeneous fiber structure with interconnected and open pores. Due to the organic origin of the raw materials, the composite material of the sapropel binder and hemp shives has a heterogeneous structure. The granulometric disintegration of different particles results in voids and uneven composition with weaker inclusions and faster deformation of the sample.

Table 3.3

Thermal conductivity of materials

Material: binder-filler	Density, kg/m^3	Thermal conductivity, W/m·K
Carboniferous and green algae sapropel – hemp	191	0.063
Carboniferous and cyanobacterial sapropel – hemp	200	0.059
Wood fiber – green algae sapropel	153	0.055
Wood fiber – cyanobacterial sapropel	202	0.060
Cyanobacterial sapropel – wood sanding dust	214	0.061
Cyanobacterial sapropel – wood sanding dust – Aerosil silica	376	0.080

In the study on sapropel and peat as a binder for wood chips (Obuka et al., 2013), the thermal conductivity of the materials reached 0.067 and 0.060 W/m·K. The study takes into account the number of freezing cycles and the humidity of the materials tested. The results show that the thermal conductivity of peat and particleboard increases, while that of sapropel and particleboard decreases during the freezing cycles. Comparing the obtained results, where the moisture content of the composite material is from the air-dry state to the moisture-saturated material (12%), the thermal conductivity coefficient is 0.050–0.060 W/m·K for sapropel-wood chips and 0.055–0.064 W/m·K for peat-wood chips, respectively. The activated peat mass with binder properties was obtained by mechanical treatment of peat in the thermal bullet planetary mill. The activated peat mass was prepared using 300 g of peat and placed in a grinding vessel with 8 grinding balls and grinding for 30 minutes at 300 rpm. Sapropel was not mechanically heat-treated before obtaining thermal insulation materials but was immediately mixed with the chips. The mixing of sapropel and wood chips (raw material weight ratio 1:3) was performed manually until a uniform mass was obtained. The resulting mass was then placed in a mold (30 × 30 cm with height adjustment) and sealed at 0.03 MPa for 3 hours to provide a denser structure of the composite material, increase its mechanical strength, reduce shrinkage of the final product, as well as shrinkage crack formation. Sapropel-peat composite plates were dried at 25 °C for 24 h and at 105 °C for 24 h.

Summary. Using natural materials and local resources, such as sapropel, as well as industrial by-products such as birch wood sanding dust and fibre, and hemp shives it is possible to develop environmentally friendly composite materials for the construction industry, adjusting properties depending on the area of utilization. Thermal conductivity results show that materials can be used to develop environmentally friendly composite materials with insulation properties.

3.4. Compressive and flexural strength of composite materials

There is an acute need in the construction industry for new types of adhesives and binders based on natural (plant and animal) substances (D'Amico et al., 2010). Synthetic adhesives used today contain toxic substances that cause health problems and environmental contamination. Most adhesives are based on formaldehyde (urea-formaldehyde and phenol-formaldehyde), which account for 92% of total adhesive consumption. Formaldehyde adhesives are made from non-renewable resources and are potentially harmful carcinogens. Research is underway worldwide to develop various alternatives to current adhesives, such as soy-based wood glues (Lei et al., 2014). Thus, one of the challenges in the woodworking industry is the development of environmentally friendly adhesives from natural and renewable resources (Y. Liu and Li, 2007).

In this study, composite materials were developed using sapropel as an adhesive. Two types of sapropel samples were used – the green algae sapropel obtained at Lake Veveru and cyanobacterial sapropel obtained at Lake Pilvelu. Characteristics such as dry matter content, moisture content and density were determined for sapropel. Adhesives were tested by gluing plywood and mechanical testing of the material: bond strength test, static bending using (Anonymous, 2000b) and (Anonymous, 2005) standard, application group (D1–D4) for sapropel as glue using (Anonymous, 2001a) and (Anonymous, 2002) standards, pulling peat with sapropel and determining strength perpendicular to the slab plane using (Anonymous, 2000a) standard.

The sapropel samples were mixed completely just before the preparation of three-layer plywood of dimensions 4 × 250 × 250 mm. Glue spreading level for Lake Veveru sapropel was 276–290 g m^2 and 264–288 g m^2 for Lake Pilvelu sapropel. The plywood was pressed under the pressure of 2.0 MPa for 24 hours, at 100 °C for first 16 hours. The samples were stored for one day at temperature 20 ± 3 °C with 65 ± 5% relative humidity until reaching equilibrium moisture content. Subsequently, the plywood panel was cut into shear specimens with the dimension of 4 × 50 × 150 mm to determine its bending strength and 4 × 25 × 200 mm to define shear strength.

The dried peat-sapropel samples were pressed under the pressure of 0.1 MPa for 48 hours. The samples were stored for one day at 20 ± 3 °C with 65 ± 5% relative humidity until reaching equilibrium moisture content. The material samples made from dried natural peat and sapropel were tested for tensile strength perpendicular to the grain direction.

Adhesives were tested by gluing plywood and mechanical testing of the material: determination of static bending strength (Fig. 3.1) and glue strength test, determination of applicability group (D1–D4) for sapropel as binder (glue), sapropel bonding of peat and tensile strength determination. perpendicular to the plane of the slab.\

The results show that the highest result in the mechanical bending test for the sapropel adhesive (Anonymous, 2001b) standard for the determination of elastic modulus and bending force was found in the Lake Pilvelu sapropel (88.7 MPa in parallel bending). In addition to determining the applicability group for the sapropel as an adhesive (durability test), the Pilvelu sapropel – beech samples show a result of 3.67 MPa. In addition, tests according to the standard EN 319 were performed to detect dried natural peat and sapropel as a glue for tensile strength perpendicular to the grain direction, results indicated: samples of peat – Pilvelu sapropel – 0.077 MPa, samples of peat – Veveru sapropel – 0.067 MPa.

The development of adhesives made from natural raw materials is a highly innovative line of research, as the expansion of the product range and global consumption increases the consumption of adhesives. The construction industry consumes 60% of all raw materials produced. Consequently, the construction industry is also one of the largest consumers of adhesives and binders in the world. As stated above, there is an acute need in the industry for new types of adhesives and binders based on natural (plant and animal) substances (D'Amico et al., 2010; Zabalza Bribián et al., 2011).

Plywood glued with sapropel sample bending test is shown in the process in Figure 3.1. The results show that the highest result in mechanical bending tests for sapropel adhesive (Anonymous, 2001b) standard – determination of modulus of elasticity and bending force) is found in Lake Pilvelu sapropel (in parallel bending – 88.7 MPa).

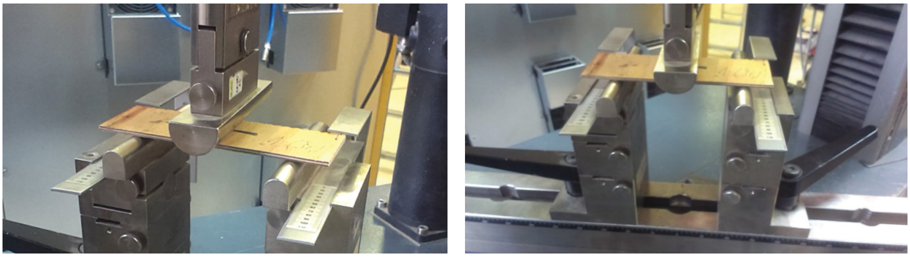

Figure 3.1. **Bending test of a sample of plywood glued with sapropel**

The lowest result, however, is shown by the same type of sapropel only perpendicular to the bend (Fig. 3.2.). The results of the study indicate that an environmentally friendly adhesive derived from sapropel can be used as a natural binder in composite materials, which has a high adhesion and retention capability.

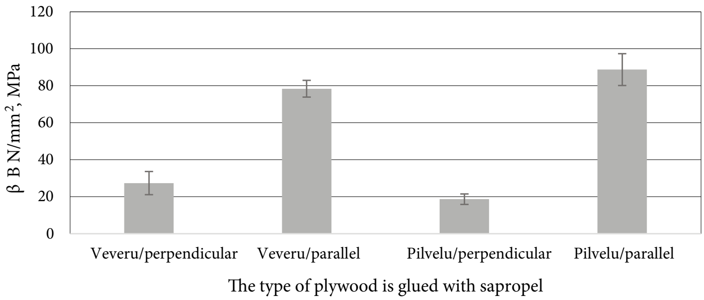

Figure 3.2. **Bending mechanical strength in parallel and perpendicular to the fiber direction**

The research direction is promising and should be continued to improve the properties of sapropel adhesive and to increase its effectiveness.

Summary. Composite materials were developed using sapropel as an adhesive. This study has demonstrated good application potential of sapropel as an adhesive, but still much work has to be done to improve results. Question posed at this part of this study, that it is a challenge to produce plywood from organic rich lake sediment (sapropel) applied as a glue, it is now possible to state that the first test results reveal that there is an opportunity to use sapropel as a potential adhesive, but there is a need for further experiments. The research extends our knowledge of using natural materials and local resources, such as sapropel, as well as birch wood veneer, and it is possible to develop environmentally friendly composite materials for the construction industry, adjusting for the need of utilization in future.

3.5. Sound insulation properties

Sound insulation must be taken into account during the construction of the building. Noise is an important problem and is considered to be environmental pollution, and it causes many health problems, the causes of which are not easy to identify. In several European countries, there are regulations that sound insulation materials must be installed in buildings to reduce the adverse effects of noise pollution. These regulations have further increased the demand for effective and inexpensive sound insulation materials (Islam and Bhat, 2019).

Sound insulation materials also consist of porous synthetic substances, including rock wool, glass wool, polyurethane or polyester, which are usually based on petrochemistry (Patnaik et al., 2015) and which have a negative impact on human health and the environment. This has led to increase in demand for environmentally friendly insulation materials (Islam and Bhat, 2019).

Study on sapropel and peat as a binder for wood chips (Obuka et al., 2014) states that ability to insulate sound is one of the important properties of any building material. Thus a study of sound insulation properties of the developed materials was carried out within the framework of the thesis (Table 3.4.). Composite materials were obtained by mechanical treatment of pear in thermal bullet planetary mill resulting in activated peat mass with binder properties. The activated peat mass was prepared using 300 g of peat and placed in a grinding vessel with 8 grinding balls and grinding for 30 minutes at 300 rpm. Sapropel was not mechanically heat-treated before obtaining thermal insulation materials but was immediately mixed with the chips. The mixing of sapropel and wood chips (raw material weight ratio 1: 3) was performed manually until a uniform mass was obtained. The resulting mass was then placed in a mold (30 × 30 cm with height adjustment) and sealed at 0.03 MPa for 3 hours to provide a denser structure of the composite material, increase its mechanical strength, reduce shrinkage of the final product, as well as shrinkage crack formation. Sapropel-peat composite plates were dried at 25 °C for 24 h and at 105 °C for 24 h.

Table 3.4

Results of sound insulation tests using 4 microphone method

Tested plate	Sound insulation, dB
Peat – wood	30
Peat – wood	32
Sapropel – wood	32
Sapropel – wood	31

The obtained biocompositematerials have a fine-porous structure with a homogeneous fibrous structure with open and interconnected pores. The obtained sound insulation results indicate very good insulation properties of the composite material. The boards have a fine-porous structure with a homogeneous fibrous structure with open and interconnected pores. Compared to other ecological thermal insulation materials, such as flax fiber thermal insulation material, the results are worse and differ by 14 dB. According to the literature, the sound insulation result of flax fiber material is 45 dB, but flax-wool thermal insulation material retains 40 dB sound absorption (Kozłowski et al., 2008). Given the sound insulation properties, it can be concluded that better sound insulation level can be reached using heavier materials. The best available sound absorption materials in Latvia are universal fiberboard, the densest samples of mineral wool and cork products.

Summary. Sound insulation indicators of peat – wood chips and sapropel – wood chip composite material are high and comparable with synthetic sound insulation materials offered on the market.

3.6. Auto-ignition test

In the study on sapropel and peat as a binder for wood chips (Obuka et al., 2014) self – ignition risk assessment of the developed materials was performed (Table 3.5.).

Table 3.5

Peat and sapropel particle boards: comparison of auto-ignition

Sample	T °C	T °C, average arithmetic
Peat – particle board	345	333
	330	
	325	
Sapropel – particle board	290	296
	295	
	302	
Pine wood chips	345	345
	340	
	350	

Based on the data obtained from the combustion test, it is possible to conclude that the auto-ignition temperature of peat particle board is higher than the auto-ignition temperature of sapropel-particle board. This is due to the fact that the samples differ in density and fiber arrangement in the samples. Respectively, the fiber arrangement of peat particle board is denser and there is less air between them, but sapropel – particle board is more fragile with significantly lower mechanical strength. This method of production allowes to obtain sample with fibrous structure that has a greater amount of air. This reduces the temperature at which the sample begins to ignite spontaneously, as there is a greater amount of oxidizing-oxygen in the air.

It is important to mention that wood is an anisotropic material and that its physical as well as mechanical properties are closely related to the direction of the fibers used (Ulpe and Kupče, 1991). After the tests, it can be concluded that the obtained materials belong to the group of combustible materials, because when the composite is exposed to the ignition source, it ignites, burns or gets charred. When the ignition source ceases to operate, material continues to burn or char. In order to improve the fire resistance of the composite material, it is necessary to take the essential fire safety measures, as well as to ensure the insulation of the material, for example, by using plasterboard sheets.

Summary. In order to improve the usability of sapropel based biocomposites, they must be treated with various means that improve fire safety and biological resistance, as this increases the durability and use of composite materials.

3.7. Biodegradability of the tested materials

Biodegradation experiments were performed by adding the composite materials to the soil amended with nutrients and a consortium of microorganisms with a high hydrolytic activity (Muter, 2015) in order to provide favorable conditions for degradation processes.

For the developed composite materials three types of raw sapropel have been used as a binder, i.e., green algae sapropel (GAS); cyanobacteria sapropel (CBS) and carbonatic sapropel (CS). Sapropel was mechanically treated by mixing together with electrical hand mixer until smooth and homogeneous material was formed. Mixing of sapropel-filler mass was done manually until homogeneous and filler was fully covered with sapropel. Binder-filler mass ratio was 6:1. Metal molds with dimensions of 30 × 30 cm and with adjustable height were used for composite material production. The mixture of raw materials was placed in layers in molds for more dense composite material structure, higher mechanical strength and for minimizing final product shrinkage. Sapropel-filler specimens were cured at the temperature of 80–105 °C for 36–72 hours until the constant weight was reached.

Fillers of biocomposite materials were used in the biodegradation test – wood fiber, birch wood sanding dust, hemp shives. Mineral binders developed in previous studies were used for these materials – dolomitic lime consisting of 100% DL60 lime (Dolomite) and hydraulic lime consisting of 60% DL60 lime and 40% calcinated kaolin clay (Clay) (Sinka and Sahmenko, 2015). Binder-filler mass ratio was 2:1. Block peat ("Laflora") was also used for composite materials biodegradation studies as a control material (Obuka et al., 2019).

3.7.1. Respiration intensity of microorganisms

The respiration intensity of microorganisms in the experimental batches was observed before and after 7-day incubation period at 37 °C. An increase of respiration intensity in the composite materials has been observed. The amended batches at the beginning of incubation showed statistically significant difference ($p<0.05$) and varied in the range from 31% to 70%, as compared to the control batch with soil and peat (Fig. 3.3 A). The highest respiration intensity was in the soil containing CS/Wood fibers, while the lowest – CS/Wood sanding dust, i.e., 7.68 ± 0.35 μg C-CO_2/h gdw and 5.92 ± 0.43 μg C-CO_2/h gdw respectively (Fig. 3.3. A). Among the types of composite materials, no statistically significant differences were found in respiration stimulating effect. In the future, peat can be used for testing as an additional substrate for the biodegradation of composite materials. The obtained first data on the respiration intensity of peat show a higher activity of microorganisms in it and thus a possible higher biodegradation potential of the created biocomposite materials.

The second test was carried out after 7-day incubation period, when readily available substrates have been exhausted (Figure 3.3.B). Respiration intensity of microorganisms after 7-day incubation period was considerably lower than that in the beginning of the experiment. This can be explained by the fact that microorganisms have already degraded easily degradable substances.

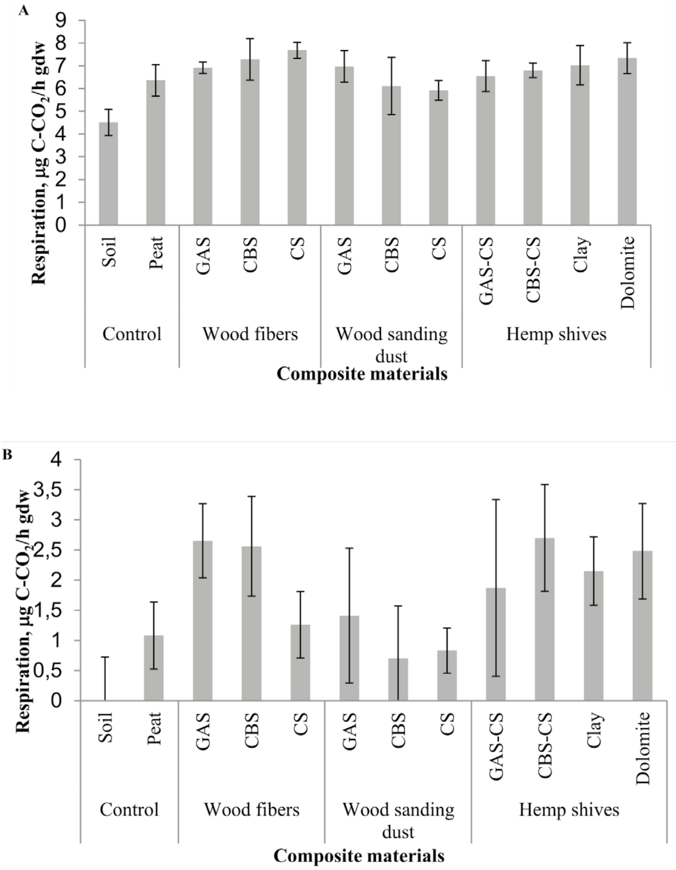

Figure 3.3. **Respiration intensity of microorganisms in a clay loam soil amended with nutrients, microbial consortium and composite materials. The ratio of a composite material to the substrate was 0.25:10.0. The substrate was prepared as described in Materials and Methods, p.2.12 and 2.13. Respiration intensity was measured before incubation (3.3.A) and after 7-day incubation period (3.3.B) of a composite material with soil at 37 °C. GAS – green algae sapropel; CBS – cyanobacteria sapropel; CS – carbonatic sapropel. Control – the soil substrate without composite materials.**

Subsequently, these data indicated to the degradation state of comparatively hardly biodegradable substances (cellulose, hemicellulose, lignin) resulting in the original material fractionation with respect to polymer stability. No respiration was detected in the control soil. The highest respiration intensity was detected in CBS-CS/Hemp shives, while the lowest – in CBS/Wood sanding dust, i.e., 2.70 ± 0.89 µg C-CO_2/h gdw and 0.70 ± 0.87 µg C-CO_2 C-CO_2/h gdw, respectively (Fig. 3.3.B.).

The obtained data can be interpreted as the potential biodegradability of the tested composite materials under given test conditions. It shows that the materials used are biodegradable at a varying rate. It is seen that it is mostly dependent on the used filler. The wood sanding dust has the lowest biodegradability as it shows the lowest respiration after 7 days, while wood fibers and hemp shives have higher biodegradability as they have higher respiration after 7 days. Sapropel binder shows similar respiration as the reference lime binders, as the used sapropel is with high carbonate percentage. The used materials demonstrate that with different extent all studied materials are biodegradable and can be used to decrease the overall environmental impact of construction materials.

3.7.2. Enzyme activity of microorganisms: fluorescein diacetate hydrolysis

One of criteria for evaluating the biodegradability of the tested materials could be an increase of microbial enzyme activity, which responded to the presence of bioavailable nutrients. FDA hydrolysis involves the activity of various enzyme groups of microorganisms, i.e., hydrolases, proteases, esterases, lipases, etc. (Green et al., 2006). As shown in Fig. 3.4., after 7-day incubation period all composite materials added to the soil stimulated FDA hydrolysis activity, comparing with the control set. After 7-day incubation period in the batch system, the lowest FDA hydrolysis activity was observed in the non-composite control (Fig. 3.4.). All tested composite materials show a stimulating effect on the enzyme activity of the microorganisms, with the highest mean value for [GAS-CS/Hemp shives], i.e., 2.01 ± 0.75 µM h gdw FDA (Fig.3.4.).

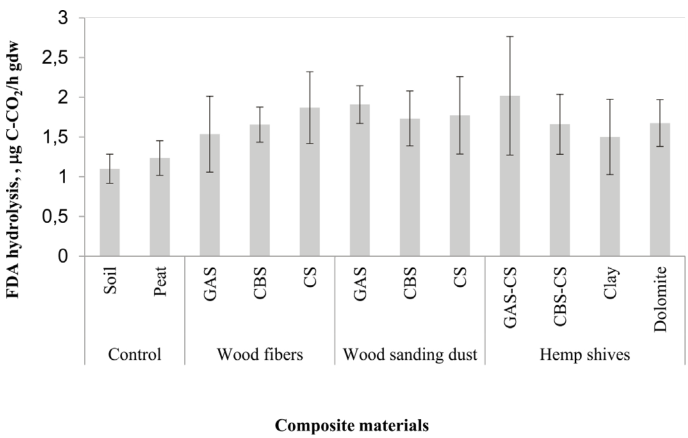

Figure 3.4. **Fluorescein diacetate hydrolysis activity of microorganisms in a clay loam soil amended with nutrients, microbial consortium and composite materials. The ratio of a composite material to the substrate was 0.25:10.0. The substrate was prepared as described in Materials and Methods. FDA activity was measured after 7-day incubation period of a composite material with soil at 37 °C. GAS – green algae sapropel; CBS – cyanobacteria sapropel; CS – carbonatic sapropel. Control – the soil substrate without composite materials.**

Comparison of the FDA hydrolysis activity showed a statistically significant ($p<0.05$) difference between control and composite materials, except CS/wood fibers.

Greater FDA hydrolysis activity may indirectly indicate more intense biodegradation processes, as it depends on the availability of nutrients, the concentration of micro-organisms, and their physical, chemical and environmental properties (Green et al., 2006; Mupambwa and Mnkeni, 2016).

Summary. Biodegradation experiments were conducted on 11 samples. The biodegradability of the obtained composites has been studied and major differences of the biodegradability potential have been found, mostly depending on the filler properties, but also on the presence of mineral matter content in the obtained composites. The obtained results demonstrate potential to use sapropel as a raw material for composites in combination with other waste materials with potential application as construction materials and design products, to extend the life of natural materials and achieve aims of reduction of waste streams.

3.8. Sapropel, peat, biochar granules for the agricultural purposes

Peat is a widespread and important resource in Latvia, 1.2 million tons of peat are extracted every year. One of the most common uses for peat is horticulture – for soil improvement. Mixing peat with soil can improve its structure and increase acidity. One of the main characteristics of peat in agriculture is its ability to retain moisture when the soil is dry, thus ensuring water exchange between plants.

On the other hand, total sapropel resources in Latvia are about 2 billion m3. The spread of sapropel and its wide range of uses makes it an important natural resource that can be used in agriculture, horticulture, forestry, livestock farming, chemical and construction industry, balneology and cosmetology (Stankeviča and Kļaviņš, 2014). In this thesis part study, sapropel and peat are considered as potential soil improvers in the form of granules. Until now sapropel in Latvia was mainly used for fertilization of fields. In addition, sapropel can be used as a binder, for example in granules development for strength enhancement (Balčiūnas et al., 2016; Obuka et al., 2015; Vincevica-Gaile et al., 2019).

The aim was to find out the possibilities of peat-sapropel and sapropel granules formation and to evaluate their properties. The sapropel used is derived from the Lake Veveru in the Latgale region of Rezekne. The Sapropel of the Lake Veveru has a moisture content of 97.66%, a low density of 1.08 g/cm^3 and an organic content of 86.25%. The second sapropel used in the study is peaty sapropel with a moisture content of 90.45%, an organic content of 81.34% and a density of 1.10 g/cm^3 (Table 3.1.).

The granules were made in the Building Materials Laboratory of Riga Technical University. During the development of the sapropel-peat and sapropel granules, the binder was machined prior to incorporation – compacted to a homogeneous mass. The study determined the physical and mechanical properties of test sapropel granules for three types of granules. Gravity density, water absorption test and granules compressive strength, environmental acidity response and electrical conductivity were determined.

Granules from pure sapropel and water pH = 7.35, granules from peaty sapropel and sapropel pH = 7.36, granules from sapropel-peat pH = 4.52 were made. The formed granules slowly decompose in the aquatic environment. In the soil environment, granule decomposition occurs as a result of physical action.

In a study on the development of environmentally friendly granules for agricultural use from sapropel and peat, bulk density (Anonymous, 1999), water absorption (Anonymous, 2013), mechanical strength (Anonymous, 2007) were determined. Gravity density of granules from pure sapropel and water is 639.6 kg/m^3, but granules from peaty sapropel – 246.1 kg/m^3, from sapropel – peat – 248.3 kg/m^3. The water absorption of granules from pure sapropel and water is ≤ 78.9%, granules from peaty sapropel – 167.8%, sapropel – peat granules – 163.9%. The mechanical strength of pure sapropel and water granules is 1.06 MPa, that of peaty sapropel – 0.46 MPa, that of sapropel-peat granules – 0.44 MPa. As a result, granules with sufficient mechanical strength for long-term storage, transport and incorporation into the soil were obtained.

Other of Latvia's valuable resources is biomass. By using it in power plants, cogeneration plants produce a by-product – bio-char. This by-product can be used rationally, for example, in agriculture. The incorporation of bio-char into the soil results in carbon sequestration and positively influences soil properties. The sorption capacity provided by the porosity and surface area of the bio-char prevents the leaching of plant elements and reduces the risk of soil contamination from reaching the plant parts (Hansen et al., 2017). Sapropel, on the other hand, is a valuable natural resource of Latvia that can be used as a binder, and it is also traditionally used as a soil improver or supplementary fertilizer (Balčiūnas et al., 2016; Obuka et al., 2015; Stankeviča and Kļaviņš, 2014). Currently, there is no production of bio-char products for agriculture in Latvia and their supply is not wide in Europe either.

The aim of the study was to investigate the possibilities of bio-char-sapropel granules formation and to evaluate their properties by using bio-char as a by-product in cogeneration plants. The study used biochar obtained by pyrolysis at 600 °C. Their raw material is various hardwoods. The sapropel used was derived from Lake Pikstere in Jekabpils region, Selonia region. This sapropel contains 96.71 ± 0.22% moisture and 82.7 ± 0.26% organic matter (dry matter).

The granules were manufactured at the Rudolfs Cimdiņš Riga Biomaterial Innovation and Development Center by extruding, grinding and then rounding a mixture of non-dried sapropel and biochar. For the specimens concerned, the sapropel binder was machined prior to incorporation – blended to a homogeneous mass. When working with this method, the most suitable ratio of biochar to sapropel for granules is 3:10 in non-dried form (or 9:1 in dry product). The result is granules with a high mechanical strength for storage, transport and incorporation into the soil.

In the result granules has a water extraction pH of 10 and an electrical conductivity of 703.5 μS/cm (gradually increasing as the pellet decomposes). In this case, the high values are determined by bio-char and can be used to adjust soil pH. The bulk density of the granules (0.31 ± 0.07 g/cm^3) is low compared to the pressed bio-char granules currently available on the market. From a logistical point of view, low density is not a desirable feature, but for soil improvement it can serve to solve the problem of soil compaction. In the aquatic environment, granules decompose slowly because both ingredients are water insoluble. Therefore, their degradation in the soil environment is due to physical effects, but the degradation of both bio-carbon and sapropel is slow (De Gisi et al., 2014).

The pellets contain 0.005–0.12 g/kg phosphorus, 0.052 g/kg nitrogen, 5.4–5.7 g/kg potassium, 19.3 19.6 g/kg calcium and 44.2 g/kg magnesium available in plants forms. In general, the composition of the elements of granules is sufficient to ensure plant development. However, for optimal plant development, some nutrients are needed in larger quantities (eg phosphorus, iron, zinc). The materials used are free of heavy metals and are considered safe for use in agriculture.

Determination of moisture was determined 7 times for each sample (Table 3.6.).

Table 3.6

Determination of moisture content (%) of biochar and sapropel granules

Original and composite material	Moisture
Sapropel, %	96.71 ± 0.22
Biochar, %	3.14 ± 0.19
Mixture, %	74.04 ± 0.27
After extrusion – cylindrical granules, %	63.19 ± 0.36
Rotational Molding – Spherical Granules, %	63.19 ± 0.36
After drying – cylindrical granules, %	3.56 ± 0.39
Rotary drying – spherical granules, %	4.13 ± 0.47

Bulk density of Lake Pikstere and biochar granules: by type of granules – cylindrical after extrusion (0.31 ± 0.07 g/cm^3), spherical after extrusion (0.47 ± 0.18 g/cm^3), spherical after rotation molding movements (1.00 ± 0.43 g/cm^3). The granules have a low bulk density compared to commercially available compressed biochar granules.

Granules contain 0.005-0.12 g/kg of phosphorus, 0.052 g/kg of nitrogen, 5.4–57.7 g/kg of potassium, 19.6 g/kg of calcium, 0.002-0.003 g/kg of iron and 44.2 g/kg of magnesium in forms available to plants. The composition of the granule elements is sufficient, but in order to ensure efficient plant development, the composition of the elements must be adapted to the needs of the soil. Analysed raw materials do not contain heavy metals and are therefore considered safe for use in agriculture.

Summary. Sapropel is suitable for use as a binder in the development of biochar, peat composites and provides sufficient strength of the granules, regardless of whether the granules are made by the extrusion method or by the rounding-agglomeration method. The use of biochar-sapropel granules in agriculture should be considered as a prospective. They are technically easy to manufacture, and their physical properties are suitable for storage and transport.

3.9. Sapropel composite material microbiological stability

Microbiological stability of sapropel and lime as binder for composite materials of hemp, sapropel as binder for wood fiber, wood wool were studied. Sapropel with high organic matter content can be used as a binder or adhesive additive in the production of environmentally friendly composite materials (Balčiūnas et al., 2016; Obuka et al., 2016).

This study used sapropel-lime, magnesium oxide-chloride, and lime binders; filler composite materials included hemp shives, wood fiber, and birch wood sanding dust. The fillers used are industrial and agricultural by-products that needs to be recycled or used repeatedly. The use of hemp-lime composite has a positive impact on the environment and is directly linked to CO_2 emissions. Both components are absorbed by CO_2 – lime during hardening (carbonation) and hemp – during growth (Shea et al., 2012). Sapropel also contains CO_2 in the form of organic substances during formation, thus being equivalent to hemp-lime materials.

Additive ALINA LIFE™ was used as an antimicrobial component. The composite materials were prepared in the Riga Technical University Laboratory of Building Materials, Institute of Materials and Structures. Mechanical strength, thermal conductivity, microbiological stability (194 samples in total) and the environmental reaction (pH) were determined for the composite materials. Prior to microbiological resistance tests, some samples were subjected to freeze-thaw cycles and artificially aged. Frost resistance test mode corresponds to frost resistance test according to EN 12390-9. Samples were aged at +20 ± 1 ° C for 1 hour and –20 ± 1 ° C for 3 hours. All samples were subjected to 30 freezing and thawing cycles. Microbiological stability was also tested on specimens that were not subjected to freezing and thawing cycles. The samples were tested using the fungi *Alternaria alternata* and *Cladosporium herbarum.*

The fungi Cladosporium herbarum and Alternaria alternata are common allergens and their spores are found in the outdoor and indoor air (Breitenbach and Simon-Nobbe, 2002). *Alternaria alternata* is a world-wide saprotrophic fungus that is capable of developing on a variety of plants and other substrates. The fungus is able to adapt to different growing conditions, but is mainly found in soil and compost materials, but it is also a plant pathogen (Doustmorad and Javad, 2015). Also found naturally in soil and compost materials, *Cladosporium herbarum* is found in air, food, textiles and many other substrates. Under certain conditions, it is also capable of developing into other fungi and healthy plant leaves (Schubert et al., 2007). Microscopic fungal genera such as *Alternaria, Epicoccum, Fusarium, Phomopsis, Cylindrosporium, Phyllosticta* and *Cladosporium* are frequently found on wood and herbaceous plants (Adamčíková and Hrubík, 2015). Both *Cladosporium* and *Alternaria* spp. high concentrations are also often found on building facades in temperate climates, as these fungi are resistant to natural sunlight. The pigments of these fungi paint the surfaces in dark tones. Because the materials we investigate are of natural origin, containing wood and fiber materials, processing is required to ensure antimicrobial activity and protection.

During the research it was found that the fungi of the genera *Sordaria*, *Alternaria* and *Fusarium* are the most common on the materials used. Isolated cases of *Penicillium*, *Acremonium*, *Paecilomyces*, *Trichoderma*, *Mucor* and *Stachybotrys* spp. – it indicates that the substrates contain sufficient moisture and nutrients for fungal development. Well-developed fungi were observed on sapropel-wood fiber and birch wood sanding dust materials, which can be explained by the fact that the pH level is neutral (pH = 6–7) or even slightly acidic (pH = 5), that wood is naturally a suitable substrate for many fungi.

Fungal development was practically non-existent on hemp-lime materials and hemp-magnesium chloride binder as well as hemp-sapropel-lime binder materials. This is due to the antimicrobial activity of cannabis (Ali et al., 2012), as well as the naturally high pH (pH = 9–12) of lime, which adversely affects fungal development.

The study proved that increased intensity (Figure 3.5.) of fungi growth occurs in materials that are made of wood fibre, wood dust and and sapropel as binder. It should be revealed that the fungi species that grow on the material depend on the type of material, filler and binder. Designation of used materials and methods can be seen in 3.7. table.

Table 3.7

Designation of used materials and methods

Designation	
Sapropel	S
Sapropel-lime-hemp composite	SLHC
Lime-hemp composite	LHC
Magnesium-hemp composite	MHC
Sapropel-wood fibre	SWF
Sapropel-wood sanding dust	SWD
Ageing in climate chamber	CH
ALINA organoclay additive coating	AO
Magnesium oxychloride coating	MH
Lime binder coating	LH
Alternaria alternata	A
Cladosporium herbarum	C
Control sample	K
Evaluation/Intensity of growth	E
Magnesium oxychloride cement	MOC
Formulated hydraulic lime	FHL
Hydraulic lime	HL
Magnesium phosphate cement	MPC
Hemp shives	HS
Flax shives	FS
Wood wool/wood fiber	WW
Wood fibre cement board	WC
ALINA additive	AL
Biocide additive	B
Fungi mixture	F
Control without additive	K

Sample preparation, mixtures and curing. The mixing of the samples was done manually. Mixtures of the samples are listed in Table 2. Mixtures of the LHC, SLHC and MHC have two different target densities – 300 and 500 kg/m^3 in order to test variation of properties at different densities.

To mix the LHC (1,2) samples and SLHC (1,2) samples, at first shives were mixed with lime and then water (for LHC) or sapropel (for SLHC) were added. The shives: water or sapropel ratio is 1:2.5 (samples 1) and 1:5 (samples 2). Added water or sapropel: lime ratio in composite materials were 1:1.

The SWD and SWF were made by mixing sapropel-filler mass. It was done manually until homogeneous mixture has been obtained at the stage where filler was fully covered with binder. Sapropel was mechanically treated by mixing together with electrical hand mixer until homogeneous material has formed. Organoclay additive was added to the mass and treated by mixing until smooth mass has formed. Metal mold (dimension of 30 × 30cm) with adjustable height was used for composite material curing. The mixture of raw materials was put in mold. Sapropel-filler samples were cured at the temperature of 80 °C for 72 hours.

For the MHC samples, at first shives were premixed with water, for hemp shives not to deprive MOC binder of the water because of its high hygroscopic nature. The shives: water ratio was 1:1.25. MgO was added in dry form, mixed with wet shives, afterwards $MgCl_2$ brine was added and blended together, MgO:$MgCl_2$ ratio was 1:0.67.

After mixing the samples were laid in molds hand compressing every ⅓ of the height. Samples were demolded after 2 days and afterwards were cured for 28 days in laboratory conditions (40 ± 10 %RH and 20 ± 2 °C) until testing.

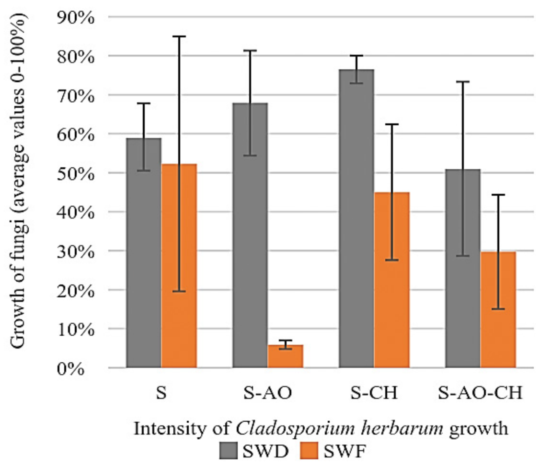

Figure 3.5. **Inhibition of Cladosporium herbarum growth: Sapropel binder materials.**

Process of SWD and SWF materials results indicated a tendency of organoclay improvement for antifungal activity to the composite materials. After intensity of fungal growth was assessed visually it was seen that the structure is not degraded comparing to materials without additive. As well climate chamber made changes to composite materials. Consequently, it can be seen that SWF-AO is 6% comparing to SWF-AO-CH, which is 30% of *Cladosporium herbarum* growth intensity (Figure 3.5.).

Fungal growth was practically not observed on hemp-lime and hemp materials – magnesium chloride binder, as well as hemp-lime sapropel-adhesive materials (Table 3.8.). This can be explained by cannabis antimicrobial effects (Ali et al., 2012), as well as lime naturally high 9–12 pH, which negatively affects the development of the fungi.

Table 3.8

Inhibition of *Cladosporium herbarum* (C); *Alternaria alternata* (A) growth
Control sample (K) growth of other fungi: MHC, LHC, SLHC materials.
Colour legend as in Table 2.3

Nr.	Sample label	E		
		A	C	K
1	MHC	1.7	1.7	1
2	MHC-MH	1	1	1
3	MHC-AO	1	1.7	1
4	SLHC	1.3	1	1
5	SLHC-LH	2	1.7	1
6	SLHC-AO	1	1.3	1
7	LHC	1	1	1
8	LHC-LH	1	1	1
9	LHC-AO	1.3	1	1
10	MHC-CH	1.5	2	2
11	MHC-CH-MH	1.5	1	1
12	MHC-CH-AO	1	1	1
13	SLHC-CH	1	1	1
14	SLHC-CH-LH	1	1	1
15	SLHC-CH-AO	2	1	1
16	LHC-CH	1	1	2
17	LHC-CH-LH	1.5	2	1
18	LHC-CH-AO	1	1	1

It must be emphasized that it is the dried wood surface that has absorbed moisture and consequently has increased susceptibility to fungi. It also proved in this research, because materials made of wood dust and fiber and sapropel as binder in evaluation of intensity of growth (Table 3.9.) got 3.3–5 which indicates visible growth more than 50% coverage to 100% (covering the whole surface of the sample). These materials have neutral 6–7 pH or slightly acidic pH 5.

Table 3.9

Inhibition of *Cladosporium herbarum; Alternaria alternata* growth
Control sample growth of other fungi: Sapropel binder materials. Colour legend as in Table 2.3

Nr.	Sample label	E		
		A	C	K
19	SWD	3.7	4	3.7
20	SWF	3.3	3.7	5
21	SWD-AO	5	4	2.3
22	SWF-AO	3.3	2.3	2.3
23	SWD-CH	3.5	4	4.5
24	SWF-CH	3.3	3.5	5
25	SWD-CH-AO	4.5	4	3
26	SWF-CH-AO	4	4.5	3.5

The results show that the composite filler particle type, composition as well as surface area have an effect on the intensity of growth of fungi. The fungi (moulds) used in the experiment are present in the cellulose-rich plant debris (Bech-Andersen, 2004; Klamer et al., 2004). Moulds are the first indicator that the building and construction materials have begun to deteriorate and lose their good qualities. The next organisms that begin to degrade the material after moulds, are bacteria and white and/ or brown rot fungi. It should be noted that the development of the fungi on materials requires less moisture than bacteria (Hyvärinen et al., 2002)once moistened, may provide ecological niches for various microbes that have not been well characterized. The aim of the current study was to determine whether fungal genera and actinobacteria were associated with seven types of moisture-damaged building materials by systematically describing the mycobiota and enumerating fungi and bacteria in these materials. Microbial analyses were obtained from 1140 visibly damaged samples of building material, viz, wood, paper, non-wooden building boards, ceramic products, mineral insulation materials, paints and glues, and plastics. Fungal and bacterial concentrations correlated well (r = 0.6. The literature describes that materials can be protected from fungal and bacterial degradation using boric acid and other antifungal and antibacterial agents, which are widely used in medicine and the wood industry material storage (Haleem Khan and Mohan Karuppayil, 2012).

Together 3 experiments were done in microbial stability tests.

For the test part 2.1. of the experiment, the samples were prepared in 70 × 70 × 70 mm cube moulds, wood wool (WW) was cut with a similar surface area. For the second stage, the samples were prepared in 40 mm diameter and 10 mm high cylindrical forms, with wood fibre cement board (WF) and WW cut with similar surface area; for the test part 2.2., additional samples with lowered mineral binder amount were also produced, using 50% and 20% of the binder amount of the first stage with the same amount of shives, producing samples with less binder coverage and microbiological protection.

Of the 75% RH material samples, only MPC and WW showed an overgrowth (Figure 3.6.); no fungal overgrowth was observed on other samples. Under such humidity conditions, only fungi that are in the category of primary colonisers can grow and they have low activity, which results in small overgrowth.

Figure 3.6. **Control samples of wood wool covered with *Trichoderma* (A) and MPC composite covered with *Penicillium* and *Aspergillus* (B).**

Table 3.10

Detected fungi at the first stage of the experiment

Type	Inoc.	C	A	B	pH
MOC	F	*Penicillium, Aspergillus, Cladosporium herbarum*	*Penicillium, Aspergillus*	0	9.76
	K	*Aspergillus, Scopulariopsis*	*Chaetomium*	0	
FHL	F	0	*Simplicillium*	*Verticillium*	11.99
	K	0	0	0	
MPC	F	*Aspergillus, Penicillium*	–	–	10.45
	K	0	–	–	
WW	F	*Trichoderma*	–	–	4.28
	K	*Aspergillus niger, Trichoderma*	–	–	
SLHC	F	*Aspergillus*	*Scopulariopsis*	0	12.18
	K	*Aspergillus, Chaetomium*	0	0	12.16

At 99 % RH, MPC showed intensity of growth level 4, wood wool showed intensity of growth level 3, and both showed macroscopic fouling with fungi (Fig. 3.6.); the remaining specimens showed intensity of growth level 1 or an increase in microscopically detected fungi. The low microbiological stability of wood wool can be explained by a low pH level of 4.28. Although magnesium phosphate cement has a high pH level of 10.45 that develops with time as the cement hardens (Jia et al., 2019), it has low microbiological stability, which is related to the monopotassium phosphate that is used as a hardener for the binder. Monopotassium phosphate water solution has a pH lower than 7 and can also be used as a c mineral fertiliser (Hegedűs et al., 2017; Shen et al., 2017)and thus phosphate fertilizers contain significant amounts of U-238, K-40 and Ra-226. These can leach out of the fertilizers used in large quantities for resupplying essential nutrients in the soil and can then enter the food chain through plants, thereby increasing the internal dose of the affected population. In the current study, the radiological risk of eight commercially available phosphate fertilizers (superphosphate, NPK, PK thus the undissolved part of the hardener can serve as a nutrient for fungal growth.

The fungal species found in the samples of the materials are summarised in Table 3.10., where it can be seen that the main fungi that developed in the samples were those that were inoculated with the suspension, but others – such as *Verticillium*, *Simplicillium*, and *Aspergillus niger* – were also found.

As the first stage of the experiment did not show enough fungal growth to be able to fully compare the different materials, it was necessary to perform the second stage of the experiment. In the first stage, humidity was increased only when a decrease in air RH was detected in the samples with humidity sensors. Although microscopic fungal growth was observed in most of the samples, it can be concluded that such humidity conditions were not sufficient to produce fungal growth large enough to be compared by visual inspection. Therefore, in the second round of experiments, the control of humidity conditions was significantly increased by adding 3 ml of sterile water twice a week, and binder amounts for mineral binders were decreased to 50% and 20% of those used in the first stage

From analysing the changes in the microbiological stability of composites depending on the concentration of the binder (Fig. 3.7), it can be concluded that a decrease in the amount of mineral binder decreased microbiological stability. For MOC, FHL, and HL biocomposites at 100% concentration the fouling assessment was 0–1.5, at 50% concentration it was 1–3, and at 20% it was 2.5–4 (Fig. 3.7.).

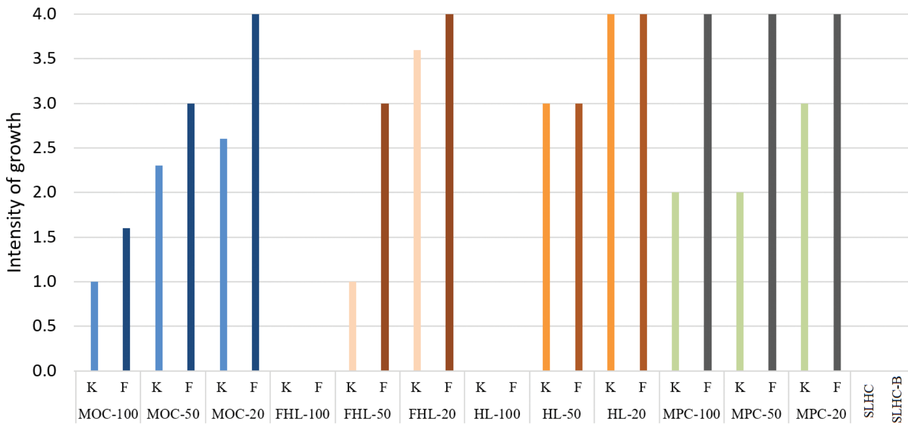

Figure 3.7. **The second stage of the experiment: fouling depending on binder**
Fouling depending on binder. Intensity of growth is evaluated after visual assessment scale (0–4) showed in Table 2.4.

The decrease in microbiological stability correlated with the lowering of pH in the specimens. Lime-based binder biocomposites (FHL and HL) showed higher microbiological stability than MOC biocomposites, since on the 100% binder specimens fouling was not observed, while on the MOC the fouling corresponded to the levels 1–2. At 50% and 20% specimens, this difference disappeared. This can be attributed to the pH level, which for the lime-based specimens was around 12 at 100% but for the MOC was 9.76, while the reduction of binder in 50% and 20% specimens resulted in a similar pH and microbiological stability (Table 3.10.).

The decrease in microbiological stability in the MPC biocomposites was less pronounced, as the intensity of growth at 100% concentration was 2–4, while at 20% it was 3–4. Such an increased intensity of growth in MPC was similar to the results of the first stage of the experiment and can be explained by the impact of the hardener, potassium phosphate. Although the growth was found on local spots, it was evaluated as level 4; this can be seen as a drawback of the visual assessment method and scale used as, for example, there was no distinction between HL-20 (Fig. 3.10.) and MPC-20 samples (Fig. 3.11.).

A comparison of control (K) and fungal inoculated (F) samples (Figure 2) showed that artificially inoculated samples had an increase of between 20% and 50%. Table 3.11. shows the diversity of fungal colonies in the samples as determined by microscopic examination of the fungi. It can be seen from the table that the fungi found in the inoculated samples, mainly *Aspergillus versicolor*, *Penicillium chrysogenum* and *Cladosporium herbarum*, were almost absent in the control samples.

The comparison of control samples and samples with improved microbial stability by organoclay additive or biocide coating (Table 3.9.) showed that both types of coating generally improved microbial stability. Organoclay-added samples showed 13.8% lower overgrowth and those with the biocide product had 9.1% lower. However, this effect was not the same for all formulations. Organoclay additive in HL binder showed no improvement, neither did biocide for MOC and FHL binders.

Figure 3.8. **Materials after microbiological stability tests**
A) hemp shives; B) flax shives, C) wood wool; D) wood fibre cement board

The microbiological stability of the biocomposite aggregate hemp shives (HS) was low – the intensity of fungal growth was 3.2–4 (Fig. 3.8). Some literature sources tend to attribute antibacterial properties to the hemp shives (Ali et al., 2012), but the experiments showed fungi fouling on them. However, when compared with the aggregate of similar origin, flax shives (FS), it can be observed that the flax shives were completely covered with fouling (Fig. 3.8.) and fungal growth started much earlier than for the hemp shives. Thus, hemp shives have somewhat better microbiological resistance than flax shives, but with the methods used in this research, they cannot be distinguished as both had macroscopic growth covering >80% of the surface and no evaluation according to the speed of fungal growth has been made, which limits a full interpretation of the research results.

The microbial resistance (Fig. 3.8.) of the reference building materials – wood wool (WW) and wood fibreboard (WF) – was also experimentally tested. The fastest growth of *Trichoderma* on wood wool was due to the low pH 3.63 (Table 3.11.), similar to the first stage of the experiment (Fig. 3.6.). However, the WF samples showed very high microbial resistance and a high pH of 11.8. Only a small amount of *Paecilomyces* was detected in most samples (Table 3.12.).

In the second stage of the experiment, it was discovered that fungi belonging to the species of *Paecilomyces* and *Stachybotrys* were the most common on the materials included in the research. In some cases, *Penicillium, Acremonium, Cladosporium, Aspergillus, Trichoderma* and *Mucor* were also observed, indicating that the substrates contained sufficient amounts of moisture and nutrients for the fungal development. Most of these fungi feed on cellulose; therefore, they can be found on cellulose-based materials (Bech-Andersen, 2004; Klamer et al., 2004). *Stachybotrys* also feeds on lignin and for this reason, it is often found on wood and its products (Vance et al., 2016), and it is also known as black mould (Ding et al., 2018). Since hemp shives contain high levels of lignin and cellulose, this type of fungi can be found on a large number of specimens (Fig. 3.9.–3.11.). The mycotoxins produced by these fungi cause allergic reactions, and they are often associated with various health problems caused by inappropriate indoor microclimate (Hossain et al., 2004).

Table 3.11

Assessment of fungal colonies growth in the second stage of experiment

Colour legend as in Table 2.4

Type	Inoc.	C	AL	B	pH
MOC-100	K	1	0	2	9.76
	F	1.6	1	1	
MOC-50	K	2.3	1	1	9.55
	F	3	1	3	
MOC-20	K	2.6	2.3	3	9.55
	F	4	3	4	
FHL-100	K	0	0	0	11.99
	F	0	0	0	
FHL-50	K	1	0	1	9.24
	F	3	3	3	
FHL-20	K	3.6	1	3	9.17
	F	4	4	4	
HL-100	K	0	0	0	12.40
	F	0	0	0	
HL-50	K	3	3	0	8.68
	F	3	3	1.5	
HL-20	K	4	4	4	8.61
	F	4	4	3	
MPC-100	K	2	2	2	10.49
	F	4	4	3	
MPC-50	K	2	2	3.5	10.47
	F	4	3	4	
MPC-20	K	3	3	3	10.32
	F	4	1	1	
HS	K	3.8	4	1	8.50
	F	4	4	4	
FS	K	4			7.25
	F	4			
WW	K	3			3.63
	F	3			
WF	K	1			11.80
	F	0			
SLHC	K	0	0	0	11.99
	F	0	0	0	
SLHC – B	K	0	0	0	12.1
	F	0	0	0	

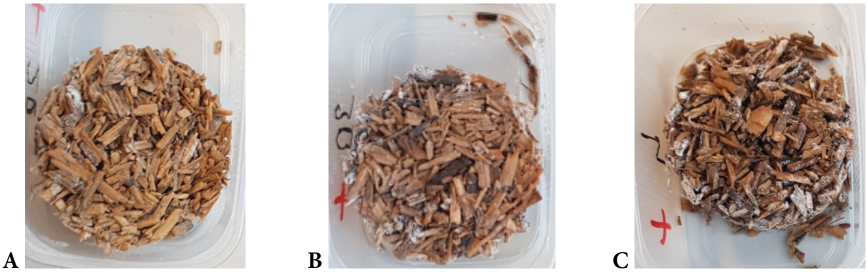

Fig. 3.9. **Magnesium oxychloride biocomposites with varying binder amount: A) MOC-100, B) MOC-50, C) MOC-20.**

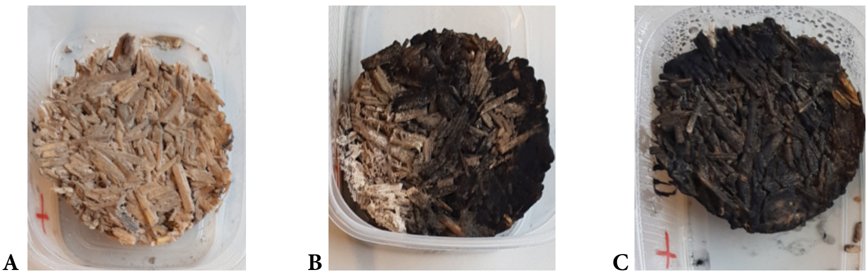

Fig. 3.10. **Hydraulic lime biocomposites with varying binder amount: A) HL-100; B) HL-50; C) HL-20.**

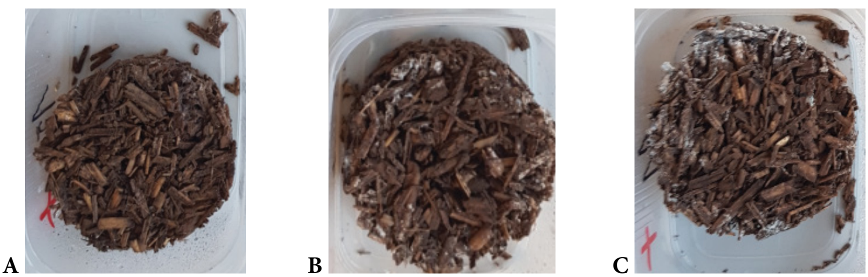

Fig. 3.11. **Magnesium phosphate biocomposites with varying binder amount: A) MPC-100; B) MPC-50; C) MPC-20.**

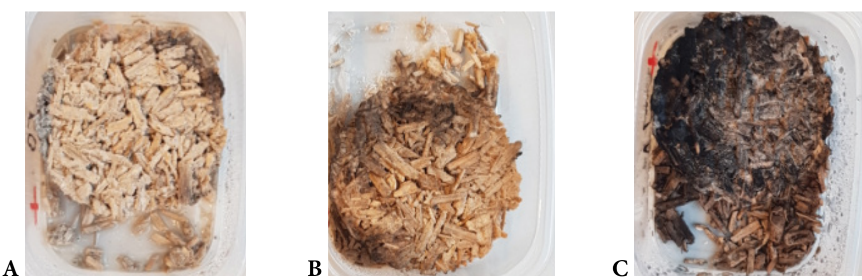

Fig. 3.12. **Formulated hydraulic lime biocomposites with varying binder amount: A) FHL-100; B) FHL-50; C) FHL-20.**

Table 3.12

Detected fungi and other organisms on samples

Type	Inoc.	C	AL	B
MOC-100	K	*Paecilomyces*	*0*	*Paecilomyces*
	F	*Paecilomyces*	*Paecilomyces*	*Paecilomyces*
MOC-50	K	*Paecilomyces*	*Paecilomyces*	*Paecilomyces*
	F	*Paecilomyces, Scopulariopsis*	*Paecilomyces*	*Paecilomyces, Aspergillus, Cladosporium*
MOC-20	K	*Paecilomyces*	*Paecilomyces*	*Paecilomyces*
	F	*Cladosporium, Paecilomyces, Scopulariopsis*	*Aspergillus, Paecilomyces, Scopulariopsis*	*Paecilomyces, Scopulariopsis*
FHL-100	K	0	0	0
	F	0	0	0
FHL-50	K	0	0	0
	F	*Scopulariopsis, Cladosporium, Aspergillus, Paecilomyces*	0	*Scopulariopsis*
FHL-20	K	*Acremonium, Paecilomyces*	*Paecilomyces*	*Scopulariopsis, Paecilomyces*
	F	*Cladosporium, Scopulariopsis*	*Paecilomyces, Scopulariopsis, Stachybotrys*	*Paecilomyces, Scopulariopsis, Cladosporium*
HL-100	K	*0*	0	0
	F	*0*	0	0
HL-50	K	*0*	0	0
	F	*Aspergillus, Cladosporium, Paecilomyces*	*Paecilomyces, Chaetomium*	*Paecilomyces*
HL-20	K	*Scopulariopsis, Paecilomyces*	*Paecilomyces*	*Paecilomyces*
	F	*Paecilomyces, Chaetomium, Penicillium, Trichoderma, Cladosporium, Coprinus comatus, Scopulariopsis, Stachybotrys*	*Paecilomyces, Coprinus comatus, Scopulariopsis*	*Paecilomyces, Scopulariopsis*
MPC-100	K	*Scopulariopsis*	*Paecilomyces*	*Paecilomyces, Scopulariopsis*
	F	*Paecilomyces, Scopulariopsis,* Actinobacteria, *Readeriella*	*Paecilomyces, Scopulariopsis*	*Paecilomyces*
MPC-50	K	*Paecilomyces, Scopulariopsis*	*Paecilomyces*	*Paecilomyces*
	F	*Readeriella, Paecilomyces, Scopulariopsis*	*Readeriella, Paecilomyces*	*Readeriella, Paecilomyces*
MPC-20	K	*Paecilomyces, Scopulariopsis*	*Paecilomyces*	*Paecilomyces*
	F	*Paecilomyces, Scopulariopsis, nematodes, Readeriella*	*nematodes, Paecilomyces, Mucor, Trichoderma*	*Paecilomyces*

HS	K	*Coprinus comatus, Paecilomyces, Geotrichum*	0	*Chaetomium*
	F	*Mucor, Cladosporium, Chaetomium, Coprinus comatus, Stachybotrys*	*Mucor, Stachybotrys, Coprinus comatus*	*Mucor, Cladosporium, Chaetomium, Stachybotrys, Alternaria*
FS	K	*Scopulariopsis, Acremonium, Coprinus comatus, Paecilomyces*	–	–
	F	Nematodes, *Paramecium, Paecilomyces, Coprinus comatus, Alternaria*	–	–
WW	K	*Paecilomyces,*	–	–
	F	*Trichoderma*	–	–
WF	K	*Paecilomyces*	–	–
	F	–	–	–
SLHC	K	0	0	0
	F	0	0	0
SLHC – B	K	0	0	0
	F	0	0	0

The environmental reaction (pH) plays an important role in the spread of fungi and bacteria in building materials and was measured in both the first and second stages of the experiment. The composite materials with pH levels up to 8 are more susceptible to colonisation by microorganisms than alkaline cement materials, which have a pH of about 12–14 and are therefore relatively insensitive to colonisation in the early state of the composite. However, over time, the carbonation process lowers the pH of cementitious alkaline materials to about 9, allowing the microorganisms to develop on the materials. studies have examined the accelerated carbon- ate contamination of mortars and show that their bioavailability is significantly increased. Thus, such composites can be a significant source of indoor air pollution (Verdier et al., 2014)mortar, etc.

Summary. Microbiological stability tests have been developed for sapropel-based new materials for application of functional properties. Biocomposite material, where sapropel was used as a binder, shows one of the highest microbiological stability results. In addition, fungi and other organisms were not detected on the samples.

The tested sapropel, lime and magnesium oxychloride cement composite material have a higher microbiological resistance than commercially used wood wool insulation; therefore, they have the potential to be used in construction under similar conditions, i.e. in structures protected from external moisture. Using visual expert conclusions, as in this study, can give a modest insight into the microbiological resistance and stability of the studied composite materials. It may also be that a fungus with a robust effect on the material can give a low growth percentage share. Organoclay-added samples showed 13.8% lower overgrowth and those with the biocide product had 9.1% lower, however incompatibility was observed with formulated hydraulic lime (20%), magnesium oxychloride cement (20%), hydraulic lime (20 %) and magnesium phosphate cement (100%) binders.

3.10. Comparison of created sapropel and peat based biocomposite materials

In order to determine which material is the most promising for use in the construction industry as a thermal insulation material, a comparison of materials was performed taking into account the study of their essential properties. Thermal conductivity, microbial resistance, mechanical strength results, microbial resistance, sound insulation, auto-ignition, biodegradability was taken into account (Table 3.10.)

Table 3.10

Sapropel and peat based biocomposites comparison

Biocomposite material	Composition	Thermal conductivity, W/m^3	Microbial resistance, scale 1–5*	Mechanical strenght, MPa Compressive strenght/ Flexural strenght	Sound insulation, dB	Auto–ignition, T	Biodegradability, relative units**
SLHC	Sapropel Lime Hemp	0.089	0	0.77	–	–	–
SWF	Sapropel Wood fiber	0.060	4	0.60	–	–	–
SWD	Sapropel Wood sanding dust	0.061	3.8	0.67	–	–	–
CS–GAS–HS	Sapropel Hemp	0.063	–	0.101/0.05	–	–	0.40
CS–CBS–HS	Sapropel Hemp	0.059	–	0.159/0.06	–	–	0.31
GAS–WW	Sapropel Wood fiber	0.055	–	0.221/ 0.069	–	–	0.35
CBS–WW	Sapropel Wood fiber	0.060	–	–	–	–	0.16
GAS –WD	Sapropel Wood sanding dust	0.061	–	0.71/ 0.164	–	–	0.11
CBS–WD–Aerosil	Sapropel Wood sanding dust Aerosil	0.080	–	0.68/ 0.203	–	–	–
Sapropel – particle board	Sapropel Wood chips	0.067	–	0.06 /0.02	31–32	296	–
Peat – particle board	Peat Wood chips	0.06	–	0.13/0.3	30–32	333	–

* Evaluation of fungal growth on materials (average values) is showed in Table or 2.3. and 2.4. Separate scales have been used in different studies, but they have been harmonized to give comparable results.
** Ratio of respiration intensity after 7-day incubation period and at the begining of incubation.

The thermal conductivity results are alike for the developed materials and they show that the materials can be used for the development of environmentally friendly composite materials with insulating properties.

The bio-based composite material, where sapropel was used as a binder, shows one of the best results of microbiological stability. Furthermore, no fungi or other organisms were detected on the samples. The compressive strength test results show that materials are stable and can be used as thermal insulation materials.

The biodegradability of the obtained biocomposite materials was studied and differences in the biodegradability potential were found, mainly depending on the properties of the filler, but also on the presence of mineral content in the obtained composites.

The comparative evaluation of the created biocomposite materials in thesis, indicates that the properties of materials support their application possibilities, and the obtained knowledge can promote development of new materials.

CONCLUSIONS

1. Organic-rich sapropel is prospective material for diverse applications: it shows high prospects to act as biological glue combined with fibrous organic materials.
2. Using local resources such as sapropel and by-products of the production process, such as birch wood sanding dust, birch wood fibers, hemp shives and wood chips, it is possible to develop environmentally friendly composite materials in construction and agriculture, adapting them to the needs of use.
3. Biological stability of natural sapropel containing biocomposites is one of key parameters for their application potential and should include detailed evaluation of composites in respect to major groups of microorganisms of concern.
4. The mechanical and thermal properties of sapropel-based composites were similar to those of synthetic as well as mineral materials, suggesting that sapropel composites could have similar use in the construction industry: as a self-bearing wall thermal insulation material that works together with the structural timber frame.
5. As the sapropel-based building materials have high organic content, they are vulnerable to biodegradation; therefore, antimicrobial additives are significant to add.
6. Microbiological stability and biodegradation tests have been developed and adapted to apply the functional properties of sapropel-based biocomposite materials.

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LATVIJAS UNIVERSITĀTE

ĢEOGRĀFIJAS UN ZEMES ZINĀTŅU FAKULTĀTE

VIDES ZINĀTNES NODAĻA

Vaira Obuka

SAPROPELIS BIOKOMPOZĪTMATERIĀLU IZSTRĀDEI: ĪPAŠĪBU IZPĒTE UN PIELIETOŠANAS IESPĒJAS

Promocijas darba kopsavilkums

Zinātņu doktores grāda iegūšanai

Zemes zinātnēs, fiziskajā ģeogrāfijā, vides zinātnēs

RĪGA, 2021

Promocijas darbs tika izstrādāts no 2015. līdz 2021. gadam Latvijas Universitātes Ģeogrāfijas un Zemes zinātņu fakultātes Vides zinātnes nodaļā.

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Doc. *Dr. geogr.* **Oskars Purmalis**, secretary of Council

Promocijas darba aizstāvēšana notiks 2021. gada 26. augustā plkst. 10:00 Latvijas Universitātes Ģeogrāfijas un Zemes zinātņu fakultātes Vides zinātnes promocijas padomes sēdē attālināti.

Ar promocijas darbu un tā kopsavilkumu var iepazīties Latvijas Universitātes Bibliotēkā, Rīgā, Kalpaka bulvāris 4.

Promocijas padomes sekretārs
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ANOTĀCIJA

Promocijas darba "SAPROPELIS BIOKOMPOZĪTMATERIĀLU IZSTRĀDEI: ĪPAŠĪBU IZPĒTE UN PIELIETOŠANAS IESPĒJAS" mērķis ir izpētīt sapropeļa īpašības un iespējas to izmantot biokompozītmateriālu izstrādei izmantošanai lauksaimniecībā, celtniecības nozarē un citās jomās, kā arī pārbaudīt iegūto materiālu īpašības attiecībā uz to pielietošanas iespējām. Biokompozītmateriālu paraugi tika veidoti, izmantojot dažādu veidu sapropeli kā saistvielu un bērza koksnes slīpputekļus, bērza koksnes šķiedru, kaņepju spaļus un šķiedru, aerosilu, mahagonijas zāģu skaidas kā pildvielas. Sapropeļa kā līmvielas īpašību pārbaudei tika izmantots bērza lobītais finieris, dižskābarža finieris un gabalkūdra. Darba teorētiskā daļā ir veikts pārskats par sapropeļa īpašībām un sastāvu, videi draudzīgu būvmateriālu izmantošanas iespējām. Izveidotie biokompozītmateriāli tika analizēti nosakot to mehānisko izturību, siltumvadītspēju, mikrobioloģisko stabilitāti, biodegradāciju, kompozītmateriālu novecināšanos, kompozītmateriālu spiedes un lieces izturību, skaņas izolācijas īpašības, pašaizdegšanās iespējas. Promocijas darbā pierādīts, ka, izmantojot vietējos resursus, piemēram, sapropeli, un ražošanas procesa blakusproduktus, piemēram, bērza koksnes slīpputekļus, koksnes šķiedras, kaņepju spaļus un šķiedru, būvniecībā un lauksaimniecībā ir iespējams izstrādāt videi draudzīgus biokompozītmateriālus, tos pielāgojot lietošanas vajadzībām. Dabiskā sapropeļa, kas ietilpst biokompozītmateriālu sastāvā, mikrobioloģiskā stabilitāte ir viens no galvenajiem parametriem to pielietošanas potenciālam, un tajā jāietver detalizēts biokomkompozītmateriālu novērtējums attiecībā uz galvenajām mikroorganismu grupām, kas ir sastopamas celtniecības materiālos. Sapropeļa biokompozītmateriālu mehāniskās un siltumizolācijas īpašības ir līdzīgas ar komerciāli pieejamiem materiāliem, kas liek secināt, ka sapropeļa biokompozītmateriālus varētu līdzīgi izmantot būvniecības nozarē.

Promocijas darba kopsavilkums sastāv no 27 lappusēm un satur vienu attēlu un četras tabulas.

Atslēgas vārdi: sapropelis, saistviela, kompozītmateriāls, mikrobioloģiskā stabilitāte, biodegradācija

IEVADS

Mūsdienu ekonomika visā pasaulē lielā mērā ir balstīta uz fosilo materiālu izmantošanu (Ingrao et al., 2018), un šī pieeja ievērojami veicina resursu izsīkšanu, vides problēmas, un, jo īpaši klimata izmaiņas. Bioekonomiku (biotehnonomiku) var uzskatīt par alternatīvu fosilo materiālu balstītai ekonomikai, un tā balstās uz biomasas vai biotehnoloģijas izmantošanu preču, pakalpojumu vai enerģijas ražošanai (Lewandowski, 2018). Ņemot vērā pasaules vides un klimata problēmas, kā arī globālo resursu samazināšanos un noplicināšanos, kas novedīs pie resursu izsīkšanas, ir nepieciešams samazināt sintētisko ķīmisko vielu lietošanu un attīstīt bioekonomiku. Videi draudzīgu materiālu paplašināta izmantošana ir uzskatāma par efektīvu rīcības instrumentu ilgtspējīgas attīstības stratēģiju ietvaros gan Eiropas Savienībā (Altozano, 2012), gan Latvijā (Latvijas Republikas Zemkopības Ministrija, 2017). Tāpēc ir svarīgi atrast un pētīt jaunus dabisko materiālus, kas būtu spējīgi aizstāt sintētiskos materiālus (Fava et al., 2015).

Organiskām vielām bagāti ezeru nogulumi – sapropelis, gitija u.c. – ir perspektīvs materiāls dažādām izmantošanas iespējām (Balčiūnas et al., 2016; Stankevica, 2020). Sapropelis ir ezeru rekultivācijas blakusprodukts, īpaši attiecībā uz eitrofiem ezeriem, kuriem ir nepieciešama ezeru nogulumu izņemšana, lai saglabātu ezeru ekosistēmu, neļaujot tiem aizaugt. Tādējādi sapropeļa ieguve un izmantošana ir ilgtspējīga no aprites ekonomikas perspektīvas, it īpaši attīstot jaunus sapropeli saturošus biokompozītmateriālus jeb biokompozītus. Lielākā daļa Latvijas ezeru ir eitrofi ezeri, kurus būtiski ietekmē antropogēnā eitrofikācija. Kopējais pieejamais sapropeļa resurss Latvijā ir ~2 miljr. m^3. Sapropeļa resursa apjoms ezeros sasniedz 700–800 milj. m^3, kamēr sapropeļa rezerves purvos ir 1,5 miljrd. m^3 (Segliņš, 2014). Sapropeli var uzskatīt par atjaunojamo resursu, jo ezeru eitrofikācija ir dabisks un nepārtraukts process. Tādējādi jaunu iespēju izstrāde, lai veicinātu sapropeļa pielietošanu, sekmē ezeru rekultivāciju, kā arī var ievērojami veicināt bioekonomikas attīstību.

Sapropeļa īpašības ir atkarīgas no daudziem apstākļiem, ierobežojot resursa tiešo pielietojumu, kas visbiežāk vērsts uz lauksaimniecības vajadzībām. Līdztekus ierobežotam pētījumu apjomam, kā arī novecojušiem sapropeļa izmantošanas pētījumiem, sapropelis kā resurss vāji ieinteresē nozares, kas darbojas jaunu produktu izstrādē. Viena no ievērojamākajām sapropeļa īpašībām, to apstrādājot un izžāvējot, ir spēja darboties kā saistvielai vai līmvielai dažādos materiālos (Balčiūnas et al., 2016; Gružāns, 1958, 1960; Klavins and Obuka, 2018). Tādējādi sapropeli var izmantot kompozītmateriālu izstrādei, pamatojoties uz dažādu materiālu grupu īpašību kombināciju, kā arī jaunu materiālu ar jaunām īpašībām izstrādei. Jaunu kompozītmateriālu izstrāde mūsdienās ir vispārēja materiālu zinātnes attīstības tendence. Parasti kompozītmateriāli ir veidoti uz sintētisku materiālu bāzes, piemēram, minerālvate, akmens vate, stikla vate, savukārt sapropeļa unikālās īpašības ļauj ieviest jaunu kompozītmateriālu grupu, ko veido matrica un šķiedru pastiprinājums – biokompozītmateriāli (Mohanty et al., 2000). Neskatoties uz to, sapropelis praktiski nav izmantots šādu materiālu ražošanai, tomēr var uzskatīt, ka šis pētījumu virziens ir ļoti perspektīvs, jo uz dabīgo materiālu balstītas saistvielas biokompozītmateriālu izveidei ir aktuālas.

Būtisks virziens darbā ar sapropeli ir tā izmantošana par saistvielu, bet par pildvielu kompozītmateriālos izmantojot papildus vēl dažādus rūpniecības un lauksaimniecības blakusproduktus. Šāda pieeja sniedz iespējas atrast jaunu pielietojumus, piemēram, kaņepju spaļiem un šķiedrai, koksnes slīpputekļiem, skaidām. Nozīmīgs etaps biokompozītmateriālu izstrādē ir pareiza jauno materiālu īpašību noteikšana (Bulota et al., 2011; Jawaid et al., 2019; Mngomezulu et al., 2014). Biokompozītmateriālu testēšana tradicionāli koncentrējās uz funkcionālo īpašību – mehāniskās izturības, lietošanas izturības, u. c. – pārbaudēm, bet bioloģiskās stabilitātes testi bieži tiek atstāti novārtā, jo testēšanas metodoloģijas nav izstrādātas un aprobētas. Tomēr, tā kā biokompozītmateriāli ir bioloģiski noārdāmi materiāl, to bioloģiskās stabilitātes pētījumiem ir svarīga loma jauno materiālu praktiskās izmantošanas veidu apzināšanā.

Promocijas darba mērķis ir pētīt sapropeļa īpašības un iespējas to izmantot biokompozītmateriālu izstrādei izmantošanai lauksaimniecībā, celtniecības nozarē un citās jomās, kā arī pārbaudīt iegūto materiālu īpašības attiecībā uz to pielietošanas iespējām.

Promocijas darba uzdevumi

1. Sapropela īpašību izpēte biokompozītmateriālu izstrādei
2. Izstrādāt principus biokompozītmateriālu ražošanai, izmantojot sapropeli
3. Sagatavot jaunus, uz pielietojumu orientētus, sapropeli saturošus biokompozītmateriālus
4. Izstrādāt biokompozītmateriālu īpašību izpētes metodoloģiju un pētīt sapropeļa biokompozītmateriālu pielietošanas iespējas.

Hipotēze

Jaunu testēšanas metodoloģiju izstrāde un aprobācija ir būtiska, lai izstrādātu sapropeli saturošus biokompozītmateriālus, īpašu vērību pievēršot to funkcionalitātei un biostabilitātei.

Zinātniskā novitāte

1. Jaunas pieejas izveide ezeru rekultivācijas atkritumu produkta – sapropeļa, īpašību izpētei un tā izmantošanas iespēju attīstīšanai dabīgu materiālu ražošanai, un izmantošanas iespēju demonstrēšanai
2. Izstrādāta dizaina koncepcija sapropeļa biokompozītmateriālu izveidei
3. Sapropeļa biokompozītmateriālu sagatavošana jaunām, uz tirgu orientētām izmantošanas iespējām būvmateriālu rūpniecībā un projektēšanā, kā arī citās jomās, tādējādi atbalstot vietēju, dabisku resursu izmantošanu
4. Sapropeli saturošu biokompozītmateriālu analītiskās raksturošanas un testēšanas metodikas izstrāde, lai pierādītu to biostabilitāti, funkcionālās īpašības un pielietošanas potenciālu

Promocijas darba rezultātu aprobācija

Promocijas pētījuma rezultāti ir aprobēti 9 zinātniskās publikācijās, no kurām 8 ir indeksētas SCOPUS un Web of science zinātniskās literatūras datu bāzēs, apspriesti 5 ziņojumos starptautiskās zinātniskās konferencēs, 6 referātos vietēja mēroga konferencēs Latvijā.

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1. LITERATŪRAS APSKATS

1.1. Sapropelis: veidošanās apstākļi un sastāvs

Sapropelis ir daļēji atjaunojams zemes dzīļu resurss (Segliņš and Brangulis, 1996), kas ir veidojies dažādos apstākļos. Sapropelis ir sīkgraudainas un irdenas saldūdens ar organiskajām vielām bagātas nogulsnes (Emeis, 2009). Sapropelī ir zems neorganiskās izcelsmes vielu saturs (Stankeviča and Kļaviņš, 2014). Sapropeļa organiskās vielas galvenokārt veido ūdenstilpē mītošo ūdensaugu (fitoplanktons) un ūdensdzīvnieku (zooplanktons un citi) atliekas (Kurzo et al., 2004), kas lielos daudzumos savairojas stāvošās vai vāji caurtekošās, aizaugošās ūdens tilpēs (Lācis, 2003). Sapropeļa sastāvu bez kramaļģēm, zilaļģēm un zaļaļģēm veido arī radiolārijas, foraminīferas, dinoflagelāti, sūkļi, dažādas vēžveidīgo sugas, kā arī baktērijas.

Ir divi sapropeļa iegulu tipi: ezeros (zem ūdens) un sauszemes, kas atrodas purvos zem kūdras slāņa (Kaķītis, 1999). Pamatojoties uz Latvijas ezeru izpētes rezultātiem, ezeros sapropeļa krājumi ir 700–800 milj. m^3, bet sapropeļa krājumi purvos sasniedz 1,5 miljr. m^3. Kopējie sapropeļa resursi Latvijā ir 2 miljr. m^3 (Segliņš, 2014), tomēr uzkrāto resursu novērtējums būtu jāpārvērtē, ņemot vērā neseno pētījumu rezultātus (Stankevica, 2020).

Viena no būtiskākajām valga sapropeļa īpašībām ir tā koloidāla struktūra. Tā nosaka sapropeļa organisko koloīdo daļiņu spēju absorbēt lielu daudzumu ūdens, tamdēļ tam ir augsta mitruma ietilpība, kas ir 70–97% (Vimba, 1956) un zema filtrācijas spēja (Liužinas et al., 2005). Sapropela relatīvais mitrums ir saistīts ar tā organisko sastāvu – jo lielāks organisko vielu daudzums, jo lielāks mitruma saturs (Stankevica, 2020).

1.2. Sapropeļa izmantošanas iespējas

Sapropelis ir pieejams ievērojamā daudzumā, tāpēc ir svarīgi izpētīt tā pielietošanas iespējas. Sapropeli var uzskatīt par atjaunojamu dabīgas izcelsmes vērtīgu resursu, un, piemēram, ezera rekultivācijas gadījumā, kas ietver nogulumu izņemšanu no ezeriem, to var uzskatīt par blakusproduktu un tādējādi to var tālāk izmantot, kā izejvielu jaunu produktu radīšanai. Sapropelim tāpat kā kūdrai ir plašas izmantošanas iespējas, kas ir atkarīgas no sapropeļa sastāva, īpašībām un resursa pieejamības. To var izmantot dažādās tautsaimniecības nozarēs, piemēram, lauksaimniecībā, medicīnā, veterinārijā, celtniecības nozarē utt.

No izmantošanas viedokļa par vērtīgāko sapropeļa tipu uzskata organisko sapropeli, tomēr tas nenozīmē, ka šis tips ir universāls un sniedz tikpat labus rezultātus visās sapropeļa izmantošanas jomās (Brakšs et al., 1960; Gružāns, 1960; Штин, 2005).

Visplašāk ir pētīta sapropela izmantošana lauksaimniecībā. Sapropeļa īpašības ietekmē tā pielietošanas potenciālu lauksaimniecībā: 1) sapropelis sekmē augsnes struktūras uzlabošanu, 2) sapropelis var bagātināt augsni ar organiskām vielām, īpaši ar humusvielām, 3) sapropelis ir barības vielu avots un var nodrošināt lēnu barības vielu izdalīšanos 4) bioloģiski aktīvās vielas sapropelī var veicināt augu augšanu (sapropelis var darboties kā biostimulants). Latvijā sapropeļa izmantošana lauka mēslošanā Latvijas Lauksaimniecības Universitātē tiek pētīta kopš 1954. gada. Kā organisko mēslojumu sapropeli var izmantot gan svaigā veidā, gan kā kompostu vai substrātu. Svarīgi ir uzsvērt, ka svaigi iegūts, neizvēdināts sapropelis satur, alumīnija, cinka, bitumvielas un neoksidētus dzelzs savienojumus, kas pirmajā izmantošanas gadā var kavēt tā pārveidošanos augiem pieejamās barības vielās, kā arī samazināt augsnes mikroorganismu aktivitāti (Kaķītis, 1999). Lai sapropelis būtu ļoti efektīvs pirmajā lietošanas gadā, to jāsajauc ar kūtsmēsliem vai vircu.

Ņemot vērā sapropeļa īpašības, ir lielas iespējas attīstīt sapropeļa izmantošanu lopkopībā, lai veicinātu lopkopības efektivitāti, putnu un dzīvnieku barības efektīvu izmantošanu. Arguments attiecībā uz sapropela izmantošanu ir saistīts ar tā biogēno raksturu un acīmredzamo nepieciešamību samazināt sintētisko produktu daudzumu.

Viens no potenciālajiem sapropeļa pielietošanas veidiem lopkopībā, ir tā izmantošana par uztura bagātinātāju, kas paaugstina dzīvnieku svaru, neizmantojot ķīmiskus preparātus. Šim mērķim ir piemērots organiskais sapropelis, kas ir dabisks un drošs mājputniem. Sapropeli bagātinot ar dabīgiem mikroelementiem un vitamīniem, to var izmantot lopkopībā kā mikroelementu un vitamīnu piedevu.

Bioloģiski aktīvas vielas – enzīmi, vitamīni, antibiotikas, aminoskābes, lipīdi, estrogēni, ogļhidrāti, kā arī humusvielas veicina sapropeļa fizioloģisko nozīmi mājputnu barības piedevās. Humusvielas, kas ir sastopamas sapropelī veicina dzīvnieku zarnu trakta mikrobioloģisko līdzsvaru un funkcionalitāti. Toties sapropelī esošais cinks un varš uzlabo dzīvnieku augšanu, imūnsistēmas funkciju (Mikulionienė and Balezentienė, 2012).

Sapropeļa pielietošanas potenciāls veselības aprūpē ir balstīts uz ilgu balneoloģijas vēsturi, kuras pamatā ir peloīdu vai medicīnisko dūņu izmantošana ārējai lietošanai un vannām, kā arī citi preparāti un materiāli. Peloīdi tiek aprakstīti, kā organisko minerālu kompleksi ar augstu organisko vielu koncentrāciju, ko var izmantot terapeitiskajās procedūrās (Badalov and Krikorova, 2012). Galvenie faktori, kas ietekmē sapropeļa lietošanas efektivitāti balneoloģijā, ir bioloģiski aktīvu vielu, piemēram, hormonu, sterīnu, aminoskābju un vitamīnu klātbūtne (Szajdak and Maryganova, 2007). Sapropelis ir izmantojams balneoterapijā un kosmetoloģijā (Badalov and Krikorova, 2012), kad iegūts no ezera vai purva un kombinācijā ar fizikāliem faktoriem (sapropeļa mitrums, siltuma noturēšanas spēja), psiholoģiskajiem aspektiem (relaksējoša atmosfēra), tā pielietošana pārliecinoši parāda biostimulējošu iedarbību, aktivizē vielmaiņu un imūnsistēmu (Anderson, 1996). Sapropeļa pielietojums vairākos pētījumos ir parādījis augstu efektivitāti kaulu un muskuļu slimību, locītavu un mugurkaula slimību, miozīta, čūlu ārstēšanā, kā arī pozitīvu ietekmi uz nervu sistēmas traucējumiem. (Bellometti et al., 1996, 2000). Svarīga ir sapropeļa spēja mazināt iekaisuma procesus, kā arī ādas slimības, īpaši hronisku ekzēmu un vairākas dermatīta formas (Carabelli et al., 1998).

Minerālvielas un organiskie savienojumi sapropeļa sastāvā nosaka tā efektivitāti dažādu slimību ārstēšanā, piemēram, perifērās un nervu sistēmas, balsta un kustību sistēmas slimības, kuņģa un zarnu trakta slimības. Metaboliskās aktivitātes pētījumos sapropelī tika noskaidrots, ka sapropeļa ārstnieciskās īpašības nosaka tā organiskās vielas, tai skaitā arī humusvielas (Курзо, 2005). Sapropelis var tikt pielietots mastīta, hroniska gastrīta, čūlu, divpadsmit pirkstu zarnas, furunkulu, ādas (apdegumus, dermatītu, ekzēmas) slimībām, kā arī hepatobiliāro sistēmu slimības ārstēšanā (Штин, 2005).

Viens no sapropeļa pielietošanas veidiem ir tā izmantošana brikešu un granulu ražošanā dzīvojamo un mājsaimniecības ēku apsildīšanai (Kozlovska-Kędziora and Petraitis, 2011; J. Kozlovska and Petraitis, 2012; Курзо, 2005; Штин, 2005). Sapropeļa brikešu izmantošana ietaupa citus enerģijas resursus, jo sapropela brikešu dedzināšanas process ir ilgāks nekā parastajām briketēm (Kozlovska-Kędziora and Petraitis, 2011; Justyna Kozlovska, 2012). Šo brikešu ražošanā sapropeli var sajaukt ar salmiem, zāģu skaidām vai kūdru (Штин, 2005). Pētījumi parādīja, ka piesārņojuma koncentrācija sapropeļa brikešu dedzināšanas procesā nepārsniedz normatīvās robežas. Šāda veida briketes var samazināt piesārņojumu un nodrošināt vienmērīgu enerģijas avota izmantošanu (Justyna Kozlovska, 2012). Izmantojot zāģu skaidu-sapropeļa briketes, tiek samazināta CO_2 emisija un uzlabota sadegšana (Штин, 2005).

Ir veikti daudzi pētījumi par sapropeļa izmantošanu ķīmiskajā rūpniecībā. Resursa pieejamības, salīdzinoši zemās pašizmaksas, ķīmiskā sastāva, ekoloģiskā drošuma dēļ sapropelis ir piemērojama izejviela urbšanas šķīdumu veidošanai, kas samazina berzi un ir vajadzīgi ģeoloģiskās izpētes dziļurbumu darbiem (Штин, 2005). Sapropelis satur augstmolekulārās vielas: dabiskus biopolimērus, celulozi, humusvielas, ogļhidrātus, lignīnu, bitumus un hemicelulozi, tā šķīduma inhibitora aktivitātes īpašības uz metāliskas virsmas koroziju un reoloģiskās īpašības, nosaka sapropeļa šķidrumu izmantošanu urbšanas iekārtu sistēmās, papildus tās ir labākas par SiO_2, aerosolu un diatomītu dispersijām (Курзо, 2005; Штин, 2005).

1.3. Sapropeļa izmantošana biokompozītmateriālu veidošanā

Šobrīd ir pieaugoša uzmanība kompozītmateriālu, īpaši biokompozītmateriālu izstrādei. Biokompozītmateriāli ir kompozītmateriāli, ko veido bioloģiskas izcelsmes matrica (sveķi, līme utt.) un šķiedru materiāla armatūra. Rūpes par vidi un sintētisko šķiedru izmaksas ir radījušas pamatu dabisko šķiedru izmantošanai kompozītos, kur matricas fāzi veido atjaunojamie vai neatjaunojamie resursi. Kompozītmateriāliem atrod jaunus un aizraujošus pielietojumus dažādās jomās, bet dominējošā ir būvniecība un celtniecības materiālu rūpniecība.

Ir pētīta sapropeļa izmantošana būvniecības nozarē būvmateriālu ražošanai. Ir pētījumi par sapropela betona tehniskajiem testiem (Brakšs et al., 1960; Gružāns, 1960), sapropeļa – kaņepju šķiedru un spaļu (Pleiksnis et al., 2016; Pleikšnis and Dovgiallo, 2015) and sapropeļa – kokskaidu (Obuka et al., 2014) kompozītmateriāliem. Vienu no jaunākajiem pētījumiem veica G. Balčiūnas, kurš pētīja sapropeļa-kaņepju-papīra ražošanas atkritumu kompozītmateriālu īpašības (Balčiūnas et al., 2016). Šajos pētījumos secināja, ka sapropeļa izmantošana par saistvielu ar dažādiem pildmateriāliem, nodrošina izveidotajiem kompozītmateriāliem augstu tehnisko kvalitāti, un tos var iekļaut gatavo produktu siltumizolācijas materiālu kategorijā. No literatūras datiem izriet, ka sapropeli var izmantot kā saistvielas piedevu dažādiem koksnes pārstrādes blakusproduktiem, papīra un kartona rūpniecības ražošanas neizmantotajiem atkritumiem, linu pārstrādes blakusproduktiem (Курзо, 2005), mazsadalījušās kūdras un līdzīgām izejvielām (Gružāns, 1958, 1960). Sapropelis ir labs aizstājējs uz olbaltumvielām bāzētām līmēm, piemēram, albumīnam, un olbaltumvielu aizstāšanas iespējas būtu ievērojams sapropeļa izmantošanas pielietojums.

Saistvielas ražošanai no sapropeļa var tikt izmantots sapropelis ar organisko vielu saturu vairāk par 85% un slāpekli vairāk par 3,3% (Курзо, 2005). Sapropeļa saistvielaslīmējošās īpašības izmantojamas, ražojot būvniecības materiālus, ar aukstiem paņēmieniem – blietēšanu, ar karstiem paņēmieniem – līmspiedē paaugstinātā spiedienā un temperatūrā (Brakšs and Miļins, 1960).

Viena no sapropeļa īpašībām ir tā spēja saistīt lielu daudzumu ūdens. Ražojot celtniecības materiālus, ir svarīgi panākt, lai kompozīmateriālam ir pēc iespējas mazāks rukums. Lai samazinātu materiāla rukumu, sapropeļbetona izgudrotāji un pētnieki iesaka izmantot sapropeli ar mitrumu līdz 60% un pildvielas ar mitrumu zem 20%. Viens no svarīgākajiem uzdevumiem būvmateriālu ražošanā nākotnē ir samazināt enerģijas patēriņu visos to dzīves ciklos, sākot no būvniecības līdz dzīves cikla beigām (Asdrubali et al., 2015).

2. MATERIĀLI UN METODES

2.1. Pētījumā izmantotie sapropeļa paraugi

Promocijas darbā tika izmantots ar organiskajām vielām bagāts sapropelis. Sapropeļa nogulumi tika ņemti no četriem Latvijas ezeriem – Padēlis, Pilvelis, Vēveru – Rēzeknes novadā, Latgalē. Piksteres ezers – Jēkabpils, Sēlijā.

2.2. Sapropeļa paraugu raksturošanas metodes

Karsēšanas zudumu noteikšana. Lai noteiktu mitrumu, karbonātu un organisko vielu saturu sapropelī, tika izmantota karsēšanas zudumu noteikšanas metode (LOI) (Heiri et al., 1993).

Bioloģiskais sastāvs. Sapropeļa paraugu bioloģisko sastāvu noteica ar gaismas mikroskopu, saskaitot un izsakot organisko vielu saturu procentos visās identificētajās organisko atlieku grupās. Izmantojot sapropeļa tipa klasifikāciju, tika identificēts sapropeļa tips, klase un izvērtētas izmantošanas iespējas (Stankeviča and Kļaviņš, 2014).

2.3. Biokompozītmateriālu izstrādei izmantotie materiāli un to raksturojums

Kaņepju šķiedras un spaļi, bērza koksnes slīpputekļi and koksnes šķiedra tika izmantota, kā pildvielas biokompozītmateriālu sagatavošanā. Biokompozītmateriālu izstrādē, kā pildviela – sabiezēšanas piedeva, tika izmantots koloidāls silīcija dioksīda produkts "Aerosil". Plašāks izmantoto materiālu apraksts atrodams rakstos (Obuka et al., 2015;Obuka et al., 2017, 2021).

Gabalkūdra (SIA "Laflora") tika izmantota biokompozītmaterialu biodegradācijas testiem, kā kontroles materiāls. Plašāks izmantoto materiālu apraksts atrodams (Obuka et al., 2019).

Bērza lobītais finieris tika izmantots, lai izveidotu saplāksni. Lai noteiktu pielietojamības grupu sapropelim kā līmei, tika izmantots dižskābarža finieris. Gabalkūdras paraugi arī tika izmantoti testiem. Plašāks izmantoto materiālu apraksts atrodams rakstā – (Obuka et al., 2016)

Lai izveidotu sapropeļa – kūdras kokskaidu siltumizolācijas plāksnes tika izmantota – Baložu kūdras ieguves kūdra, kā arī Pilveļu ezera sapropelis. Plašāks izmantoto materiālu apraksts atrodams (Obuka et al., 2014)

Papildus sapropelim tika izmantotas arī komerciāli pieejamas saistvielas: magnija oksihlorīda cements (MOC), hidrauliskais kaļķis (HL), formulētais hidrauliskais kaļķis (FHL), magnija fosfāta cements (MPC). Plašāks izmantoto materiālu apraksts atrodams (Obuka et al., 2017, 2021)

2.4. Kompozītmateriālu sagatavošana

Kompozītmateriālu izstrādei mikrobioloģiskās stabilitātes testiem, kā saistvielu izmantoja neapstrādātu sapropeli. Biokompozītmateriāli tika izgatavoti arī izmantojot neorganiskas saistvielas, piemēram, kaļķi. Papildus informāciju par kompozītmateriālu sagatavošanu pieejama (Obuka et al., 2017).

Kompozītmateriāla sagatavošanai, kur sapropeli testēja kā līmi, sapropeļa paraugi tika pilnībā sajaukti tieši pirms trīsslāņu saplākšņa sagatavošanas ar izmēriem 4 × 250 × 250 mm. Papildus informāciju par kompozītmateriālu sagatavošanu var atrast rakstā (Obuka et al., 2016).

Lai izveidotu sapropeļa – kūdras kokskaidu siltumizolācijas plāksnes, aktivētās kūdras masa ar saistvielas īpašībām tika iegūta kūdru apstrādājot mehāniski – termisko ložu planetārajās dzirnavās RETSCH PM 400. Papildus informāciju par kompozītmateriālu sagatavošanu var atrast rakstā (Obuka et al., 2014)

2.5. Biokompozītu materiālu testēšanas metodes

Biokompozītmateriāliem (bērza koksnes – sapropeļa (SWD), koksnes šķiedras – sapropeļa (SWF)) 4% sausnas masas koncentrācijā tika pievienots SIA ALINA produkts ALINA LIFE^{TM} organomāli. Iegūto biokompozītmateriālu novecināšana klimata kamerā tika veikta, pakļaujot paraugus 30 sasalšanas un atkausēšanas cikliem. Papildus informācija par mikrobioloģiskās stabilitātes testiem var atrast rakstā (Obuka et al., 2017).

Siltumvadītspēja tika mērīta, izmantojot LaserComp FOX 600 siltuma plūsmas mērītāju (Obuka et al., 2015). Spiedes un lieces izturības pārbaudei paraugi tika īpaši sagatavoti (zāģēti nepieciešamajos izmēros). Papildus informācija par šo metodi ir atrodama rakstā (Obuka et al., 2015).

Kompozītmateriālu mehāniskās izturības testi (stiprības noteikšana statiskā liecē un līmējuma stiprības pārbaude, pielietojamības grupas noteikšana, stiprības noteikšana stiepē), kur sapropelis tika pārbaudīts kā līmviela, papildus informācija par metodi ir atrodama rakstā (Obuka et al., 2016).

Materiāliem tika veikta arī skaņas izolācijas pārbaude. Papildus informācija par šo metodi ir atrodama rakstā (Obuka et al., 2014).

Lai raksturotu kompozītmateriālu degšanas raksturlielumus, tika veiktas degšanas testi (Obuka et al., 2014).

Lai salīdzinātu izveidoto biokompozītmateriālu biodegradāciju, tika izstrādāta eksperimenta shēma (Obuka et al., 2019). Mikroorganismu ar substrātu inducētās elpošanas intensitāte tika pārbaudīta izmantojot zināmas metodes (Rowell, 2014; Zibilske, 1994; Гавиленко et al., 1975) un tās pielāgojot (Obuka et al., 2019).

Šajā pētījumā izmantotais elpošanas tests tika attiecināts uz substrāta izraisītu elpošanu (SIR), jo kopā ar paraugu augsnei tika pievienoti oglekļa avoti. Tomēr SIR mērīšanas standarta principi (piemēram, inkubācija 4 stundas) netika ņemti vērā šī pētījuma īpašo uzdevumu dēļ. Bioloģiskās noārdīšanās procesa stimulēšanai tika veikta bioaugmentācija un 7 dienu inkubācija.

Pēc 7 dienu inkubācijas perioda tika veikta fluoresceīna diacetāta (FDA) hidrolīzes aktivitātes noteikšana (Obuka et al., 2019).

Kopā, lai pārbaudītu mikrobioloģisko stabilitāti tika veikti 3 eksperimenti. Tika veikts sapropela biokompozītmateriālu, LHC un MHC kompozītmateriālu mikrobioloģiskās stabilitātes salīdzinājums, mākslīgi inokulējot sēņu suspensijas *Alternaria alternata* un *Cladosporium herbarum* uz materiāliem. Papildus informācija par metodi ir rakstā – (Obuka et al., 2017).

Tika veikti divi eksperimenti, lai noteiktu mikrobioloģisko stabilitāti otrajā testa daļā. Abos eksperimenta posmos materiāla paraugi tika mākslīgi inokulēti ar sešu sēņu suspensiju:

1) *Aspergillus versicolor* MSCL 1346;
2) *Penicillium chrysogenum* MSCL 281;
3) *Alternaria alternata* MSCL 280;
4) *Cladosporium herbarum* MSCL 258;
5) *Chaetomium* sp. MSCL 851;
6) *Trichoderma asperellum* MSCL 309.

Papildu informācija par metodi ir rakstā (Obuka et al., 2021).

Eksperimenta pirmajā posmā analizētos materiāla paraugus inkubēja divos mitruma režīmos – RH 75% un 99%, 20 °C (Obuka et al., 2021). Eksperimenta otrajā posmā paraugi tika turēti tikai pie relatīvā mitruma 99% un temperatūras 20 ± 2 °C (Obuka et al., 2021).

Pirmajā eksperimenta posmā otrajā mikrobioloģiskās stabilitātes testā tika izmantota ACTICIDE FD biocīds. Eksperimenta otrajā posmā biocīds BACTERICIDE. Abos eksperimentos mikrobioloģiskās aizsardzības nolūkiem tika izmantots SIA ALINA produkts ALINA LIFE^{TM} organomālu pārklājums (Obuka et al., 2021).

Sapropeļa, sapropeļa – kūdras granulas izmantošanai lauksaimniecībā tika testētas. Pētījumā tika veiktas testēšanas granulu fizikālo-mehānisko īpašību noteikšanai 3 veidu granulām (sapropelis, kūdrains sapropelis, sapropeļa-kūdras granulas). Tika noteikts bēruma blīvums, izmantojot standartu LVS EN 1097-3 (Anonymous, 1999), ūdensuzsūce izmantojot standartu LVS EN 1097-6 (Anonymous, 2013), mehāniskā izturība, izmantojot standartu EN 1606 (Anonymous, 2007), vides skābuma reakcija un elektrovadītspēja.

Lai sagatavotu bioogles-sapropeļa granulas lauksaimniecības vajadzībām, kā pildviela tika izmantota bioogle. Tika izmantotas divu veidu bioogles: bioogle (B), lapkoku bioogle (LB.). Granulu kompozītmateriāli tika izveidoti, manuāli sajaucot mitru sapropeli un bioogli, līdz tika sasniegta viendabīga konsistence. Lai noteiktu labāko variantu, tika izmantotas dažādas biooglu un sapropeļa proporcijas (1:3, 1:4, 1:6, 1:8 un 1:10). Masu tālāk sadalīja divos paraugos, un katra daļa tika ievietota sagatavotās metāla formās. Vienu paraugu žāvēja gaissausā vidē (relatīvais gaisa mitrums 14-20%), bet otru žāvēja krāsnī 80 ° C temperatūrā. Gaissausā vidē žāvēts paraugs tika svērts katru stundu pirmās 3 stundas un vēlreiz pēc 24 stundu izveides brīža. Krāsnī žāvētu paraugu svēra ik pēc 15 minūtēm. Bioogles- sapropeļa granulu granulēšana, īpatnējās virsmas laukums, ūdensuzsūce un mehāniskās izturības testi ir aprakstīti rakstā (Vincevica-Gaile et al., 2019).

3. REZULTĀTI UN DISKUSIJA

3.1. Sapropeļa īpašības

Sapropeļa nogulumi tika ņemti no četriem Latvijas ezeriem – Padēlis, Pilveļu, Vēveru – Rēzeknes novadā, Latgalē. Piksteres ezers – Jēkabpils, Sēlijā.

Šo ezeru sapropelis ir pētīts iepriekš, un to var uzskatīt par biokompozītmateriālu izstrādāšanā perspektīvu. Sapropeļa paraugu raksturojums ir uzskaitīts 3.1. tabulā.

3.1. tabula

Sapropeļa paraugu raksturojums

Ezers	Mitrums, %	Organiskās vielas, %	Karbonāti, %	Blīvums, g/cm^3
Padēlis	85,97	15,27	35,57	1,24
Pilveļu	94,99	84,51	1,26	1,10
Vēveru	97,66	86,25	1,18	1,08
Piksteres	96,45	82,67	17,33	1,028

Izmantotie sapropeļa paraugi atspoguļo sapropeļa tipus, kurus var izmantot kā saistvielu materiālos.

3.2. Sapropeļa biokompozītmateriālu izstrāde

Kā potenciālu pildvielu sapropeļa bāzes biokompozītmateriālu veidošanā var uzskatīt dabiskas šķiedas un vispirms – kaņepi. Lai izpētītu iespējas kaņepju šķiedru un spaļu izmantošanai kompozītmateriālu iegūšanai, tika izmantotas arī komerciāli pieejamu saistvielu piedevas: magnija oksihlorīda cements, hidrauliskais kaļķis, formulētais hidrauliskais kaļķis. Iegūtās kompozīcijas salīdzināja savā starpā un ar literatūrā pieejamajiem datiem. Kaņepju šķiedras un spaļi, koksnes šķiedra un bērza koksnes slīpputekļi ir izmantoti, kā pildvielas biokompozītmateriālu izstrādē. Šie pildvielas ir lauksaimniecības un kokapstrādes rūpniecības blakusprodukti, kuriem jārod atkārtota izmantošana.

Pētījuma mērķis bija noskaidrot biokompozītmateriāluizveides un izmantošanas potenciālu, izmantojot sapropeli un kaļķi kā saistvielu un kaņepju spaļus un šķiedru, koksnes šķiedru un bērza koksnes slīpputekļus kā pildvielu, un noteikt to optimālās īpašības. Blīvums, siltumvadītspēja, un mehāniskā izturība tika noteikta izveidotajiem paraugiem. Iegūto kompozītmateriālu spiedes stiprība testos ir parādīta 3.2. tabulā un tā parāda, ka iegūtos materiālus var izmantot kā siltumizolācijas materiālus, jo to stiprība atbilst normatīvajā regulējumā pastāvošām prasībām.

3.2. tabula

Kompozītmateriālu raksturojums

Apzīmējums	Sastāvs	Īpašības	
Sapropeļa-kaļķa-kaņepju kompozīts SLHC 1-2	Sapropelis Kaļķis Kaņepju šķiedra un spaļi	Izejvielu attiecība (pildviela : saistviela : saistviela)	1 : 2.5 : 2.5
		Blīvums kg/m^3	306,88; 296,31
		Siltumvadītspēja, W/m·K	–
		Mehāniskā izturība, MPa	0,25
Sapropeļa-kaļķa-kaņepju kompozīts SLHC 3-4	Sapropelis Kaļķis Kaņepju šķiedra un spaļi	Izejvielu attiecība (pildviela : saistviela : saistviela)	1 : 5 : 5
		Blīvums kg/m^3	533,58; 540,59
		Siltumvadītspēja, W/m·K	0,089
		Mehāniskā izturība, MPa	0,77
Kaļķa-kaņepju kompozīts LHC 1-2	Kaļķis Kaņepju šķiedra un spaļi	Izejvielu attiecība (pildviela : saistviela : saistviela)	1 : 2.5 : 2.5
		Blīvums kg/m^3	294,09; 302,40
		Siltumvadītspēja, W/m·K	–
		Mehāniskā izturība, MPa	0,29
Kaļķa-kaņepju kompozīts LHC 3-4	Kaļķis Kaņepju šķiedra un spaļi	Izejvielu attiecība (pildviela : saistviela : saistviela)	1 : 5 : 5
		Blīvums kg/m^3	498,32; 562,93
		Siltumvadītspēja, W/m·K	0,099
		Mehāniskā izturība, MPa	0,90
Kaļķa-kaņepju kompozīts LHC	Kaļķis Kaņepju šķiedra un spaļi	Izejvielu attiecība (pildviela : saistviela : saistviela)	1 : 5 : 5
		Blīvums kg/m^3	408,10
		Siltumvadītspēja, W/m·K	0,086
		Mehāniskā izturība, MPa	0,61
Sapropeļa-koksnes šķiedras kompozīts SWF	Sapropelis Koksnes šķiedra	Izejvielu attiecība (pildviela : saistviela)	1 : 6
		Blīvums kg/m^3	319
		Siltumvadītspēja, W/m·K	0,19
		Mehāniskā izturība, MPa	0,060
Sapropeļa-bērza koksnes slīputekļu kompozīts SWD	Sapropelis Koksnes bērza slīpputekļi	Izejvielu attiecība pildviela : saistviela)	1 : 6
		Blīvums kg/m^3	470
		Siltumvadītspēja, W/m·K	0,061
		Mehāniskā izturība, MPa	0,67
Magnija-kaņepju kompozīts MHC 1	Magnija oksīds Kaņepju šķiedra un spaļi	Izejvielu attiecība (pildviela : saistviela : saistviela : saistviela)	1 : 1.25 : 0.9 : 1.33
		Blīvums kg/m^3	302,3
		Siltumvadītspēja, W/m·K	0,076
		Mehāniskā izturība, MPa	0,25
Magnija-kaņepju kompozīts MHC 2	Magnija oksīds Kaņepju šķiedra un spaļi	Izejvielu attiecība (pildviela : saistviela : saistviela : saistviela)	1 : 1.25 : 2 : 0.6
		Blīvums kg/m^3	504,4
		Siltumvadītspēja, W/m·K	0,111
		Mehāniskā izturība, MPa	1,12

Iegūtie rezultāti rāda, ka kaļķu un kaņepju kompozītmateriāla (blīvums 408,10 kg/m^3) siltumvadītspēja ir vidēji zema – 0,086 W/m·K. Līdzīgas vērtības tika iegūtas sapropeļa-kaļķa-kaņepju biokompozītmateriālam – 0,089 W/m·K. Iegūtie rezultāti ir apmierinoši, līdzīgi tiem materiāliem, kuros pasaulē praktiski izmanto kaņepju šķiedras un spaļus, un ar pašreizējo regulējumu sienai, kas izolēta ar šādiem materiāliem, jābūt aptuveni 400 mm biezai, lai sasniegtu normatīvās vērtības (Sinka et al., 2014).

Pētījumā par sapropeļa – kūdras kokskaidu siltumizolācijas plāksnēm (Obuka et al., 2013), tika noteikta materiālu mehāniskā izturība. Atkarībā no mitruma daudzuma mainās plātnes spiedes pretestība. Sapropeļa-kokskaidu plātnes izturība ir 0,06 MPa, bet kūdras – kokskaidu – 0,13 MPa. Turpretī lieces pretestība parāda, ka sapropeļa – kokskaidu plātnei izturība ir 0,02 MPa, bet kūdras-kokskaidu plātnei – 0,3 MPa. Šie spiedes pretestības rezultāti norāda uz to, ka kompozītmateriālu stiprība ir pietiekama, lai ar tiem veiktu montāžas darbus, kā arī līmējošus savienojumus. Papildus informācija par iegūtajiem rezultātiem ir atrodama publikācijā (Obuka et al., 2014).

Iegūtie rezultāti rāda, ka kompozītmateriāliem ar bērza koksnes slīputekļiem, kā pildvielu un zaļaļģu sapropeli, kā saistvielu ir augstākas kompresijas deformācijas vērtības perpendikulāri un paralēli parauga veidošanās virzienam. Perpendikulāro deformāciju spiedes rezultāti ir diapazonā no 0,67 līdz 0,76 MPa. Lineāro deformāciju rezultāts ir attiecīgi 0,72 un 0,67 MPa. Rezultāti, kas iegūti no mehāniskās izturības testiem, parāda, ka materiāli ir pietiekami izturīgi, lai tos varētu izmantot montāžas darbos un veidotu līmējošos savienojumus. Papildu informācija par testa rezultātiem ir atrodama rakstā (Obuka et al., 2015).

3.3. Kompozītmateriālu siltumvadītspējas pārbaude

Pētījumā par sapropeli kā saistvielu biokompozītmateriāliem tika veikts siltumvadītspējas tests, izmantojot dažādus sapropeļus un pildvielas (Obuka et al., 2015). Trīs sapropeļa veidi tika izmantoti: Vēveru ezera (zaļaļģu) un Pilveļu ezera (zilaļģu) un sapropelis no Padeļa ezera (karbonātiskais). Kaņepju spaļi un šķiedra, koksnes šķiedra, bērza koksnes slīputekļi tika izmantoti kā pildvielas. Izstrādātajiem kompozītmateriāliem kā saistvielu izmantoja neapstrādātu sapropeli. Iegūtie rezultāti ir apskatāmi 3.3. tabulā.

3.3. tabula

Kompozītmateriālu siltumvadītspējas rezultāti

Materiāls: saistviela-pildviela	Blīvums, kg/m^3	Siltumvadītspēja, W/m·K
Karbonātiskais uz zaļaļģu sapropelis – kaņepju spaļi un šķiedras	191	0,063
Karbonātiskais uz zillaļģu sapropelis – kaņepju spaļi un šķiedras	200	0,059
Koksnes šķiedra – zaļaļģu sapropelis	153	0,055
Koksnes šķiedra – zaļaļģu sapropelis	202	0,060
Zillaļģu sapropelis – koksnes bērza slīputekļi	214	0,061
Zillaļģu sapropelis – koksnes bērza slīputekļi – Aerosils	376	0,080

Attiecīgi siltumvadītspējas labākie rādītāji ir biokompozītmateriālam, kas ir iegūts izmantojot koksnes šķiedras un Vēveru ezera zaļaļģu sapropeli kā saistvielu. Rezultāti norāda ka šie biokompozītmateriāli ir ar līdzīgiem rādītājiem un ar līdzīgām izmantošanas iespējām un potenciālu. Izveidotajiem biokompozītmateriāliem ir zema siltumvadītspēja to jauktās, porainās struktūras dēļ, un tiem ir viendabīga šķiedru struktūra ar savstarpēji savienotām un atvērtām porām. Izejvielu organiskās izcelsmes dēļ sapropeļa saistvielas un kaņepju spaļu un šķiedru biokompozītmateriālam ir neviendabīga struktūra. Granulometriski atšķirīgām daļiņām sakārtojoties, rodas tukšumi un nevienmērīga struktūra, ar ieslēgumiem, paraugam ātrāk deformējoties. Papildus informācija par testa rezultātiem ir atrodama rakstā (Obuka et al., 2015).

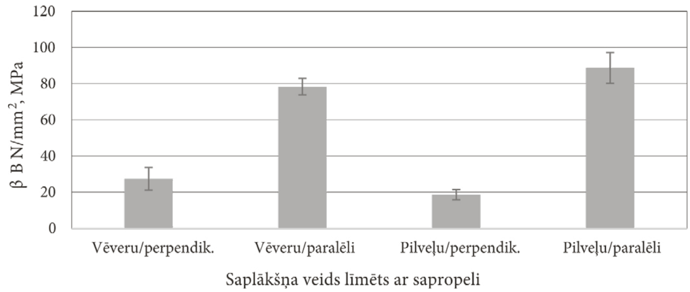
Pētījumā par sapropeļa – kūdras kokskaidu siltumizolācijas plāksnēm (Obuka et al., 2014) siltumvadītspējas rezultāti sasniedza 0,067 un 0,060 W/m·K. Pētījumā tika ņemts vērā sasaldēšanas ciklu skaits un testēto materiālu mitrums. Kūdras– kokskaidu plātnei veicot saldēšanas ciklu ietekmes izpēti, tās siltumvadītspēja nedaudz palielinās, taču sapropeļa–kokskaidu plātnes siltumvadītspējas koeficients samazinās, kas ir labāk. Salīdzinot iegūtos rezultātus, kur biokompozītmateriāla mitruma saturs ir no sausgaisa līdz mitrumam piesātinātam materiālam (12%), siltumvadītspējas koeficients sapropeļa-kokskaidu plātnei ir 0,050-0,060 W/m·K un kūdras – kokskaidu plātnei attiecīgi 0,055-0,064 W/m·K.

3.3. Kompozītmateriālu spiedes un lieces izturības testi

Šajā pētījumā tika izstrādāti kompozītmateriāli, sapropeli izmantojot kā līmvielu. Tika izmantoti divu veidu sapropeļa paraugi – zaļaļģu sapropelis, kas iegūts Vēveru ezerā un zilaļģu sapropelis, kas iegūts Pilveļu ezerā. Sapropelim tika noteikti tādi raksturlielumi kā sausnas saturs, mitruma saturs un blīvums. Līmes tika pārbaudītas, līmējot saplāksni un pārbaudot kompozītmateriālus mehāniski: stiprības noteikšana statiskā liecē un līmējuma stiprības pārbaude izmantojot (Anonymous, 2000b) un (Anonymous, 2005) standartu, pielietojamības grupas (D1–D4) noteikšana sapropelim kā līmvielai izmantojot standartu (Anonymous, 2001a) un izmantojot (Anonymous, 2002) standartu, gabalkūdras salīmēšana ar sapropeli un stiprības noteikšana stiepē perpendikulāti plātnes plaknei noteikšana izmantojot (Anonymous, 2000a) standartmetodi.

No rezultātiem izriet, ka robežstiprības liecē mehāniskajām pārbaudēm sapropeļa līmvielai (Anonymous, 2001b), augstāko rezultātu uzrāda Pilveļu ezera sapropelis paralēli liecē – 88,7 MPa. Zemāko rezultātu rāda tāda paša veida sapropelis, kas ir testēts tikai perpendikulāri liecei (3.2. attēls). Papildus nosakot pielietojamības grupas (D1–D4) noteikšana sapropelim kā līmei, rezultāti rāda, ka Pilveļu sapropelis – dižskābardis paraugi sasniedz 3,67 MPa. Papildus tests saskaņā ar standartu (Anonymous, 2000a) tika taisīts gabalkūdrai un sapropelim kā līmvielai, lai noteiktu stiprības noteikšanu stiepē perpendikulāri plātnes plaknei, rezultāti rāda, ka līmēto paraugu gabalkūdra–Pilveļu sapropelis, lieces mehāniskā izturība sasniedz – 0,077 MPa, gabalkūdra – Vēveru sapropelis sasniedz 0,067 MPa.

Pētījuma rezultāti norāda uz to, ka videi draudzīga līmviela, iegūta no sapropeļa, kompozītmateriālu izstrādē ir izmantojama kā dabiska saistviela, kurai piemīt augsta spēja salīmēt un noturēt veidojuma formu.



3.2. attēls. **Lieces mehāniskā izturība paralēli un perpendikulāri šķiedru virzienam**

Pētījuma virziens ir perspektīvs un tas ir jāturpina, radot jaunus risinājumus sapropeļa līmvielas īpašību uzlabošanai, tās efektivitātes celšanai.

3.5. Skaņas izolācijas īpašības

Pētījumā par sapropeli un kūdru, kā saistvielu un kokskaidām kā pildvielu (Obuka et al., 2014), ir noteikts, ka viena no nozīmīgām jebkura būvmateriāla īpašībām ir to spēja izolēt skaņu Tādējādi promocijas darba ietvaros tika veikts izstrādāto materiālu skaņas izolācijas īpašību pētījums (3.4. tabula).

3.4. tabula

Skaņas izolācijas testu rezultāti, izmantojot 4 mikrofonu metodi

Testētā plātne	Skaņas izolācijas, dB
Kūdra – kokskaidas	30
Kūdra – kokskaidas	32
Sapropelis – kokskaidas	32
Sapropelis – kokskaidas	31

Iegūtajiem biokompozītmateriāliem ir smalki poraina struktūra ar viendabīgu šķiedru struktūru ar atvērtām un savstarpēji savienotām porām. Iegūtie skaņas izolācijas rezultāti liecina par to, ka biokompozītmateriāli ir ar ļoti labām izolācijas īpašībām. Salīdzinot ar citiem ekoloģiskajiem siltumizolācijas materiāliem, piemēram, linu šķiedru siltumizolācijas materiālu, rezultāti ir sliktāki, un tie atšķiras par 14 dB. Linu šķiedru materiālam skaņas absorbcijas rezultāts pēc literatūras datiem ir 45 dB, bet linu – vilnas siltumizolācijas materiāls nodrošina 40 dB skaņas absorbciju (Kozłowski et al., 2008). Ņemot vērā skaņas izolācijas īpašības, var secināt, ka labāku skaņas izolācijas līmeni var sasniegt, izmantojot smagākus materiālus.

3.6. Pašaizdegšanās tests

Pētījumā par sapropeli un kūdru, kā saistvielu un kokskaidām kā pildvielu (Obuka et al., 2014) tika veikts izstrādāto materiālu pašaizdegšanas riska novērtējums. Uz degšanas pārbaudes iegūto datu pamata ir iespējams secināt to, ka kūdras kokskaidu plātnes pašaizdegšanās temperatūra ir augstāka, nekā sapropeļu–kokskaidu plātnes pašaizdegšanās temperatūra. Lai uzlabotu materiālu lietojamību, tie jāapstrādā ar dažādiem līdzekļiem, kas uzlabo ugunsdrošību un bioloģisko izturību, jo tas uzlabo kompozītmateriālu izturību, izmantošanas iespējas, dzīves ciklu.

3.7. Biodegradācijas testi

Biodegradācijas eksperimentus veica, testējamajiem biokompozītmateriāliem pievienojot augsni, barības vielas un mikroorganismu konsorciju ar celulolītisko aktivitāti, (Muter, 2015) lai nodrošinātu labvēlīgus apstākļus noārdīšanās procesiem.

Trīs sapropeļa veidi tika izmantoti: Vēveru ezera (zaļaļģu-GAS) un Pilveļu ezera (zilaļģu-CBS) un sapropelis no Padēļa ezera (karbonātiskais-CS).

Biodegradācijas testā tika izmantoti biokompozītmateriālu pildvielas – koksnes šķiedra, bērza koksnes slīpputekļi, kaņepju šķiedras un spaļi. Šiem materiāliem tika izmantotas minerālās saistvielas, kas izstrādātas iepriekšējos pētījumos – dolomītmilti kas sastāv no 100% DL60 kaļķa (Dolomīts) un hidrauliskais kaļķis, kas sastāv no 60% DL60 kaļķa un 40% kalcinēta kaolīna māla (Māls) (Sinka and Sahmenko, 2015). Saistvielas un pildvielas masas attiecība bija 2:1. Gabalkūdra ("Laflora") tika izmantota arī kompozītmateriālu biodegradācijas pētījumos kā kontroles materiāls (Obuka et al., 2019).

3.7.1. Mikroorganismu elpošanas intensitāte

Biodegradācijas procesu vēroja sākumā un pēc 7 dienām pie 37 °C. Tika novērots elpošanas intensitātes pieaugums kompozītmateriālos. Paraugi inkubācijas sākumā uzrādīja statistiski nozīmīgu atšķirību ($p<0,05$) un elpošanas intensitāte svārstījās diapazonā no 31% līdz 70%, salīdzinot ar kontroli (augsni un kūdru). Papildinformāciju par šī pētījuma rezultātiem var atrast (Obuka et al., 2019).

Rezultāti rāda, ka dažādos apjomos visi pētītie biokompozītmateriāli ir bioloģiski noārdāmi, nodrošinot degradācijas procesam piemērotus apstākļus. Tas parāda, ka izmantotie materiāli ir bioloģiski noārdāmi dažādā laika posmā. Ir secināms, ka tas galvenokārt ir atkarīgs no izmantotās pildvielas. Koksnes bērza slīpputekļiem ir viszemākā bioloģiskā noārdīšanās spēja, jo tiem uzrādās vismazākā elpošanas intensitāte pēc 7 dienām, savukārt koksnes šķiedrām un kaņepju spaļiem un šķiedrām ir augstāka bioloģiskā noārdīšanās spēja pēc 7 dienu inkubācijas. Rezultāti rāda, ka dažādos apjomos visi pētītie biokompozītmateriāli ir bioloģiski noārdāmi un tos var izmantot, lai samazinātu būvmateriālu kopējo ietekmi uz vidi pēc to dzīves cikla beigām.

3.7.2. Fluoresceīna diacetāta (FDA) hidrolīzes aktivitātes noteikšana

Viens no pārbaudīto materiālu bioloģiskās noārdīšanās novērtēšanas kritērijiem ir mikroorganismu enzīmu aktivitātes palielināšanās, kas reaģē uz biopieejamo barības vielu klātbūtni. Kā zināms, mikroorganismu dažādas enzīmu grupas, t.i., hidrolāzes, proteāzes, esterāzes lipāzes u. c., piedalās FDA hidrolīzē. (Green et al., 2006). Papildinformāciju par šī pētījuma rezultātiem var atrast (Obuka et al., 2019).

FDA hidrolīzes aktivitātes salīdzinājums parādīja statistiski nozīmīgu ($p<0,05$) atšķirību starp kontroli un kompozītmateriāliem, izņemot CS/koksnes šķiedras materiālu. Lielāka FDA hidrolīzes aktivitāte var netieši norādīt uz intensīvākiem bionoārdīšanās procesiem, jo tā ir atkarīga no barības vielu pieejamības, mikroorganismu koncentrācijas, kā arī no to fizioloģiskā stāvokļa, ķīmiskā sastāva un vides fizikālajām īpašībām (Green et al., 2006; Mupambwa and Mnkeni, 2016).

3.8. Sapropelis, kūdra, bioogle: granulu izstrāde izmantošanai lauksaimniecībā

Šajā promocijas darba daļā sapropelis un kūdra tika pētīti, kā potenciālie augsnes ielabotāji granulu veidā. Līdz šim sapropelis Latvijā galvenokārt tika izmantots lauku mēslošanai, kā papildmēslojums. Turklāt sapropeli var izmantot kā saistvielu, piemēram, granulu izstrādē stiprības uzlabošanai (Balčiūnas et al., 2016; Obuka et al., 2015; Vincevica-Gaile et al., 2019).

Mērķis bija noskaidrot kūdras-sapropeļa un sapropeļa granulu veidošanas iespējas un novērtēt to īpašības. Sapropeļa-kūdras un sapropeļa granulu izstrādes laikā saistviela pirms iestrādāšanas tika apstrādāta līdz viendabīgai masai. Pētījumā tika veiktas testēšanas granulu fizikāli-mehānisko īpašību noteikšana 3 veidu granulām. Tika noteikts bēruma blīvums (Anonymous, 1999), ūdensuzsūce (Anonymous, 2013), granulu spiedes stiprība (Anonymous, 2007), vides skābuma reakcija un elektrovadītspēja.

Iegūto granulu no tīra sapropeļa un ūdens pH ir 7,35, bet granulām no kūdrainā sapropeļa pH ir 7,36, no sapropeļa-kūdras granulām pH ir 4,52. Izveidotās granulas ūdens vidē sadalās lēni. Augsnes vidē granulu sadalīšanās notiek fiziskas iedarbības rezultātā.

Bēruma blīvums granulām no tīra sapropeļa un ūdens ir 639,6 kg/m^3, bet granulām no kūdrainā sapropeļa ir 246,1kg/m^3, sapropeļa-kūdras 248,3 kg/m^3. Ūdensuzsūce granulām no tīra sapropeļa un ūdens ir ≤78,9%, bet granulām no kūdrainā sapropeļa ir 167,8%, bet sapropeļa-kūdras 163,9%. Granulu mehāniskā izturība no tīra sapropeļa un ūdens ir 1,06 MPa, bet granulām no kūdrainā sapropeļa ir 0,46 MPa, bet sapropeļa-kūdras ir 0,44 MPa. Rezultātā tika iegūtas granulas, kuru mehāniskā izturība ir pietiekama, lai tās varētu ilglaicīgi uzglabāt, pārvadāt un iestrādāt augsnē.

Promocijas darbā tika pētītas arī bioogles-sapropeļa granulas. Mērķis bija noskaidrot biogļu-sapropeļa granulu izveidošanas iespējas un izvērtēt to īpašības, par izejmateriālu izmantojot biogli, kas rodas kā blakusprodukts koģenerācijas stacijās. Ūdens vidē granulas sadalās lēni, jo abas sastāvdaļas ir ūdenī nešķīstošas vielas. Tādēļ augsnes vidē to sadalīšanās notiek fiziskas iedarbības rezultātā, bet gan bioogles, gan sapropeļa noārdīšanās noris lēni (De Gisi et al., 2014).

Piksteres ezera sapropeļa un bioogles granulu bēruma blīvums: pēc granulu veida – cilindriska (iegūtas pēc ekstrūzijas metodes) – $0,31 \pm 0,07$ g/cm^3, apaļas (iegūtas ar noapaļošanas – aglomerācijas metodi) – 0,47 ± 0,18 g/cm^3, apaļas (iegūtas pēc ekstrūzijas metodes) –1,00 ± 0,43 g/cm^3. Granulu tilpummasa ir zema salīdzinājumā ar presētajām biiogļu granulām, kas šobrīd galvenokārt pieejamas tirgū. Izmantotajos materiālos nav konstatēts smago metālu piesārņojums, un no šī aspekta tie uzskatāmi par droši lietojamiem lauksaimniecībā.

3.9. Sapropeļa biokompozītmateriālu mikrobioloģiskās stabilitātes pētījums

Sapropeļa-kaļķa, magnija oksihlorīda kā saistvielas un kaņepju spaļu un šķiedras kā pildvielas, sapropeļa kā saistvielas un bērza koksnes slīpputekļu, koksnes šķiedras kā pildvielas mikrobioloģiskā stabilitāte tika pētīta. Izmantotās pildvielas ir rūpniecības un lauksaimniecības blakusprodukti, kas jāpārstrādā vai jāizmanto atkārtoti. Antimikrobiāla piedeva biokompozītmateriāliem – SIA ALINA produkts ALINA LIFE^{TM} organomāli. Paraugi tika testēti, izmantojot sēnes *Alternaria alternata* un *Cladosporium herbarum,* tās mākslīgi inokulējot uz paraugu virsmas.

Darba gaitā tika noskaidrots, ka uz izmantotajiem materiāliem visbiežāk ir sastopamas *Sordaria, Alternaria* un *Fusarium* ģints sēnes. Atsevišķos gadījumos tika konstatētas arī *Penicillium*, *Acremonium, Paecilomyces, Trichoderma, Mucor* un *Stachybotrys* spp., kas liecina par to, ka substrāti satur pietiekamu mitrumu un barības vielu daudzumu sēņu attīstībai. Labi izteikta sēņu attīstība tika novērota uz sapropeļa-koksnes šķiedras un bērza koksnes slīpputekļu materiāliem, kas ir skaidrojams ar to neitrālo pH 6–7, vai pat nedaudz skābo pH 5, kā arī to, ka koksne dabiski ir piemērots substrāts daudzām sēnēm.

Sēņu attīstība praktiski netika novērota uz kaņepju-kaļķa materiāliem un kaņepju – magnija hlorīda saistvielas, kā arī kaņepju–sapropeļa–kaļķa saistvielas materiāliem. Tas skaidrojams ar kaņepju antimikrobiālo iedarbību (Ali et al., 2012), kā arī kaļķa dabiski augsto pH 9–12, kas negatīvi ietekmē sēņu attīstību.

Pētījums pierādīja, ka paaugstināta sēņu augšanas intensitāte notiek materiālos, kas izgatavoti no koksnes šķiedras, bērza koksnes slīpputekļiem un sapropeļa kā saistvielas. Sēņu sugas, kas aug uz biokompozītmateriāla, ir atkarīgas no materiāla veida, pildvielas, materiāla virsmas un saistvielas.

Sēņu augšana praktiski netika novērota kaņepju-kaļķa un kaņepju-magnija oksihlorīda, kā arī kaņepju-kaļķa-sapropeļa biokompozīmateriāliem. Papildinformāciju par šī pētījuma rezultātiem var atrast (Obuka et al., 2017).

Tika veikti divi eksperimenti, lai noteiktu mikrobioloģisko stabilitāti otrajā testa daļā. Testā 2.1. paraugi tika sagatavoti 70 × 70 × 70 mm kubu veidnēs, koksnes vate tika sagriezta ar līdzīgu virsmas laukumu. Testā 2.2. paraugi tika sagatavoti 40 mm diametrā un 10 mm augstās cilindriskās formās, arī fibrolīts un koksnes vate tika sagatavoti tāpat. Testā 2.2. tika izgatavoti arī papildus paraugi ar pazeminātu saistvielas daudzumu, izmantojot 50% un 20% no pirmajā eksperimentā izmantotās saistvielas daudzuma ar tādu pašu daudzumu kaņepju šķiedru un spaļu, iegūstot paraugus ar mazāku saistvielas daudzumu un mikrobioloģisko aizsardzību.

Analizējot kompozītmateriālu mikrobioloģiskās stabilitātes izmaiņas atkarībā no saistvielas koncentrācijas, var secināt, ka minerālo saistvielu daudzuma samazināšanās samazināja mikrobioloģisko stabilitāti. MOC (magnija oksihlorīda cements-kaņepju), FHL (formulēts hidrauliskais kaļķis-kaņepju) un HL (hidrauliskais kaļķis-kaņepju) biokompozītmateriāliem ar 100% saistvielas koncentrāciju augšanas intensitātes novērtējums ir 0–1,5, ar 50% saistvielas koncentrāciju augšanas intensitātes novērtējums ir 1–3, bet ar 20% tas ir 2,5–4.

Mikrobioloģiskās stabilitātes samazināšanās korelēja ar pH pazemināšanos paraugos. Uz kaļķu bāzes saistvielu kompozītmateriāli (FHL un HL) uzrādīja augstāku mikrobioloģisko stabilitāti nekā MOC kompozītmateriāli, jo 100% saistvielu paraugos netika novērota sēņu augšana, savukārt MOC sēņu augšanas intensitāte atbilda 1.–2. novērtējumam. Ar 50% un 20% sasitvielas daudzumu paraugos šī atšķirība pazuda. To var attiecināt uz pH līmeni paraugos, kas uz kaļķu bāzes paraugiem bija aptuveni 12 pie 100%, bet MOC – 9,76, savukārt saistvielas samazināšanās 50% un 20% paraugos uzrādīja līdzīgu pH un mikrobioloģisko stabilitāti. Mikrobioloģiskās stabilitātes samazināšanās MPC kompozītmateriālos nebija tik izteikta, jo augšanas intensitāte 100% koncentrācijā bija 2–4, bet pie 20% – 3–4. Šāda paaugstināta MPC augšanas intensitāte bija līdzīga eksperimenta pirmā posma rezultātiem un izskaidrojama ar cietinātāja, kālija fosfāta, ietekmi.

Testā 2.1., tika atklāts, ka sēnes pieder pie *Paecilomyces* and *Stachybotrys* pētījumā iekļautajos kompozītmateriālos bija visizplatītākās. Dažos gadījumos, *Penicillium, Acremonium, Cladosporium, Aspergillus, Trichoderma* and *Mucor* tika novēroti arī, parādot, ka substrāti satur pietiekamu mitrumu un barības vielu daudzumu sēņu attīstībai. Lielākā daļa šo sēņu barojas ar celulozi; tāpēc tās var atrast uz celulozes bagātiem materiāliem (Bech-Andersen, 2004; Klamer et al., 2004). *Stachybotrys* barojas arī ar lignīnu, un šī iemesla dēļ tas bieži sastopams uz koksnes un tās izstrādājumiem (Vance et al., 2016), un to sauc arī par melno pelējumu (Ding et al., 2018).

Biokompozītmateriālu, kuru pamatā ir sapropelis, funkcionālo īpašību pielietošanai tika izstrādāti un pielāgoti mikrobioloģiskās stabilitātes testi. Biokompozītmateriāli, ar sapropeli kā saistvielu, uzrāda vienu no augstākajiem mikrobioloģiskās stabilitātes rezultātiem, tas ir, sēnes un citi organismi paraugos netika konstatēti

Sapropeļa, kaļķa un magnija oksihlorīda cementa kompozītmateriālam ir lielāka mikrobioloģiskā pretestība nekā komerciāli pieejamiem materiāliem, kā, piemēram, koksnes vatei; tāpēc tos ir iespējams izmantot būvniecībā līdzīgos apstākļos, t.i., konstrukcijās, kas aizsargātas no ārēja mitruma. Izmantojot vizuālo novērtējuma metodi šajā pētījumā, var iegūt ieskatu pētīto biokompozītmateriālu mikrobioloģiskajā rezistencē un stabilitātē. Paraugiem, kuriem tika pievienoti organomāli, to apaugums bija par 13,8% mazāks, bet tiem, kuriem bija biocīds pievienots, – par 9,1% mazāks, tomēr tika novērota nesaderība ar formulētu hidraulisko kaļķi (20%), magnija oksihlorīda cementu (20%), hidraulisko kaļķi (20%) un magnija fosfātu cementa (100%) saistvielām. Papildinformāciju par šī pētījuma rezultātiem var atrast (Obuka et al., 2021).

SECINĀJUMI

1. Ar organiskām vielām bagāts sapropelis ir perspektīvs dabas resurss, lai tam rastu dažādas pielietošanas iespējas celtniecībā un lauksaimniecībā, izmantojot to, kā saistvielu, kombinējot ar dažādiem ražošanas blakusproduktiem.
2. Izmantojot vietējos resursus, piemēram, sapropeli un ražošanas procesa blakusproduktus, piemēram, bērza koksnes slīputekļus, koksnes šķiedras, kaņepju spaļus un šķiedru, būvniecībā un lauksaimniecībā ir iespējams izstrādāt videi draudzīgus kompozītmateriālus, tos pielāgojot lietošanas vajadzībām.
3. Dabiskā sapropeļa, kas ir biokompozītmateriālu sastāvā, mikrobioloģiskā stabilitāte ir viens no galvenajiem parametriem to pielietošanas nodrošināšanai, un testu skaitā jāietver detalizēts biokomkompozītmateriālu novērtējums attiecībā uz galvenajām mikroorganismu grupām, kas ir sastopamas celtniecības materiālos.
4. Sapropeļa biokompozītmateriālu mehāniskās un siltumvadītspējas īpašības ir līdzīgas ar komerciāliem produktiem, tāpēc biokompozītmateriālus varētu izmantot līdzīgi tiem būvniecības nozarē.
5. Izveidotajiem būvniecības biokompozītmateriāliem ir augsts organisko vielu saturs, tie ir neaizsargāti pret bioloģisko noārdīšanos, tāpēc ir svarīgi pievienot antimikrobiālas piedevas.
6. Mikrobioloģiskās stabilitātes un biodegradācijas testi ir izstrādāti un pielāgoti, lai tos varētu izmantot uz sapropeli balstītu biokompozītmateriālu funkcionālo īpašību testēšanai.

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LIST OF PUBLICATIONS

Paper 1

LOCAL KNOWLEDGE AND RESOURCES AS DRIVING FORCES OF SUSTAINABLE BIOECONOMY

Local Knowledge and Resources as Driving Forces of Sustainable Bioeconomy

Maris Klavins and Vaira Obuka

Abstract A major driving force to promote the idea of sustainable bioeconomy could be local experiences, skills and knowledge in respect to the use of local and natural materials (at first, biomaterials). Sustainable bioeconomy is a concept under development, and as such it requires argumentation and demonstration of efficiency. The aim of this chapter is to study the local knowledge of the Baltic region in terms of the applicability of local biomaterials in production. In the context of bioeconomy, there is an evident need to identify the possibilities for the use of natural and local materials as well as the knowledge to manage these resources. Natural materials of the Baltic region, such as hemp, straw, timber, grain processing products (husk), reeds, moss and flax, will be studied in the historical context and in the use for innovations in modern bioeconomy. In addition, such resources as clay, organic lake sediments (sapropel), peat, sludge, ash, coal and biochar will be evaluated as potential source materials for the manufacture of innovative products. Regarding the use of natural resources, different sectors will be analysed, for example, agriculture and construction. The obtained results will give an insight into the knowledge and traditions of the Baltic region concerning the use of natural materials as a key for sustainability.

Keywords Sustainable development · Bioeconomy · Natural materials
Building materials · Knowledge integration

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1 Introduction

Bioeconomy in our time is considered as one of the key concepts supporting development. In European Union, bioeconomy is an essential element included in the development strategy and supporting sustainable development. The position is firmly stated in the European Commission's "Strategy for a sustainable bioeconomy to ensure smart green growth in Europe" (European Commission 2012) as well as in the "European strategy and action plan towards a sustainable bio-based economy by 2020" (European Commission 2010). As a new concept, the term "bioeconomy" or "bio-based economy" requires some clarification, and discussions on the proper understanding of the content of the term continue.

However, in general, the European Commission's definition can serve as the starting point for understanding the concept: "The term 'Bioeconomy' means an economy using biological resources from the land and sea as well as waste, including food wastes, as inputs to industry and energy production. It also covers the use of bio-based process for sustainable industries" (European Commission 2012). Work on the definition of the concept bioeconomy continues, and there is a consensus that it should have a much broader scope, considering the need in developing future systems of the use of natural resources as well as delivery of societal benefits and public goods (Schmid et al. 2012). This definition reveals not only the planned outcomes of the implementation of the concept of bioeconomy and aims of such implementation but also helps to understand the need to reorganise the existing basic principles of economic development, in particular, to reduce the dependence on fossil resources (including fossil fuels) and their unlimited exploitation, taking into account the quantitative limits of non-renewable resources.

The implementation of the concept of bioeconomy can significantly contribute to reaching the UN Sustainable Development Goals (2015). Bioeconomy is considered to be capable of meeting the major challenges that Europe and the world are facing: (a) increasing populations that must be fed; (b) depletion of natural resources; (c) impacts of ever increasing environmental pressures; and (d) climate change. The goal of bioeconomy is to move towards a more innovative and low-emissions economy, meeting demands for sustainable agriculture and fisheries, food security and the sustainable use of renewable biological resources for industrial purposes. The indirect aims of bioeconomy promotion includes environmental aims (reduction of greenhouse gas emissions, reduction of pollution due to mining of non-renewable resources, reduction of waste streams), new breath in economic developments (creation of new products, markets, jobs) and political aims (reduction of dependence on countries rich in resources, for example, Middle Eastern countries, Russia, China and others). At the same time, bioeconomy will support innovation, improve the quality and safety of food, support the development of rural and special costal communities and improve the efficiency of agricultural, food and general industrial production and distribution systems. Bioeconomy can promote building of low-carbon societies and thus achieve far-reaching aims.

Development of bioeconomy is urgent for EU member States with often limited national availability of non-renewable resources and to a similar extent also for developing countries. The widest positive response to the need to implement this concept in the reorganisation of economic production this concept is received in EU and Japan (Priefer et al. 2017). Several EU Member States (e.g., Latvia) have defined bioeconomy as one of the directions of national development and as part of smart specialisation plans.

The EU Bioeconomy Action Plan is based on three pillars (European Commission 2012):

1. Strengthening of research in biosciences and life sciences and supporting innovations by providing significant EU and national funding;
2. Stakeholders' involvement and development of synergies between different sectors of economies and society;
3. Enhancement of markets and supporting competitive activities as well as improving resource efficiency.

Largely, developments in bioeconomy are associated with research progress, focusing on agricultural and food technologies, biomass processing and biotechnology, while omitting the need to achieve noticeable progress in transforming waste streams into valuables, recovery of essential elements (for example, phosphorus compounds) and other directions of activities. On the one hand, the existing progress is largely based on research achievements: major progress in biosciences, development of new technologies and their implementation. Further aims are related to the development of innovation capacities. However, traditional knowledge and historical approaches relevant in pre-industrial era can also be a source of new knowledge.

In the context of bioeconomy, there is an evident need to identify the possibilities for the use of natural and local materials as well as the knowledge to manage these resources. The aim of this paper is to study the local knowledge of the Baltic region in terms of the applicability of local biomaterials for production in the context of developments in the field of bioeconomy. Natural materials of the Baltic region, such as hemp, straw, timber, grain processing products (husk), reeds, moss and flax, will be studied in the historical context and in the use for innovations in modern bioeconomy.

1. Natural and traditional use of biomaterials for bioeconomy

From a historical perspective, natural materials are the only ones available for humans. A well-known example of the use of natural materials is medicine, where natural, biologically active substances are used as drugs. More than half of the existing active substances on the market are either directly obtained from plants and animals or inspired by nature. One of the major branches in current biopharmacy—phytochemistry—is engaged in search of new active substances by analysing plants and their composition (Shah 2009). Not only active, isolated substances but also extracts of plants and animal source materials are directly used in healthcare, cosmetics and other applications. Considering the size of the biopharmaceutical market and its relation to large-scale chemical industry, the significance of natural substances and their applications are remarkable, and this segment of industry constantly grows and also makes way into bioeconomy. Scientific research in this field plays an important role. In addition, it is important to emphasize that cooperation between the state, business and academia plays a key role in developing of well-founded, high value-added products and technologies.Another major field of revival of traditional knowledge to support the development of bioeconomy is agriculture. Even most advanced agricultural technologies are largely relying on traditional knowledge and experiences and historical traditions. In these days, traditional knowledge is more and more often considered as a source of knowledge to advance contemporary agriculture globally, to support the development of new technologies in agriculture and to disseminate the traditional, local, knowledge globally. An example of such approach is the use of biochar to improve fertility of soils and reclaim poor, degraded soils (Lehmann and Joseph 2012). The origins of the use of biochar are in the traditional, native South American cultures. Biochar, a product of low-temperature pyrolysis of waste biomass, can slow down carbon turnover and thus enhance carbon sequestration in soils, restore ecosystem services and increase the fertility (and thus also productivity) of the soil. Further, biochar increases the water and nutrient holding capacity of the soil and is therefore beneficial for stressed soils. At the same time, biochar in soils is much more refractory in respect to mineralisation than conventional compost and can aid in the utilisation of organic wastes by returning the organic material and fertilisers to production as well as to the carbon cycle. So, the use of biochar is a telling example of a sustainable approach where traditional knowledge helps boosting bioeconomy.

Next, building materials are also examplary in this respect. The use of natural and local materials as well as traditional approaches is embodied in the concept of vernacular architecture and materials and their application in the construction industry. Vernacular materials can be considered as an alternative for sustainable construction, as they have significantly lower environmental impacts in comparison to industrially-produced ones (Oliver 2006; Sassi 2006). One of the main challenges for vernacular building is related to energy savings during the production of building materials, as the traditional construction industry is one of the largest energy-consuming sectors of the economy, being responsible for almost one third of all carbon emissions (Urge-Vorsatz et al. 2007). The use of natural materials, avoiding energy-intensive technologies, can help significantly reduce the greenhouse gas emissions.

2. Natural materials for bioeconomy: use of sapropel

A prospective material with a widely diverse application potential is the sedimentary deposit in waterbodies—sapropel. Sapropel is formed due to sedimentation of organic substances produced by living organisms, and thus a major source of sapropel organic matter are the decay products of algae, macrophytes as well as planktonic organisms (Leonova et al. 2011; Liužinas et al. 2005). At the same time, the contribution of mineral substances, like alumosilicates, silica and iron oxides entering from the waterbody basin is also significant. Sapropel occurs all over the world, but most intensive accumulation takes place in temperate climatic zones in Asia and Europe. Largest amounts of sapropel are found in Russia and also in the Baltic countries. Just in Latvia, the estimated sapropel resources are about 2 billion m^3. On the one hand, considering the permanently ongoing sedimentation processes in waterbodies, sapropel can be considerd as a renewable resource, especially in eutrophic waterbodies. On other hand, one of the key steps of waterbody recultivation is the removal of sediment mass. Thus, the extraction of sapropel is essential in achieving the recovery aims of eutrophic waterbodies, and sapropel mining is a means to restore the quality of water. In terms of the sapropel properties application, significant studies have been carried out in Latvia (Stankevia et al. 2016; Stankeviča 2012).

The main components of sapropel are organic materials, inorganic (mineral) substances and living organisms. The colour of sapropel varies from black to brownish, dark green to even purple, and the colour indicates the humification degree of organic material (humic substances are black to dark brown) as well as the presence of plant pigments (chlorophyll remaims can make sapropel greenish). The organic substances in sapropel are most valuable for the majority of applications, and their amount varies in a wide range—from 15% up to 90% and more (Stankeviča and Kļaviņš 2013). The organic matter of sapropel consists of C 50.8–59.2, O 27.9–35.2, H 6.7–7.4, N 4.7–5.4 and S 0.6–1.4%. Depending on the formation conditions, sapropel can contain groups of organic substances, such as humic substances 5.1–61.9%, hemicellulose 9.8–52.5%, aminoacids 9.8–17.8%, celulose 0.4–6.0%, bitumens and waxes 6.8–15.2%. Sapropel also contains many trace elements: Si, Al, Fe, Ca, Be, Sr, Mg, Ti, Na, K, V, Cr, Mi, Ag, Mo, Ga, Pb, As, Sn, P, S, Na, Sc, Ni, As, Rb, Y, V, I, Zr, Nb, Mo, Cd, Cs, Ba, La, Ce, Hf and Th (Leonova et al. 2011).

One of the most important properties of moist sapropel is its colloidal suspended phase structure, which determines the ability of the organic colloidal particles of sapropel to absorb large quantities of water. So, it has a high moisture absorbtion capacity—from 70 to 97%—and a low filtration rate (Liužinas et al. 2005). The relative humidity of sapropel is associated with organic matter, and its value increases with the content of organic matter.

Useful characteristics of organically rich lake sediments are their adhesive properties and water repellence (Balčiūnas et al. 2016; Obuka et al. 2016). The adhesive capacity of sapropel is due to its components of animal and vegetable residues. Green algae shells consist mostly of cellulose, which has weak decomposing properties. Organic sapropel, whose organic matter proportion is formed by green algae, is rich in cellulose but poor in minerals, as it consists of ash and low-level humic substances formed mainly by peat meristem. It should be noted that the high content of organic nitrogen, including free amino acids, contribute to the adhesive properties of sapropel (Balčiūnas et al. 2016; Obuka et al. 2016).

The organic adhesion capacity of lake sediments also affects the composition of humic molecule structure and concentration. This contributes to the emergence of strong links between the molecules of the material at the time of creation. The molecules of humic substances remain flexible, and their presence improve the durability and strength of the material. Therefore, with the above mentioned properties, it is expedient to use sapropel as an adhesive in various ecological construction and plaster/finishing materials.

The adhesive properties of sapropel are practicable in the production of composite materials for construction industry, interior design objects with both cold compaction techniques and hot–glue press at elevated temperature and pressure (Zach et al. 2013; Mounika et al. 2012). Thus, a prospective area of application of sapropel includes creation of different composites, for example, sapropel—wood fibre, sapropel—hemp shives and sapropel—wood sanding dust, sapropel—flax fibre and moss In these composite materials sapropel is used as a binder.

Sapropel samples have different origins (lake) and different moisture (%), organic matter (%) and carbonate (%) content. For example, a sapropel sample from Lake Padelis contains 35.57% carbonates and 85.97% moisture, its colour is pale gray-pink and density −1.24 g/cm^3. A sapropel sample from Lake Pilvelis, in turn, is dark greenish-brown, with homogeneous, jelly-like structure and a density of 1.10 g/cm^3. A sapropel sample from Lake Veveru has a high moisture level −97.66%, low density −1.08 g/cm^3, and its organic matter content reaches 86.25%.

The thermal properties of composite materials (sapropel—wood sanding dust and 'Aerosil'; wood sanding dust; wood fibre; hemp shives) was analysed. (Obuka et al. 2015).The silica product Aerosil (colloidal silicon dioxide), is a thickening agent, used as a filler for composite materials. It creates a smooth mixture, which is often used in combination with other fillers. Particular attention was paid to shrinkage cracks that affected the quality of material for further tests. In this case, gypsum was used to fill the cracks (sapropel—wood sanding dust and 'Aerosil'), so as to make the material fit for the thermal conductivity test. The measurement results also indicate a higher thermal conductivity of the material, that is, 0.080 W/m*K. Such a high result can be explained by the fact that not all of the cracks were sufficiently filled. In addition, gypsum may have influenced the result, as its thermal conductivity is around 0.18 W/m*K. The thermal conductivity test of sapropel—filler composite was carried out with variable types of sapropel and fillers. The results obtained are shown in Table 1.

Table 1 The thermal conductivity of studied materials

Material: binder-filler	Density, kg/m^3	Thermal conductivity, W/m*K
Sample 1,3—hemp shives	191	0.063
Sample 1,2—hemp shives	200	0.059
Sample 3—wood fibre	153	0.055
Sample 3—wood fibre	202	0.060
Sample 3—wood sanding dust	214	0.061
Sample 3—wood sanding dust—'Aerosil'	376	0.080

Fig. 1 Sample 1,3—hemp shives (authors photo)

According to the results obtained, the composite made of sapropel sample 3—wood fibre (density 153 kg/m^3) has the superior results (Fig. 1). Visually, this material differs from the composite of sapropel sample 3—wood fibre (Fig. 2) that has a density of 202 kg/m^3, because it has a denser structure and comparatively better resistance to deformation. In any case, the results indicate that these composites have similar characteristics and thus have a similar potential of use. The thermal conductivity of air-dried composites is relatively low because of the organic origin of the raw materials, detailed and mixed cellural structure and homogeneous fibres with interconnected and open pores.

Since the composites of sapropel—hemp shives, due to different sizes of particles, have a heterogenous structure with cavities and uneven composition with weaker inclusions, they deform more quickly. However, the composite (density 376 kg/m^3) made of wood sanding dust and 'Aerosil' with sapropel sample 3 binder and the composite made of sapropel sample 3 and wood sanding dust (Fig. 3) with density 214 kg/m^3 both formed shrinkage cracks during drying, indicating the inferiority of technology. The structure of the composite is made of densely grouped wood sanding dust particles mixed with a sapropel binder.

In a study of sapropel—sawdust and peat—sawdust composite materials (Obuka et al. 2013) the obtained thermal conductivity measurement results were 0.067 W/m*K and 0.060 W/m*K. The study considered the freezing cycles and moisture of tested materials. It shows that the thermal conductivity coefficient of the sapropel—sawdust composite becomes lower after freezing cycles. This is explained by the fact that the refrigeration process causes moisture loss and drying of the plate. This causes composite pores to fill with air, which is known to be the best heat insulation material. It is explained in literature that humidity in the

Fig. 2 Sample 3—wood fibre (authors photo)

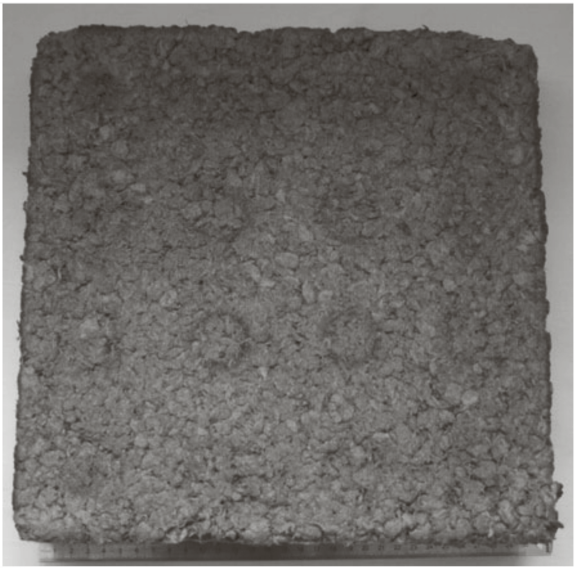
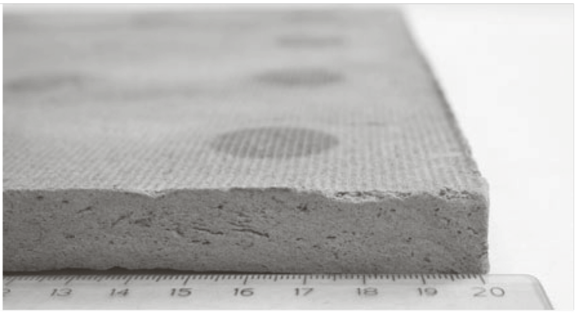


Fig. 3 Sample 3—wood sanding dust (authors photo)



composite reaches the wood fibre saturation point, and so the mechanical properties of the material do not deteriorate. If a composite material is resistant to freezing cycles, such material is usable in North European conditions. The thermal conductivity coefficient for the sapropel—sawdust composite material is 0.050–0.060 W/m*K and for the peat—sawdust composite material—0.055–0.064 W/m*K. The obtained results are similar to composite materials made of sapropel—wood sanding dust and 'Aerosil'; wood sanding dust; wood fibre; hemp shives (Fig. 4).

In Binici et al. (2014) study of the insulation materials made from sunflower stems, textiles and agricultural by-products as fillers, epoxy resin was used as a binder for better fibre strength and binding efficiency. An average thermal conductivity coefficient of 0.1642 W/m*K was obtained. However, the thermal conductivity coefficient of a sample with less epoxy resin added and made only from sunflower stems and sunflower stem fibres reached 0.0728 W/m*K


Fig. 4 Sample 1,2—hemp shives (authors photo)

(Binici et al. 2014). In a study of bamboo fibre and polyester composite, Mounika et al. (2012) conclude that the thermal conductivity coefficient decreases with an increase in the proportion of fibre. The thermal conductivity coefficient ranged from 0.185 to 0.196 W/m*K (Binici et al. 2014). Literature on materials based on natural fibres from renewable raw material sources (flax, hemp, wood, bamboo, sheep wool) shows very good sound and thermal insulation properties. This is due to the low density of the materials and natural character of input fibres ("airy", lightweight material).

In a study of lime-hemp concrete, a variety of binders were compared, including metakaolin obtained by burning kaolin clay (40% by mass) at 800 °C and dolomitic lime (60% by mass) produced by Saulkalne Ltd. Eight different types of hemp shives were used as fillers. The obtained results show that the lime-hemp concrete material has a density of 312–337 kg/m^3, and its thermal conductivity is more diverse and ranges from 0.0718 to 0.0778 W/m*K (Sinka et al. 2015).

In a study of the use of agricultural waste in sustainable construction materials, Madurwar et al. compared measurements of insulation materials of different origins. The results ranged from 0.046 to 0.056 W/m*K for rice husks and from 0.118 to 0.240 W/m*K for oil palm leaves. The authors concluded that there are significant similarities between the corn cob and extruded polystyrene (XPS) materials in terms of microstructure and chemical composition. Materials made from rice husk and coconut coir reached the best results (Shea et al. 2012).

The results obtainted for compressive deformation (Fig. 5) show that the composites with a filler of birchwood sanding dust and 'Aerosil' have good results. The compressive deformation results vary from 0.724 MPa for the sapropel sample 3—wood sanding dust composite to 0.674 MPa for sapropel sample 3—wood

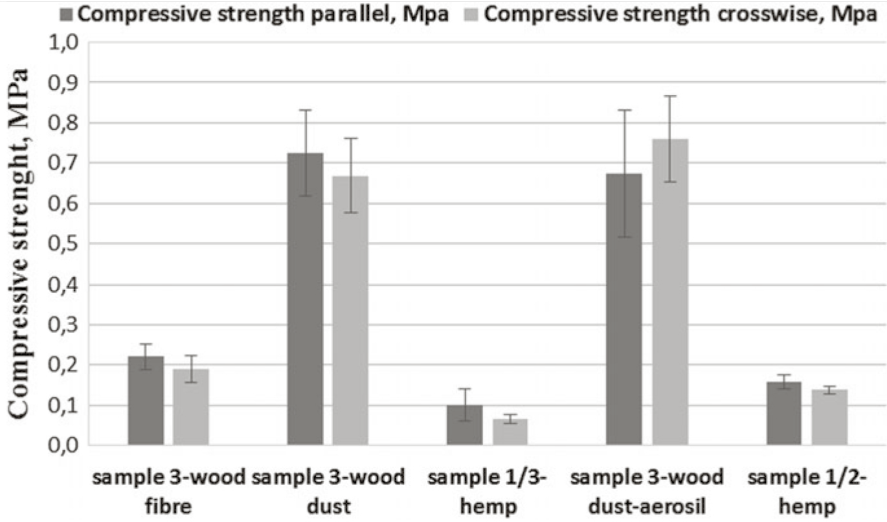


Fig. 5 Compressive strength of different composites, parallel and crosswise

sanding dust and 'Aerosil' as a filler, while the compressive strength crosswise shows 0.669 and 0.760 MPa respectively.

In compressive deformation, the composites made from hemp shives and wood fibre as a filler obtain a rate of 0.221 MPa for sapropel sample 3—wood fibre and hemp shives materials 0.101 (Sample 1,3—hemp shives) and 0.159 MPa (Sample 1,2—hemp shives), while the compressive strength crosswise measurement shows 0.191, 0.066 and 0.138 MPa respectively. These results are relatively lower due to lower intensity of filler and binder bonding. The mixing of binder with filler is more complex, because it is more difficult for the binder to enter the filler's structure, as the particles of the former are larger.

This was observed with the wood fibre composite and sample 3 as the binder. However, birch wood sanding dust and 'Aerosil' binder, consisting of dust particles, mixes with filler evenly, entering the structure of the filler. The structure of the material is smoother, increasing the mechanical resistance of the composite. The sample preparation techniques affect the compressive strength results: the preceding crushing of the material disrupts its structure. The use of various fillers and binders affects the physical and mechanical properties of composite materials; so, the hidrophysical and mechanical properties of composites can be changed by changing the types of fillers and binders.

Compared to the compressive strength results, the flexural deformation strength results (Fig. 6) show that the material strength is relatively lower. This can be seen from the results: for example, the samples made from hemp shives show lower results. The reason could be the granulometric composition, as there are many large shives that create voids and uneven composition with weaker inclusions, resulting in a faster deformation of the samples. In the process of making the wood

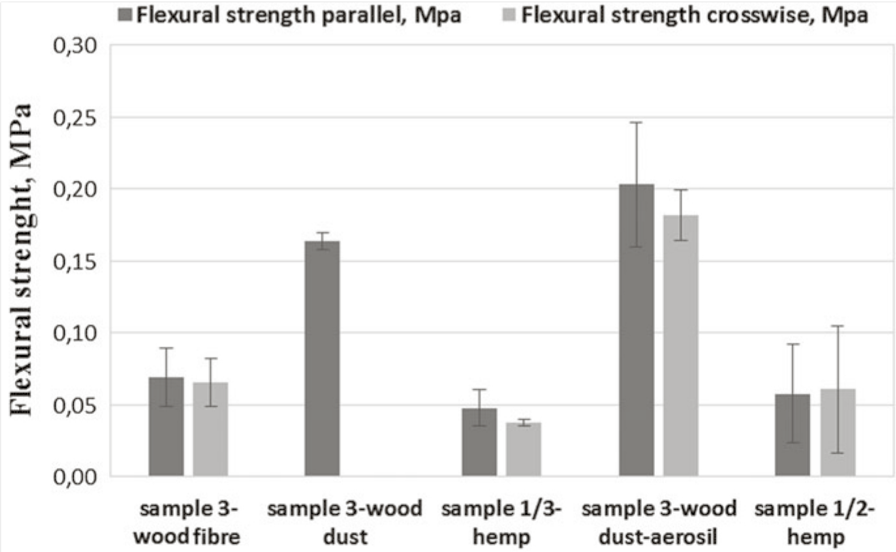


Fig. 6 Flexural strengths of different composites, parallel and crosswise

fibre—sapropel composite, the mixing of the binder with the filler is more complex, because it is more difficult for the binder to enter the structure of the filler forming tangles and air gaps. Voids remain that reduce the mechanical strength.

In flexural deformation strength, the composites made from hemp shives and wood sanding dust as a filler obtain a rate of 0.069 MPa for sapropel sample 3—wood fibre and 0.164 MPa (sapropel sample 3—wood sanding dust) and 0.203 MPa (sapropel sample 3—wood sanding dust—'Aerosil'), while the compressive strength crosswise shows 0.066 MPa for sapropel sample 3—wood fibre and 0.182 MPa for sapropel sample 3—wood sanding dust—'Aerosil' respectively. These results are relatively lower due to lower intensity of the filler and binder bonding. The mixing of the binder with the filler is more complex, because it is more difficult for the binder to enter the structure of the filler, as the particles of the former are larger and longer when using the composite of sample 1,2 sapropel. The reason for this could be the higher adhesive capacity and lower moisture content of sapropel.

In a study of the composite material of sapropel and peat sawdust, similar composites were created, and the results show that the filler and binder types and the preparation technology options change the compressive and flexural deformation strengths of the composite. According to the indicated results, the average compressive resistance was 0.03 MPa, and the compressive resistance of the peat—sawdust composite (activated peat binder) also was 0.3 MPa.

Comparing the results of this work with those of the research of sapropel—concrete, the materials made of wood fibre and hemp shives have lower rates. During preparation, 1% NaOH solution was added. The results obtained in the studies showed the compressive strength of 0.55 MPa for absolutely dry composite materials and 0.56 MPa for air-dried composite materials. In a study of lime-hemp concrete, a variety of binders, including metakaolin and dolomitic lime, were compared. The obtained results show the compressive strength range from 0.140 to 0.337 MPa and the flexural strength range from 0.021 to 0.059 MPa for different lime-hemp concrete materials (Sinka et al. 2015).

In a study of a composite material made from agricultural by-products, it was concluded that durian peel and coconut-fiber composites yield the highest strength indicators: from 2.9 to 36 MPa. The results of a study of a composite of sunflower stems and epoxy resin, in turn, show the compressive strength test scores of 0.283–0.312 MPa and the flexural deformation strength scores from 0.06 to 0.09 MPa.

Discussed results of composite materials made of sapropel as a binder and different filler materials (Obuka et al. 2016), shows competitive outcome of basic properties of composite materials. Results represent enough high compressive strength, thermal conductivity for possible insulation and construction materials.

Such kind of materials made of local and natural resources are significant research topic to discuss. Strengthening of research in sustainable, environmentally friendly materials and local resources field as well supporting innovations, is important to continue and implement in industry throught bioeconomy instruments. As mentioned before from a historical perspective, natural and local materials are the only ones available for humans and it is needful to find best practice for creating innovative, high added value products using local knowledge. In respect of decreasing the dependence on fossil resources (including fossil fuels) and creating new jobs, local arrangements of entrepeneurship in depleting remote rural areas.

2 Conclusions

From natural materials and local resources, such as sapropel, and industrial by-products, such as birch wood sanding dust and fibre and hemp shives, sawdust it is possible to develop environmentally friendly composite materials for construction for various needs of utilisation. The particle granulometric composition, surface area and other characteristics of the filler have an effect on the binding with sapropel as a binder. Composite materials are characterised by a relatively high mechanical strength, shape-holding ability and easily amenable texture imprint. One of the most important properties of these materials in today's application scope is the ability to sequester CO_2, as both the binder and the filler are bio-based. The mechanical and thermal properties of bio-based materials were evaluated and compared to similar materials. The mechanical and thermal properties of sapropel-based composites were similar to those of synthetic as well as mineral materials, suggesting that sapropel composites could have similar use in the construction industry: as a self-bearing wall thermal insulation material that works together with the structural timber frame. As the sapropel-based materials have high organic content, they are vulnerable to biodegradation; therefore, antimicrobial additives are significant to add.

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Paper 2

SAPROPEL AND LIME AS BINDERS FOR DEVELOPMENT OF COMPOSITE MATERIALS

SAPROPEL AND LIME AS BINDERS FOR DEVELOPMENT OF COMPOSITE MATERIALS

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ABSTRACT: The aim of this paper is to study possibilities to obtain composite materials using organic rich lake sediments (further – sapropel) and lime as binders and hemp shives, wood fibre, and wood sanding dust as fillers. The mechanical and thermal properties of the obtained composite materials are investigated and compared to similar composites, such as lime-hemp concrete (LHC) and magnesium oxychloride hemp composite (MHC). Because of the high amount of organic content these materials are prone to biodegradation, therefore the materials were coated with ALINA LIFE ™ organoclay additive that helps to extend product life-time, reducing rate of biodegradation. The effect of the coating on the resistance against fungi *Alternaria alternata* and *Cladosporiumherbarum* was investigated in two conditions: before and after experimental accelerated ageing of materials in climate camera. Results indicated that the composites made of sapropel and lime have similar mechanical properties as LHC and MHC: compressive strength of 0.77 MPa for sapropel-lime binder compared to 0.90 MPa for LHC and 1.12 MPa for MHC. As organoclay additive provided higher resistance to biodegradation, sapropel-lime composites have shown sufficient amount of positive properties to be considered for application in construction material industry and as an object for further research.
Keywords: biodegradability, biomass, biobased products, hemp, sapropel, hydraulic lime

1 INTRODUCTION

Development of ecological materials and their use is increasing in various sectors of the economy such as construction sector and agriculture. Construction material industry is one of the biggest emitters of CO_2 [1] together with energy produced for building heating and ventilation needs due to poor insulation [2], therefore the both sectors need ecological composite materials with good thermal insulation capabilities.

Use of environmentally friendly materials does not cause additional pollution in the environment, and the use of raw materials is promoting energy efficiency during the production. After the end of lifetime, ecological materials decompose relatively quickly and can be fully recycled. Development of such materials is necessary because environmentally sound handling of existing resources is an important issue. By-products of agriculture and wood industry (straw, hemp shives, wood waste, etc.) can be used for production of new ecological materials. It is important to evaluate the opportunities and efficiency the use of natural resources and industry by-products to create innovative products with high added value.

Sapropel is a partially renewable geological resource, it is a fine-grained organic-rich sediment or sedimentary rock, and it refers to lacustrine environment inland waters [42] [3]. Sapropel with high content of organic matter can be applied in agriculture and horticulture as a soil fertilizer and soil amendment, as well as it has a potential to be used in building industry as a binder or adhesive substance [4] [5] [40]. Organic-rich lake sediment – sapropel – is a valuable and available resource of natural origin. In Latvia, it is estimated that the reserves of sapropel in inland waters is around 700-800 million m^3, furthermore 1.5 billion m^3 underlie the peat layer, which makes 2 billion m^3 in total. Sapropel sediments have adhesive properties with high ability to bind as well as shape holding ability and plasticity [4], therefore in current study it was used as a binder. As its use as a binder does not require heating at high temperatures, it has low embodied energy and thus low CO_2 footprint, making it very appropriate for use in ecological composite insulation materials.

To achieve good ecological credentials for the composite material, a filler that has low contribution to greenhouse gas (GHG) emissions was also used. Locally produced organic materials and by-products were used as filler material - hemp shives, wood sanding dust and wood fiber. Hemp shives is an industrial by-product from hemp fiber production, which is used to produce lime-hemp concrete (LHC), a new type of building insulation material that is being used more widely in recent years due to its low thermal conductivity and high thermal capacity [6], high moisture transfer and moisture buffering capacity [7] [8] and good sound insulation capabilities [9]. Wood-based fillers have also been used for insulation materials as there is constant search for use of shavings and dust from wood product [10] and also have shown good thermal insulation capabilities [11] [12].

Both types of filler have excellent properties regarding GHG emissions - as they are organic, they have absorbed and sequestered CO_2 in them during their growth. These negative CO_2 emissions affect the whole composite - making it CO_2 neutral or even negative as in case of LHC [13] [14].

Traditionally lime-based binders are used with hemp filler, as lime enables the material to have excellent hygrothermal properties, as well as offers some protection from biodegradation due to high alkalinity. On the other hand, lime is responsible for the largest share of CO_2 emissions in LHC composites [13] [14], thus a binder that could reduce these emissions is necessary.

Two kinds of alternative binders were used in this research - first one is sapropel, second one is magnesium oxychloride cement (MOC). MOC, also known as Sorel cement, was introduced shortly after Portland cement [15] although only recently it is starting to regain its popularity due to its high early strength and compatibility with organic aggregates [16]. It has been credited to have superior environmental characteristics when compared to lime binders as magnesium has lower calcination temperature than lime [16] although its effect on biocomposite biodegradation resistance should be evaluated, as magnesium binders have lower pH levels than lime binders.

However, often in their lifetime natural materials are affected by various microorganisms. Most common biodegradation does fungi, due to high tolerance against moisture, pH and temperature fluctuations. Therefore, all over the world people face unwanted problems of issues made because of fungi [17] [18] [19] [20].

Biodegradation or microbial material degradation is of a great importance in human life and the natural life cycle. If one of the aspects is the creation of easily recyclable materials, then the development of enduring anti-microbial/resistant materials also has a big importance. Fungi are one of the biggest groups of organisms involved in biodegradation [17]. Although for thousands of years fungi have produced mycotoxins, their impact on the human health and their economic potentials have only been pertinent in last few decades [20]. Indeed, microscopic fungi are the most common microorganisms found in dwellings. This is again due to fungi high tolerance to relative humidity, fluctuations of temperature, availability of nutrients and other aspects. Furthermore, the mold fungi are particularly resistant to low pH and relatively humidity values, which greatly complicates the fight against them. Fungi-produced enzymes are capable of destroying organic substances, thus causing damage to both functional and visual attractiveness of the property [19] [20]. Approximately from 15% to 40% of population in Northern Europe and the America is exposed to a variety of indoor fungal developments, which lowers the quality of life in those dwellings. Since an average European spends 1.6 hours in fresh air per day, the living space air quality is extremely important. Fungi development primarily takes place in uninhabited buildings and buildings with high humidity. It is estimated that only in the UK more than 400 million pounds are spent every year to prevent fungi caused damage in buildings [21] [24].

Humidity is one of the most important fungal development contributing factors. Any water vapour in domestic activities, such as cooking and taking a shower, rises level of relative humidity in the room, which can lead to the accumulation of condensate on different surfaces. Not only furniture is at risk but also windows and outer walls of buildings. About 80% of evidence on development of fungi are found in timber, paper and plaster materials [21].

In this study composite materials were coated with ALINA organoclay additive developed at LLC ALINA. This product group is a new type of additives for building finishing materials preventing the negative impact of biodegradation, thus prolonging durability of materials and eliminating usage of biocides for material protection. Such additives are very important for highly organic based materials as sapropel-hemp, sapropel-wood fibre, wood dust composites. Clay is one of the most common sedimentary rocks in Latvia as well as worldwide. The use of clay application is very wide, it is used in construction, cosmetics and other production sectors, but only a few clay types have natural anti-microbial activity [24]. Therefore, research involving new organoclay additives is important because it would not only enhance the application of clay in the areas, where it is already used, but would help to discover new aspects of its use.

Cladosporiumherbarum and *Alternaria alternata* are saprophytic fungi. These species are very common and often contaminate air. In natural conditions, they are found in many substrates – in composites, plant debris, soil, in wooden materials and they are also plant pathogens. In indoor conditions they develop on foodstuffs, textiles, walls and elsewhere [25] [26].

Fungi from both *Cladosporium* and *Alternaria genera* are allergic agents. Since they are able to grow on the walls, their elimination is important not only from a medical point of view, but also from the point of view of preservation of cultural heritage. The major fungal growth is observed in buildings with high relative humidity.

The aim of this study was to explore options for composite material production using sapropel and lime as binders and hemp, wood fiber, wood sanding dust as fillers, and to determine the optimal properties, as well as to characterize properties of the obtained composite material.

2 MATERIALS AND METHODS

The following designation for materials and some methods, such as ageing in climate chamber and evaluation of intensity of growth were used in this research (Table 1).

Table I: Designation of used materials and methods

Designation	
Sapropel	S
Sapropel-lime-hemp composite	SLHC
Lime-hemp composite	LHC
Magnesium-hemp composite	MHC
Sapropel-wood fibre	SWF
Sapropel-wood dust	SWD
Ageing in climate chamber	CH
ALINA organoclay additive coating	AO
Magnesium oxychloride coating	MH
Lime binder coating	LH
Alternaria alternata	A
Cladosporiumherbarum	C
Control sample	K
Evaluation/Intensity of growth	E

2.1 Filler

Hemp shives ("Bialobrezeskie") were taken from "Zalers" Ltd. Hemp shive mixture includes 1.7% fibre and 2.2% dust by weight, the rest is shives with different sizes – 3.7% are in length 10-20 mm, 92.0% – 0.63-10 mm, 0.5% are longer than 20 mm. Their bulk density is 108.36 kg/m^3, moisture content 11.75% and thermal conductivity is 0.058 W/m*K.

Also birch wood sanding dust (wood dust) and fiber (wood fibers) were selected as fillers for production of composite materials. Birch wood sanding dust and fibre are industrial by-products from JSC "Latvijasfinieris" – a plywood manufacturing company. Birch wood fibre is up to 15 mm long with the diameter up to 0.1 mm.

2.2 Binder

One of the binders used in this research is magnesium oxychloride cement (MOC) which requires highly reactive magnesium oxide. The caustic magnesium oxide, supplied by the Austrian company RHI AG Ltd, CCM RKMH-F, was with MgO content at least 73% and low calcination temperature (750-800°C). Magnesium chloride for MOC used is magnesium chloride hexahydrate that is produced in Germany. The used hydraulic lime (HL) is formulated hydraulic lime FHL5. In this research, organic rich freshwater sediments (further – sapropel) were used. Sapropel sediments were sampled from lake located in Jekabpils District, Latgale Region (Latvia).

2.3 Sapropel properties

Loss on ignition (LOI) method [27] was applied in order to estimate moisture content, content of carbonate matter, organic matter, mineral matter and ash content in sapropel. Firstly, the moisture content in sediments was determined after drying at 105°C for 12 h. Secondly, the content of organic matter, ash and carbonates wasanalyzed by ashing samples sequentially at 550°C for 4 h and at 900°C for 2 h [28] [27].

The composition of biological samples (sapropel) was determined with a light microscope, counting and expressing as a percentage of organic matter content by groups in all identified groups of organic residues. Sapropel type, class, grade and application possibilities were identified using sapropel type classification [29]. Detection of pH and electric conductivity (EC) for sapropel was done with potentiometric analysis methods. Measurements were done for 100 mL supernatants made of 5g air-dried sample with HANNA pH 213 pH-meter [30] and HANNA HI 9932 conductivity meter [31]. Bulk density for non-homogenised (Non-H) and homogenised (H) sapropel were calculated and expressed as sample mass in grams divided with sample volume in cubic centimetres [32].

2.4 Sample preparation, mixtures and curing

The mixing of the samples was done manually. Mixtures of the samples are listed in Table 2. Mixtures of the LHC, SLHC and MHC have two different target densities - 300 and 500 kg/m^3 in order to test variation of properties at different densities.

To mix the LHC (1,2) samples and SLHC (1,2) samples, at first shives were mixed with lime and then water (for LHC) or sapropel (for SLHC) were added. The shives:water or sapropel ratio is 1:2.5 (samples 1) and 1:5 (samples 2). Added water or sapropel:lime ratio in composite materials was 1:1.

The SWD and SWF were made by mixing sapropel-filler mass. It was done manually until homogeneous mixture has been obtained at the stage where filler was fully covered with binder. Sapropel was mechanically treated by mixing together with electrical hand mixer until homogeneous material has been formed. Organoclay additive ALINA was added to the mass and treated by mixing until smooth mass has been formed. Metal mold (dimension of 30×30cm) with adjustable height was used for composite material curing. The mixture of raw materials was put in mold. Sapropel-filler samples were cured at the temperature of 80°C for 72 hours.

For the MHC samples, at first shives were premixed with water, for hemp shives not to deprive MOC binder of the water because of its high hygroscopic nature. The shives: water ratio was 1:1.25. MgO was added in dry form, mixed with wet shives, afterwards $MgCl_2$ brine was added and blended together, MgO:$MgCl_2$ ratio was 1:0.67.

After mixing the samples were laid in molds hand compressing every ⅓ of the height. Samples were demolded after 2 days and afterwards were cured for 28 days in laboratory conditions (40±10 %RH and 20±2°C) until testing.

Table II: Mixtures of the samples

Type	*Filler type*	*Filler*	*Water for filler*	*S*	*HL*	*MgO*	*$MgCl_2$ brine 1:1*	*Water for binder*
SLHC(1)	hemp shives	1	-	2.5	2.5	-	-	-
SLHC(2)	hemp shives	1	-	5	5	-	-	-
LHC(1)	hemp shives	1	-	2.5	2.5	-	-	-
LHC(2)	hemp shives	1	-	5	5	-	-	-
MHC(1)	hemp shives	1	1.25	-	-	0.9	0.6	-
MHC(2)	hemp shives	1	1.25	-	-	2	1.33	-
SWF	wood fiber	1	-	6	-	-	-	-
SWD	wood dust	1	-	6	-	-	-	-

2.4.1 Sample preparation for biodegradation tests

Organoclay additive LLC ALINA was added to materials in 4% concentration of dry mass (wood fibre or dust in SWD/SWF). In addition, organoclay additive was added to materials in 4% concentration of added lime or MOC in case of SLHC, LHC, MHC composite materials as a coating. Among the material samples, there were three that were coated with ALINA, three that were coated with lime and three without any coating.

2.5 Compressive strength and thermal conductivity

As the samples contain filler that has high elasticity and relatively low binder amount, the maximum compressive strength cannot be measured at rupture. Instead, a compressive strength at 10% deformation is measured, according to EN 826 guidelines, similar as for thermal insulation materials. The tests were performed on Zwick Z100 universal testing machine applying the force at a 10 mm/min speed.

Thermal conductivity of the samples was tested on Laser Comp FOX600 heat flow meter in accordance to the EN 12667 guidelines. Temperatures of the plates were set at 0°C at the upper and 20°C at the lower plate.

2.6 Climate chamber

Ageing in climate chamber was done by exposing the samples to 30 freeze-thaw cycles, with temperature amplitude of -20°C (3 hours) to +20°C (1 hour), which corresponds to EN 12390-9.

Climate chamber ageing test comprised of thirty cycles in of two weeks. After the test samples were inspected visually and no cracked or crumbled material was detected. In total 197 material samples were tested.

2.7 Artificial inoculation with fungi/biodegradation resistance test

Comparison of microbiological resistance of sapropel-based composite materials, LHC and MHC was carried out. Artificial infection with fungi *Alternaria alternata* MSCL 280 and *Cladosporiumherbarum* MSCL 258 was used in biodegradation resistance tests before and after experimental accelerated ageing of materials in climate camera. Fungi were grown in Petri dishes with Malt extract agar for 7 days at room temperature and afterwards fungal spores and mycelial fragments were scraped off the agar surface and vortexed to make a suspension with optical density OD_{545} 0.16. Triplicate samples of each building material were inoculated with fungal suspension. Each sample was watered (inoculated) with 3-5 ml of the suspension.

Inoculated samples were kept under the same conditions (20±2°C) and watered with sterile distilled water every second or third day to keep moist. Fungal growth on the materials was examined visually every 3-4 days. When the growth was observed the fungi were identified microscopically at least to the generic level. Intensity of fungal growth was assessed according to the scale:

0 - No growth can be seen under the microscope,
1 - Visible growth up to 50% coverage,
3 - Visible growth, 50-80% coverage,
4 - Visible growth, practically the entire sample surface area (80%) covered, the surface of the sample can be seen only in few parts,
5 - Whole surface of the sample (100%) covered.

Table III: Evaluation of fungi growth on materials (average values)

Evaluation/Intensity of growth	Colour in table 5;6
1-2	0%<50%
2-3	50%≤80%
3-4	80<99%
4-5	100%

For measurements of evaluation of fungi growth on materials was used ImageJ2 data processing software (NIH Image, USA).

In addition, pH measurements for composite materials were made after biodegradation test.

3 RESULTS AND DISCUSSION

3.1 Sapropel binder properties

In this research sapropel was used as a binder. Sapropel sediments were sampled from lake Pikstere, located in Jekabpils District, Latgale Region, Latvia. Sapropel samples differ from each other in terms of organic matter, moisture and carbonate as well as ash content. Properties of natural binder (sapropel) samples: Lake - Piksteres, sapropel type - green algae, Moisture - 96.45%, organic matter content in dry matter - 82.67%, ash content of dry matter - 17.33%, pH (water extract) - 6.89, electric conductivity - 124.75 mS/cm^2, Non-H density - 1.028 g/m^3, H density-1.069 g/m^3. Colour – greenish brown.

3.2 Mechanical and thermal conductivity properties of composite materials

Mechanical and thermal conductivity properties are summarized in Table 4, two different densities were achieved for hemp filled samples: 300 and 500 kg/m3 +/- 10%. SWF achieved density of 319 kg/m3, SWD - 470 kg/m3. Compressive strength is similar to all hemp-based materials 0.25-0.29 for 300 kg/m^3 and 0.77 to 1.12 for 500 kg/m^3 samples, force deformation curve is also similar - almost linear for low density samples, and steeper with more pronounced binder collapse point for high density samples, as sample properties are more similar to those of a filler at 300 kg/m^3, and start to function like a binder at 500 kg/m^3.

It can be seen that compressive strength is slightly influenced by sapropel addition, lowering resulting compressive strength. It can be explained with the fact that compressive strength of pure sapropel binder is lower than that of lime-based binder. Also, the magnesium-based binder shows slightly higher results than lime-based binders, due to its compatibility with organic fillers [16]. Wood-based samples have relatively lower compressive strength (0.19 and 0.67 MPa), but as filler and binder are different from previous mixtures, it cannot be directly compared. From application point of view 0.2 MPa is the lower boundary of compressive strength that composite material should have, when used as in-fill between formwork [33] in self-bearing wall together with structural timber frame.

Results from thermal conductivity tests show that density has lower correlation with thermal conductivity than compressive strength, as MHC 2 has the lowest density of 500 kg/m^3 samples – 504 kg/m^3, but has the highest thermal conductivity. Preliminary results for hemp concrete show that conductivity increases together with compressive strength as inner structure of composite has more connected binder structures, thus providing higher compressive strength and higher thermal conductivity.

In general, the test results showed that it is possible to substitute a half of lime binder with sapropel without compromising the strength of biocomposite. Also, MHC binder showed promising results in strength, although somewhat higher thermal conductivity. Wood-based composites had slightly lower compressive strength, but also had lower thermal conductivity due to filler used and low thermal conductivity of sapropel binder.

The achieved results are in line with similar LHC [6] and sapropel-hemp materials [34] [5] and all tested materials are useable as thermal insulation composites, thus all will be tested for biodegradation.

Table IV: Mechanical resistance, thermal conductivity and density of the studied materials

Type	Density, kg/m^3	Compressive strength, N/mm^2	Thermal conductivity, W/m*K
SLHC(1)	301.6	0.25	-
SLHC(2)	537.1	0.77	0.089
LHC(1)	298.7	0.29	-
LHC(2)	530.6	0.90	0.099
MHC(1)	302.3	0.25	0.076
MHC(2)	504.4	1.12	0.111
SWF	319.0	0.19	0.060
SWD	470.0	0.67	0.061

3.3 Biodegradation resistance against *Alternaria alternata* and *Cladosporiumherbarum*

LLC ALINA product "ALINA LIFE ™" was used as additive to control the degradation of composite materials. Biodegradation of composite materials was evaluated. This product group is a new type of additive for building surfacing materials and colors, it reduces the negative impact of environmental exposure, thus prolonging the longevity and reducing the use of biocides to protect the materials.

Research results showed that the most common fungi found in composite materials is *Sordaria*, *Alternaria* and *Fusarium* genus fungi. In some cases, there was also *Penicillium*, *Acremonium*, *Paecilomyces*, *Trichoderma*, and *Stachybotrys*, *Mucor spp*., that indicates that the substrates contain sufficient moisture and nutrients for the fungal development.

The study proved that increased intensity of fungi growth occurs in materials that are made of wood dust and wood fibre and sapropel as binder. It should be mentioned that the fungi species that grow on the material depend on the type of material, filler and binder.

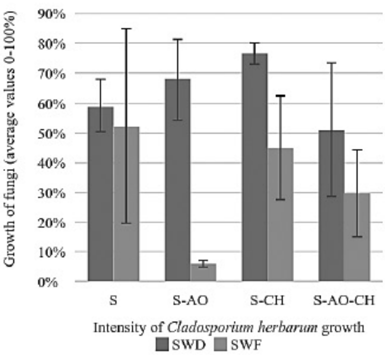

Figure 1: Biodegradation/intensity of *Cladosporium-herbarum* growth: Sapropel binder materials

In evaluation process of SWD and SWF materials results indicated a tendency of organoclay improvement for antifungal activity to the composite materials. After intensity of fungal growth was assessed visually it was seen that the structure is not degraded comparing to materials without additive. As well climate chamber made changes to composite materials. Consequently, it can be seen that SWF-AO is 6% comparing to SWF-AO-CH, which is 30% of *Cladosporiumherbarum* growth intensity (Figure 1).

Fungi *Cladosporiumherbarum* and *Alternaria alternata* are common allergy triggers, the spores are present in the outdoor as well as in indoor air [39] *Alternaria alternata*is a worldwide saprotroph fungus that is able to grow on a variety of plants and other substrates. The fungus is able to adapt to different growing conditions, but mainly can be found in soil and compost material as well as a plant pathogen [26] *Cladosporiumherbarum* also is naturally occurring in soil and compost material, this fungus has also been found in the air, food, textile and many other substrates. Appropriate conditions affect its ability to evolve to other fungi and healthy plant leaves [25]. Microscopic fungi genera, such as *Alternaria*, *Epicoccum*, *Fusarium*, *Phomopsis*, *Cylindrosporium*, *Phyllosticta* and *Cladosporium*can often be seen on the wood and on plants [35]. Both *Cladosporium*and *Alternaria spp.* are often found in high concentrations on building facades in temperate climate zone as well, because they are resistant to natural solar radiation. The pigments of these fungi darken the surfaces. As the materials studied in this research have natural origin and they contain wood and fiber filler, it is necessary to ensure appropriate treatment to ensure their antimicrobial protection.

Fungi development was practically not observed on hemp-lime and hemp materials - magnesium chloride binder, as well as hemp-lime sapropel-adhesive materials (Table 5). This is explained by cannabis antimicrobial effects [36], as well as lime naturally high 9-12 pH, which negatively affects the development of the fungi.

Table V: Biodegradation/intensity of *Cladosporium-herbarum*(C); *Alternaria alternata*(A) growth. Control sample (K) growth of other fungi: MHC, LHC, SLHC materials. Colour legend as in Table III

Nr.	*Sample label*	*E*		
		A	*C*	*K*
1	MHC	1.7	1.7	1
2	MHC-MH	1	1	1
3	MHC-AO	1	1.7	1
4	SLHC	1.3	1	1
5	SLHC-LH	2	1.7	1
6	SLHC-AO	1	1.3	1
7	LHC	1	1	1
8	LHC-LH	1	1	1
9	LHC-AO	1.3	1	1
10	MHC-CH	1.5	2	2
11	MHC-CH-MH	1.5	1	1
12	MHC-CH-AO	1	1	1
13	SLHC-CH	1	1	1
14	SLHC-CH-LH	1	1	1
15	SLHC-CH-AO	2	1	1
16	LHC-CH	1	1	2
17	LHC-CH-LH	1.5	2	1
18	LHC-CH-AO	1	1	1

Fungi can colonize nearly all natural and synthetic materials, especially if they are hygroscopic or wet. Inorganic materials are often colonized because they adsorb dust and serve as a good substrate for fungi, such as *Aspergillus fumigatus* and *Aspergillus versicolor.Cladosporium* and *Penicillium* (*Penicillium brevicompactum* and *Penicillium expansum)* are listed as one of the most common species. It must be emphasized that it is the dried wood surface that has absorbed moisture and consequently has increased susceptibility to fungi. It also proved in this research, because materials made of wood dust and fiber and sapropel as binder in evaluation of intensity of growth (Table 6) got 3.3 – 5 which indicates visible growth more than 50% coverage to 100% (covering the whole surface of the sample). These materials have neutral 6-7 pH or slightly acidic pH 5.

Table VI: Biodegradation/intensity of *Cladosporium-herbarum; Alternaria alternata*growth. Control sample growth of other fungi: Sapropel binder materials. Colour legend as in Table III

Nr.	*Sample label*	*E*		
		A	*C*	*K*
19	SWD	3.7	4	3.7
20	SWF	3.3	3.7	5
21	SWD-AO	5	4	2.3
22	SWF-AO	3.3	2.3	2.3
23	SWD-CH	3.5	4	4.5
24	SWF-CH	3.3	3.5	5
25	SWD-CH-AO	4.5	4	3
26	SWF-CH-AO	4	4.5	3.5

The results show that the composite filler particle type, composition as well as surface area have an effect on the intensity of growth of fungi. The fungi (moulds) used in the experiment are present in the cellulose-rich plant debris [22] [23]. Moulds are the first indicator that the building and construction materials have begun to deteriorate and lose their good qualities. The next organisms that begin to degrade the material after moulds, are bacteria and white and/or brown rot fungi. It should be noted that the development of the fungi on materials requires less moisture than bacteria [37]. The literature describes that materials can be protected from fungal and bacterial degradation using boric acid and other antifungal and antibacterial agents, which are widely used in medicine and the wood industry material storage [38].

Internal wall coverings used in buildings, such as the folding of gypsum board, as it is hygroscopic, are very conducive to the growth of *Stachybotryschartarum*. Paper and glue used for indoor surfaces stimulate the growth of other indoor fungi species. Polyurethane, used in insulation materials, is not resistant to the growth of *Paecilomycesvariotii*, *Trichoderma harzianum* and *Penicillium* species. *Aspergillus* and *Penicillium* grows on carelessly painted surfaces, but *Aureobasidium pullulans* is found in poor-quality colors. *Alternaria*, *Cladosporium* and *Aspergillus* can be found on acrylic painted surface (Haong et al., 2009).

4 CONCLUSIONS

One of the most important properties of these materials is their ability to sequester CO_2 as both the binder and filler are bio-based.

In the current study, mechanical and thermal properties of these materials were evaluated and compared to similar materials with bio-based fillers but mineral binders LHC and MHC. Mechanical and thermal properties of sapropel-based composites were similar to those of LHC and MHC, suggesting that sapropel composites could have similar use in construction industry as self-bearing wall thermal insulation material that works together with structural timber frame.

As sapropel-based materials are with high organic content, they are vulnerable to biodegradation. Consequently, in the current study their resistance was enhanced with organoclay additives and tested against various fungi on both fresh and aged materials.

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7 LOGO SPACE

Paper 3

SAPROPEL AS AN ADHESIVE: ASSESSMENT OF ESSENTIAL PROPERTIES

SAPROPEL AS AN ADHESIVE: ASSESSMENT OF ESSENTIAL PROPERTIES

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Abstract
Recently, a renewed interest in non-harmful, environmentally friendly adhesives has ensued among the industry professionals, both environmental and healthcare scientists. In this study, organic rich lake sediments (sapropel) from two lakes located in Latgale Region of Latvia were used as a glue to investigate the potential use of such adhesive for manufacture of composite materials from wood. Sapropel is a valuable resource with multiple areas of application, e.g., agriculture, balneology. Available amount of sapropel in Latvia is estimated at up to 2 billion m^3. Prior the tests, characterization of sapropel samples was done. Properties of the obtained composite material samples from wood and sapropel, as well as the mechanical properties were investigated. Tests involved the assessment of static bending strength and shear strength tests, durability according to their operating performance (D_1-D_4), as well as dried natural peat tensile strength perpendicular to the grain direction were determined and compared to the literature data; and the opportunities to use new composite materials in accordance with to the standards were discussed. The results of the study revealed an insight into possibilities to develop products of higher added value from sapropel as adhesive in combination with various resources. Results indicated that the samples made from Lake Pilvelis sapropel gain to better results of bending strength determination (parallel bending - 88.7 MPa). The aim of this study was to explore options to produce veneer using two kinds of sapropel as a glue and to determine the optimal properties according to the standards, as well as to characterize properties of the obtained composite material.
Key words: natural adhesive, sapropel, static bending strength, tensile strength, wood composite materials.

Introduction

Over the past century, there has been a dramatic increase in the growth of the material consumption; thus, the necessity for a wider use of local resources and available natural materials is among the priorities worldwide. Development of natural adhesives is a highly innovative research area, as the product range and the expansion of global consumption will also increase the adhesive consumption. The global market of adhesives was estimated to be 8 977 m^3 in 2013, and it is expected to reach 12 392 m^3 by 2020, growing at a CARG of 4.7% from 2014 to 2020 (Kattakota, 2015). At the world level, sectors of civil engineering and building construction consume 60% of raw materials extracted from the lithosphere; thereby, the construction sector is one of the largest consumption sectors of adhesives in the world. Due to the rising environmental and economic concerns, there is an acute need for natural glues made from materials of animal and plant origin containing, for example, proteins or starch as a binding agent (Bribián, Capilla, & Usón, 2011; Stefano *et al.*, 2009).

Most of the adhesives currently used contain toxic substances, pollute the environment and induce serious human and animal health risks. Major groups of glue are produced on a formaldehyde and vinyl basis, covering 92% of the overall adhesive consumption. Furthermore, formaldehyde adhesives are made from non-renewable resources. Accordingly, the wood composite industry currently has one of the challenges to look for possibilities of environmentally friendly adhesives derived from renewable resources (Yuan & Kaichang, 2006).

Sapropel is a partially renewable geological resource (Segliņš & Brangulis, 2002); it is a fine-grained organic-rich sediment or sedimentary rock and refers to inland waters of lacustrine environment (Emeis, 2009). Sapropel is a valuable resource of natural origin. It is estimated that available reserves of sapropel in Latvia amount to 700 – 800 million m^3, and 1.5 billion m^3 underlie the peat layer, but in total 2 billion m^3 are deposed (Segliņš & Brangulis, 2002). Sapropel can be used in different economic fields such as agriculture, veterinary medicine, livestock farming, construction, medicine, balneology, and cosmetic applications. It is assessed that sapropel has adhesive properties with high ability to bind as well as a plasticity and shape holding ability (Obuka *et al.*, 2015). Therefore, it can be used as a binder for manufacturing of environmentally friendly materials. In this research, water repellence and adhesive properties are underlined as significant characteristics of sapropel (Brakšs *et al.*, 1960; Gružāns, 1960; Штин, 2005). The aim of this study was to explore options to produce veneer using two kinds of sapropel as a glue and to determine the optimal properties according to the standards, as well as to characterize properties of the obtained composite material.

Materials and Methods

Descriptionof sapropel samples

Organic rich freshwater sediments (sapropel) were extracted from the lakes and used as an adhesive material. Sapropel sediments were sampled from two lakes in Latvia – Lake Veveru and Lake Pilvelis, located in Rezekne District, Latgale Region.

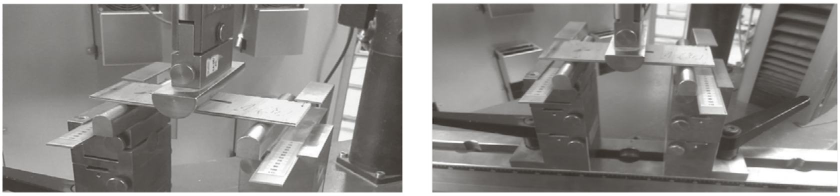

Figure 1. Veneer – sapropel static bending strength test.

Raw material of composites

Birch wood veneer with a thickness of 1.5 mm and moisture content of 6% was used for the preparation of plywood. Samples for determination of tensile shear strength: beech wood planks with a thickness of 5 mm and moisture content of 6% and with density 700 – 750 kg m^3 were used for the preparation of composite material samples for the tests. Peat samples: dried natural peat was used for tests with the moisture content of 16.4% and with density 90 – 250 kg m^3.

Loss on ignition

Loss on ignition (LOI) method was applied in order to estimate the content of carbonate matter, moisture content and the organic matter of sediments. Moisture content of sapropel was determined after drying at 105 ± 1 °C, following organic matter estimation at 550 °C for 4 h. The content of mineral substances was determined after heating at 900 °C for 2 h (Heiri, Lotter, & Lemcke, 2001). The content of dry matter was estimated after drying at 105 ± 1 °C according to standard EN 827.

Sample preparation and testing

Static bending strength (parallel and perpendicular to the grain direction), shear strength test according EN 314-1 (requirements) and EN 314-2 standards were tested (Figure 1). The sapropel samples were mixed completely just before the preparation of three-layer plywood of dimensions 4×250×250 mm. Glue spreading level for Lake Veveru sapropel was 276 – 290 g m^2 and 264 – 288 g m^2 for Lake Pilvelis sapropel. The plywood was pressed under the pressure of 2.0 MPa for 24 hours, at 100 °C for first 16 hours. The samples were stored for one day at temperature 20 ± 3 °C with 65 ± 5% relative humidity until reaching equilibrium moisture content. Subsequently, the plywood panel was cut into shear specimens with the dimension of 4×50×150 mm to determine its bending strength and 4×25×200 mm to define shear strength.

Adhesive strength of sapropel durability according to their operating performance conformity to EN 205 standard was measured. The sapropel samples were mixed completely just before the preparation of beech blanks fabrication of dimensions 10×75×600 mm. Glue spreading for Lake Veveru sapropel and Lake Pilvelis sapropel was 290 – 310 g m^2. In addition to understanding the sapropel properties used as a glue, comparing to glue that already exists in market, the samples made with PVA - Polyvinyl acetate glue were used. The planks were pressed at 100 °C under the pressure of 1.0 MPa for 24 hours. The samples were stored for one day at 20 ± 3 °C with 65 ± 5% relative humidity until reaching equilibrium moisture content. Subsequently, the plywood panel was cut into shear specimens with the dimension of 10×20×150 mm to determine the tension shear strength.

Dried natural peat and sapropel as a glue were tested for tensile strength perpendicular to the grain direction according to standard EN 319. The sapropel samples were mixed completely just before the preparation of the samples of dimensions 32×50×50 mm. Glue spreading level was 1600 g m^2 for Lake Veveru and Lake Pilvelis sapropel. The driedpeat-sapropel samples were pressed under the pressure of 0.1 MPa for 48 hours. The samples were stored for one day at 20 ± 3 °C with 65 ± 5% relative humidity until reaching equilibrium moisture content. The material samples made from dried natural peat and sapropel were tested for tensile strength perpendicular to the grain direction.

After cooling specimens at ambient conditions, the test specimens were measured for the previously mentioned methods using Zwick Z100 universal testing machine. The data in this research were processed by routine statistical analysis and displayed by the standard deviation.

Results and Discussion

Within the study, an adhesive for veneer was made using two kinds of sapropel derived from Lake Pilvelis (cyanobacteria sapropel) and Lake Veveru (green algae sapropel). The following characteristics of the sapropel samples were determined: solid content, moisture, density, and dry ash content (Heiri *et al.*, 2001). Sapropel samples differ from one another in terms of moisture (%), organic matter content (%), amount of carbonates (%) and solid content (%). For example, the Lake Pilvelis sapropel sample contains 1.26% carbonates, its moisture is 85.97%, and the

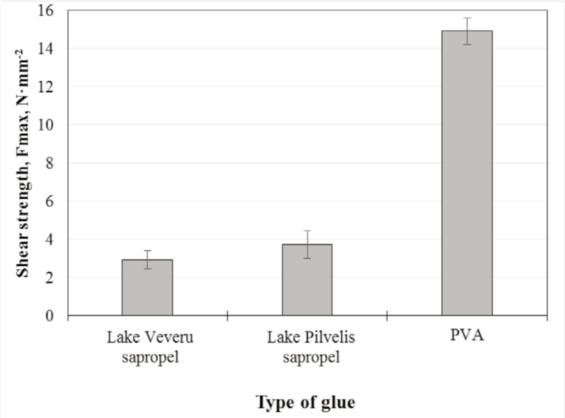

Figure 2. Durability test according to adhesive operating performance.

colour is dark greenish brown with homogeneous and jelly-like structure, with density 1.10 g cm^3 and solid content 30.1%. The moisture level of Lake Veveru sapropel sample is higher – 97.66%; it has lower density – 1.08 g cm^3 and the organic matter content reaches 86.25%, but solid content is 27.1%.

Adhesive strength of sapropel was tested by gluing veneer, plywood and natural dried peat. Several tests were performed: static bending strength (parallel and perpendicular to the grain direction) and shear strength testing, durability according to their operating performance dried natural peat (sapropel as a glue) tensile strength perpendicular to the grain direction. The total number of tested samples is 110.

Shear strength properties of wood composites bonded with Lake Pilvelis and Lake Veveru sapropel, as well as PVA (Polyvinyl acetate) glue was compared according to standard EN 205 (Figure 2).

As anticipated, the PVA bonded wood composites yielded the highest strength comparing to Lake Veveru and Lake Pilvelis sapropel samples. Comparing both sapropel samples, Lake Pilvelis sapropel showed a bit higher bonding strength by 28%. Compared to PVA, the dry strength of Lake Pilvelis sapropel used as an adhesive was about 4 times lower, respectively, while PVA-beech plywood sample achieved 15.11 $N \cdot mm^{-2}$, but Pilvelis beech test result was only 3.67 $N \cdot mm^{-2}$. In literature it is possible to find information about similar tests done with recovered sludge protein used as an adhesive (Pervaiz & Sain, 2011). If comparing in the article stated results with results of sapropel used as an adhesive in the current study, it is possible to say that shear strength properties are quite similar. Shear strength for recovered sludge protein used as an adhesive was about 2 $N \cdot mm^{-2}$ (Pervaiz & Sain, 2011).

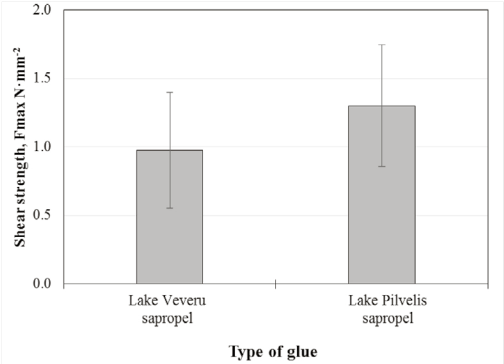

Figure 3. Plywood bonding quality using sapropel as a glue.

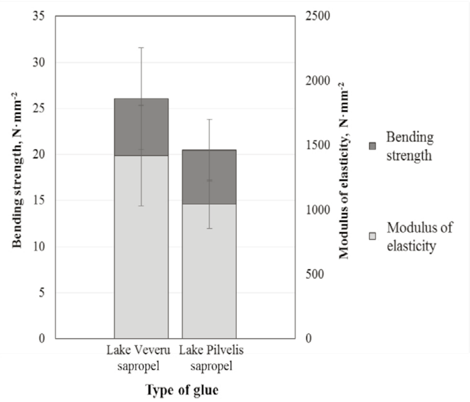

Figure 4. Bending strength parallel of plywood composites.

Bonding quality was determined according to the requirements of standard EN 314-1, the only exception was that samples were not treated in water. Two types of sapropel were tested (Figure 3).

Bonding quality test results using Lake Veveru sapropel showed shear strength Fmax 0.98 ± 0.42 N·mm^{-2}, while using Lake Veveru sapropel Fmax 1.30 ± 0.45 N·mm^{-2}. Results of samples made with Lake Pilvelis sapropel showed higher results by 33%. According to the requirements of standard EN 314-2 for plywood bonding, the quality of composite material must be at least 1 N·mm^{-2}, otherwise wood particles left on tested bond area have to be taken in consideration. All tested samples had 0% of wood particles. It was possible to state, that the sapropel as a glue was not penetrating into wood. Since the requirements of standard EN 314-1 were applied only for sample formation, it was not possible to find any comparison of other similar composite materials described in literature.

Values of elasticity modulus were estimated for specimens with plywood orientation parallel (Figure 4) and crosswise (Figure 5) to the specimen longitudinal direction. Modulus of elasticity and bending strength was done according to the requirements of standard EN 310.

Bending strength for Lake Veveru sapropel samples orientated parallel to the specimen longitudinal direction was 26.08 ± 5.50 N·mm^{-2}, modulus of elasticity 1419.80 ± 387.74 N·mm^{-2}. Bending strength for Lake Pilvelis sapropel samples orientated parallel to the specimen longitudinal direction was 20.47 ± 3.36 N·mm^{-2}, modulus of elasticity 1043.80 ± 187.70 N·mm^{-2}. Samples using Lake Veveru sapropel as an adhesive showed by 27% higher bending strength and by 36% higher modulus of elasticity.

Bending strength for Lake Veveru sapropel samples orientated crosswise to the specimen longitudinal direction was 88.55 ± 19.68 N·mm^{-2}, modulus of elasticity 16424.10 ± 2558.30 N·mm^{-2}. Bending strength for Lake Pilvelis sapropel samples oriented crosswise to the specimen longitudinal direction was 86.44 ± 11.79 N·mm^{-2}, modulus of elasticity 1043.80 ± 187.70 N·mm^{-2}. Samples using Lake Veveru sapropel as an adhesive showed by 2% higher bending strength and by 15% higher modulus of elasticity.

The results obtained from the bending strength parallel and crosswise to the grain direction of plywood composites revealed that the composites where Lake Veveru sapropel was used as an adhesive had better results among the analysed sapropel samples. According to the standard EN 636, it is possible to determine bending strength and bending modulus classes for plywood. Referencing to the standard EN 636, samples with Lake Veveru and Lake Pilvelis sapropel used as an adhesive corresponded to the class F10/40 E5/120.

In addition, tests according to the standard EN 319 were performed to detect dried natural peat and sapropel as a glue for tensile strength perpendicular to the grain direction. The results obtained were as follows: 0.077 MPa for Lake Pilvelis sapropel used as an adhesive, but for Lake Veveru sapropel used as an adhesive - 0.067 MPa. This test of dried natural peat and sapropel used as a glue for tensile strength test showed that the material strength (dried natural peat) is relatively lower; thus, the test results do not reveal the real properties of sapropel used as a glue. It is important to mention that the adhesive seam strength is higher than the material's ability to hold off the tensile test. High porosity is the reason of low mechanical strength of the derived dried peat composite material.

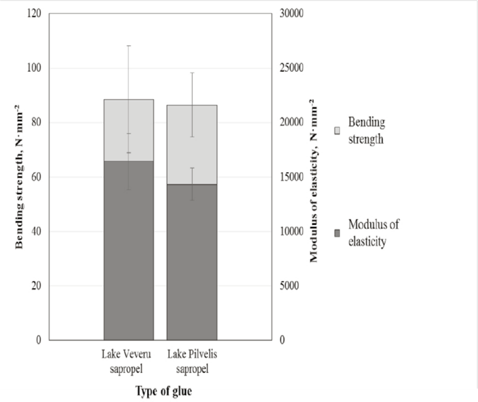

Figure 5. Bending strength crosswise of plywood composites.

As a further study area, the modification in adhesion strength of sapropel adhesives might incorporate bio-chemical modifications, such as enzymatic treatments, and the purification of crude proteins to the next level. Various different crosslinkers (Lei *et al.*, 2014), for example, epoxy resin (EPR), melamine-formaldehyde (MF) and their mixture EPR+MF, SPI (soy protein based glue) were used and compared in other studies. More promising possibility lies in mixing sapropel with other high strength adhesives such as PF, which can also improve water resistant characteristics of these bio-based glues.

Several reports have shown that secondary sludge (SS) from a kraft paper mill can be used as a source of biomass to recover protein and investigate its potential use as a wood adhesive. As mentioned in the literature review, other results are comparable to this research (Pervaiz & Sain, 2011), and the results of our study showed shear strengths of wood composites bonded with different adhesives, in this case secondary sludge, 1.0 MPa, Therefore, recovered sludge protein (RSP) adhesive showed two times better result than sapropel as a glue in this research.

Conclusions

Returning to the question posed at the beginning of this study, that it is a challenge to produce plywood from organic rich lake sediment (sapropel) applied as a glue, it is now possible to state that the first test results reveal that there is an opportunity to use sapropel as a potential adhesive, but there is a need for further experiments. Performed tests indicated that higher adhesive properties can be attributed to Lake Pilvelis sapropel which is richer in solid content. Shear strength properties tests showed Lake Pilvelis samples possessing a higher bonding strength by 28%. Bonding quality test also showed higher results by 33%. It would be interesting to assess the effects of sapropel modification and after that to form new experiments with more detailed investigation. The present study confirms previous findings and offers additional evidence, which suggests that the granulometric composition of the material (size of particles), surface area and other characteristics of the material used as a glue, binder or filler have an effect on the binding with sapropel. The advantage of this study was a practical demonstration that sapropel can be used as an adhesive for plywood manufacturing. The research extends our knowledge of using natural materials and local resources, such as sapropel, as well as birch wood veneer, and it is possible to develop environmentally friendly composite materials for the construction industry, adjusting for the need of utilization in future.

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Paper 4

SAPROPEL AS A BINDER: PROPERTIES AND APPLICATION POSSIBILITIES FOR COMPOSITE MATERIALS

Sapropel as a Binder: Properties and Application Possibilities for Composite Materials

Sapropel as a Binder: Properties and Application Possibilities for Composite Materials

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Abstract. Recent development trends largely look for possibilities of a wider use of natural materials and local resources. In this perspective, the use of organic rich lake sediment – sapropel – as a binding material in line with other environmentally friendly filling materials can be considered as a challenge. Sapropel itself is a valuable resource with multiple areas of application, for example, medicine, veterinary, agriculture, livestock farming, balneology, cosmetic applications, construction, and its application options have been widely studied in the 20th century in the Baltic countries, Ukraine and Russia. Birch wood fibre and sanding dust, hemp shives, 'Aerosil' are used as a filler and three types of sapropel are used as a binder in making composites. After material preparation and curing, physical and mechanical properties - density, thermal conductivity, compressive and flexural strength, were determined and compared to the data in the literature, and the opportunities to use them in the ecological construction were considered. The obtained results give insight into possibilities to use sapropel as a raw material, which can be considered as prospective material for construction materials and design products.

1. Introduction

Sapropel is a partially renewable geological resource [1], it is a fine-grained organic-rich sediment or sedimentary rock, it refers to lacustrine environment inland waters [2]. Organic rich lake sediment – sapropel – is a valuable resource of natural origin. In Latvia, its estimated reserves amount to 700-800 million m^3, 1.5 billion m^3 underlie the peat layer, 2 billion m^3 in total [1]. Sapropel, like, for example, peat has extensive opportunities and can be used in many fields, which vary depending on the composition of sapropel and its properties, and the availability of resources. Sapropel can be used in

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various economic fields such as agriculture, medicine, veterinary medicine, construction, livestock farming, balneology, cosmetic applications. Sapropel has adhesive properties with high abilities to glue as well as shape holding ability; it can be used as a binder for manufacturing of environmentally friendly, natural nanostructured materials. Development of composites made from sapropel as a binder and birch wood sanding dust and fibre, hemp shives as a filler contributes to the rational use of natural resources, recultivation of the lakes and production of renewable energy, obtaining materials with the possibilities to manufacture ecological construction products.

Sapropel is the bottom deposits of fresh water bodies containing organic matter up to more than 15% [3]. Sapropel is formed from residues of the plankton and benthos rests – phytoplankton and zooplankton [4]. These elements multiply in large quantities, especially in standing or poorly through running shallow overgrown lakes [5].

One of the most important properties of moist sapropel is a colloidal suspended phase structure, which determines the ability of sapropel organic colloidal particles to absorb large quantities of water, so it has a high moisture capacity, which amounts to 70-97% [6] and low filtration rate [7]. Relative humidity of sapropel is associated with organic matter and its value increases with the content of organic matter [8].

In this research, significant characteristics of organic rich lake sediments are adhesive properties and water repellence [9], [10], [11]. Adhesive capacity of sapropel is determined by the presence of animal and vegetable residues. Green algae shells consist mostly of cellulose, which has weak decomposing properties. Organic sapropel proportion of matter is formed by green algae and is rich with cellulose but is poor in minerals, it consists of ash content, low humic substance level content, formed mainly by peat meristem [12]. It should be noted that the adhesive properties give higher organic nitrogen amounts of sapropel, also including free amino acids [4].

Composition of sapropel can be affected by molecular structure of humic substances and their quantity, respectively, if the content of humic substances increases then ramification of peripheral parts of molecules also increases. This contributes to the emergence of strong links between the molecules of the material at the time of creation. Molecules of humic substances remain flexible, malleable composite material comprises particles capable of providing material durability and high strength [4]. Therefore, it is rational to use sapropel with the above-mentioned properties as an adhesive for various ecological construction materials – plaster/finishing materials and thermal insulation materials, which could replace the traditionally used materials – stone wool and expanded polystyrene. Adhesive properties of sapropel are important in the production of building materials, i. e., if cold techniques compaction and techniques with hot glue presses at elevated temperature and pressure are applied [13].

The aim of this study is to explore different options to produce sapropel-wood fibre, sapropel-hemp shives, and sapropel-wood sanding dust composites and to determine the optimal composition ratio of certain raw material components and to characterize the resulting material properties.

2. Materials and methods

2.1. Sapropel sampling
In this research, organic rich freshwater sediments (further – sapropel) were used. Sapropel sediments were sampled from three lakes in Latvia – Padelis, Pilcenes and Pilvelu, located in Rezekne District, Latgale Region.

Table 1. Characteristics of the sapropel samples.

Lake	Sample Nr.	Moisture,%	Organic matter,%	Carbonates,%
Padelis	Sample 1	85.97	15.27	35.57
Pilvelu	Sample 2	94.99	84.51	1.26
Veveru	Sample 3	97.66	86.25	1.18

Sapropel samples differ from one another in terms of moisture (%), organic matter (%) and carbonates (%). Characteristics of the sapropel samples are shown in table 1. For example, Lake Padelis sapropel sample contains 35.57% carbonates, moisture is 85.97%, but colour – pale gray-pink and its density is 1.24 g/cm^3. Lake Pilvelis sapropel sample is dark greenish brown with homogeneous and jelly-like structure and density of 1.10 g/cm^3. Lake Veveru sapropel sample moisture level is high – 97.66%, it has low density – 1.08 g/cm^3 and organic matter reaches 86.25%.

2.2. Loss on ignition
Loss on ignition (LOI) method was applied in order to estimate moisture content, content of carbonate matter and organic matter of sediments [14]. Moisture content of sapropel was determined after drying at 105°C, following organic matter estimation at 550°C for 4 h. The content of mineral substances was determined after heating at 900°C for 2 h.

2.3. Fillers for composite materials
Birch wood sanding dust (also known as wood dust) and fibre (also known as wood fibers), and hemp shives were selected as fillers for production of composite materials. Birch wood sanding dust and fibre is industrial by-product from JSC "Latvijas finieris" – a plywood manufacturing company. Birch wood fibre is up to 15 mm long and up to 0.1 mm thick in diameter. In addition, hemp shives ("Bialobrezeskie") were taken from "Zalers" Ltd. Hemp shive slices were maximal 5.5 cm long and up to 0.6 cm thick in diameter. In producing of composites, an additional thickening additive filler was used – colloidal silica product "Aerosil". It is a filler that creates a smooth mixture, often in combination with other fillers.

2.4. Sample preparation and curing
For the developed composite materials raw sapropel was used as a binder (adhesive). Mixing of sapropel-filler mass was done manually until homogeneous and smooth mixture was reached at the stage where filler was fully covered with sapropel. Sapropel was mechanically treated by mixing together with electrical hand mixer until smooth and homogeneous material was formed. Metal mould with dimension of 30×30 cm and with adjustable height was used for composite material production. The mixture of raw materials was laid in by layers in mold for more dense composite material structure, higher mechanical strength and for minimizing final product shrinkage. Sapropel-filler samples were cured at the temperature of 80 – 105°C for 36 – 72 hours.

2.5. Thermal conductivity test

Before the thermal conductivity test, the density of the samples was calculated by weighting the samples and measuring the dimensions. Thermal conductivity was measured using LaserComp FOX 600 heat-flow measurer. Test settings were 0°C upper and 20°C lower plate. Automatic determination of sample thickness was chosen for this study.

2.6. Compressive and flexural strength tests

For testing compressive and flexural strength, the samples were specially prepared (sawed in necessary dimensions). The dimensions were 27-60×27-55×27-55 mm cubic forms for compressive tests (parallel and crosswise to the tamping direction) and 27-60×27-55×120 mm pieces for flexural strength tests. Mechanical tests were performed on ZWICK Z100 universal testing machine. For compressive strength, a stress at 10% deformation was recorded, for compressive crosswise and flexural strength – until failure. For sapropel-hemp shives, a layer of gypsum was spread over the interfaces to ensure even pressure application.

3. Results and discussion

3.1. Thermal conductivity test results

Paying particular attention to shrinkage cracks, thermal properties of the composite materials (wood sanding dust and 'Aerosil' with sample 2) were tested by heating the material in the oven. Shrinkage cracks impacted the quality of material for further tests, but in this case gypsum was used to fill the cracks and to do a thermal conductivity test. The measurement results also indicate a higher thermal conductivity of the material, that is, 0.080 W/m*K. This value can be explained by the fact that all the cracks were not sufficiently filled, gypsum also influenced the result, as thermal conductivity of gypsum is around 0.18 W/m*K. Thermal conductivity test of sapropel – filler composite was carried out by changing the types of sapropel and fillers. The results obtained are shown in table 2.

Table 2. Thermal conductivity of the studied materials.

Material: binder-filler	Density, kg/m^3	Thermal conductivity, W/m*K
Sample 1 and sample 3 - hemp shives	191	0.063
Sample 1 and sample 2 - hemp shives	200	0.059
Sample 3 - wood fibre	153	0.055
Sample 3 - wood fibre	202	0.060
Sample 3 - wood sanding dust	214	0.061
Sample 3 – wood sanding dust - 'Aerosil'	376	0.080

According to the results obtained, the composite made from sapropel sample 3-wood fibre (density 153 kg/m^3) has the best results of thermal conductivity. From visual aspect, it is a material different from another sample 3 sapropel-wood fibre (figure 2) with density 202 kg/m^3, because it has a denser structure and it has comparatively better resistance with respect to deformation. Results indicate that these composites have similar characteristics, thereby they have similar possibilities of use and potential. Thermal conductivity of air-dried composites is relatively low because of the organic origin of raw materials, detailed cellural mixed structure and homogeneous fibres with interconnected and open pores.

Figure 1. Sample 1 and sample 3 – hemp shives.

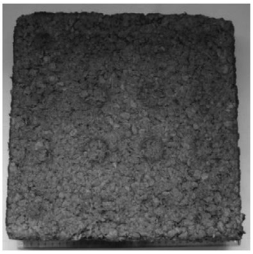

Figure 2. Sample 3 – wood fibre.

While sapropel-hemp shives composites (figure 1 and 4) are characterized by a heterogeneous structure due to different size of particles, having cavities and uneven composition with weaker inclusions, deforming more quickly. However, composite (density 376 kg/m^3) made from wood sanding dust and 'Aerosil' with sample 3 sapropel binder, and composite made from sample 3 sapropel and wood sanding dust (figure 3) with density 214 kg/m^3, formed shrinkage cracks during drying indicating the inferiority of the technology. Composite structure is made of densely grouped wood sanding dust particles with a sapropel binder.

In the study of sapropel-sawdust and peat-sawdust composite materials [15], the results obtained in thermal conductivity measurements were 0.067 W/m*K and 0.060 W/m*K. The study considered the freezing cycles and moisture of the tested materials. It shows that sapropel-sawdust thermal conductivity coefficient becomes lower after freezing cycles. If the composite material is resistant to freezing cycles, this material is applicable for Latvian conditions [15]. When compared with the results obtained, where composite's humidity is from air - dry state and a moisture saturated material (12%), thermal conductivity coefficient for sapropel-sawdust composite material is 0.050 – 0.060 W/m*K and for peat-sawdust composite material is 0.055 – 0.064 W/m*K, respectively, which is very similar to the results of this research. In the study of sapropel-straw panels where composition is similar to the composites created in this research and the samples from the study of sapropel and peat sawdust composite material [15], the result obtained is 0.055 W/m*K and it is stressed that with varying fillers and sapropel ratio, it is possible to produce a more effective thermal conductivity material [16].

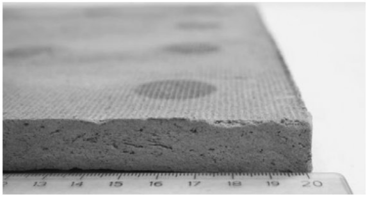

Figure 3. Sample 3 – wood sanding dust.

Figure 4. Sample 1 and sample 2 – hemp shives.

In the study by Binici and colleagues on the insulation materials made from the sunflower stems, textiles and agricultural by-products as a filler, epoxy resin was used as the binder for better fiber strength and binding efficiency. An average thermal conductivity coefficient of 0.1642 W/m * K was obtained. However, the thermal conductivity coefficient of the sample with less epoxy resin added and made only from sunflower stems and sunflower stem fibers reached 0.0728 W/m*K [17]. In research of bamboo fiber and polyester composite Mounika et al. conclude that thermal conductivity coefficient decreases with the increase in the proportion of fiber. Thermal conductivity coefficient ranged from 0.185 to 0.196 W/m*K [18]. Literature on materials based on natural fibres from renewable raw material resources (flax, hemp, wood, bamboo, sheep's wool) shows that they possess very good sound and thermal insulation properties. This is due to material's low density and natural character of input fibres ("airy", lightweight material) [19], [20].

In the study about lime-hemp concrete, a variety of binders were compared, including metakaolin, obtained by burning kaolin clay (40% by mass) at 800°C and dolomitic lime (60% by mass), produced by "Saulkalne" Ltd. 8 different types of hemp shives were used as filler. The obtained results shows lime-hemp concrete material has a density of 312-337 kg/m^3, thermal conductivity of the material is more diverse than its density – from 0.0718 to 0.0778 W/m*K [21].

In the research about the use of agricultural waste in sustainable construction materials, Madurwar et al. compared the measurements of insulation materials of different origin. The results ranged from 0.046 to 0.056 W/m*K for rice husks to 0.118 to 0.240 W/m*K for oil palm leaves. The authors concluded that there are significant similarities between the corn's cob and the extruded polystyrene (XPS) material in terms of microstructure and chemical composition. Materials made from rice husk and coconut coir demonstrated the best results [22]. Previously discussed results of thermal conductivity showed similar values comparing with the results obtained in the current study.

3.2. Mechanical resistance and stability test results

The results obtained from the compressive deformation test (figure 5) show that composites where sample 3 sapropel was used as a binder with a filler of birchwood sanding dust and 'Aerosil' have the best result among the analysed samples. Compressive deformation results vary from 0.724 MPa sample 3 sapropel-wood sanding dust composite to 0.674 MPa for sample 3 sapropel-wood sanding dust and 'Aerosil' as a filler, while compressive strength crosswise shows respectively 0.669 MPa and 0.760 MPa.

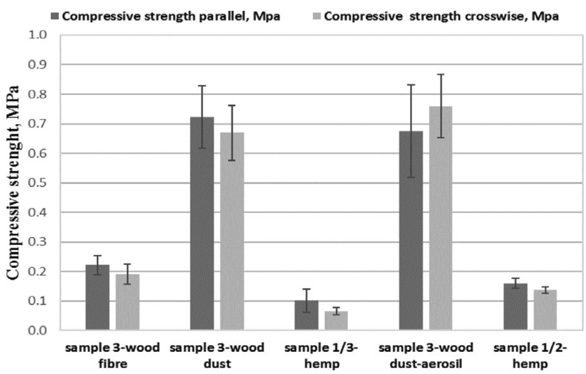

Figure 5. Compressive strength parallel and crosswise of different composites.

Composites made from hemp shives and wood fibre as a filler in compressive deformation obtain the rate of 0.221MPa for sample 3 sapropel-wood fibre and hemp shives materials 0.101 (Sample 1 and 3 – hemp shives) and 0.159 MPa (Sample 1 and sample 2 – hemp shives), while compressive strength crosswise shows respectively 0.191 MPa, 0.066 MPa and 0.138 MPa. The aforementioned materials have relatively lower rates due to lower intensity of filler and binder bonding. The mixing of the binder with the filler is more complex, because for the binder it is more difficult to enter the filler structure as its particles are larger. This was observed with wood fibre composite and sample 3 as a binder. However, filler (birch wood sanding dust and 'Aerosil'), which contains a mass of dust particles, mixes with the binder evenly, entering filler's structure. The structure of the material is smoother and will increase the mechanical resistance of the composite. Compressive strength results are influenced by the mode of sample preparation as they are sawn before, disrupting the structure of the material. The use of various fillers and binders affects physical and mechanical properties of composite materials, so changing the type of fillers and binders can induce change in physical and mechanical properties.

Comparing to the compressive strength results, the flexural strength results (figure 6) show that the material strength is relatively lower. It can be seen considering the results that the samples which have been made from hemp shives show lower values, the reason could be granulometric composition, as there are many large shives that create voids and uneven composition with weaker inclusions resulting in faster deformation of the samples [21]. In the process of making wood fibre-sapropel composite, the mixing of the binder with the filler is more complex, because for the binder it is more difficult to enter the filler structure, forming tangles and air gaps. Therefore, there are voids which can reduce mechanical strength of the obtained material.

Composites made from hemp shives and wood sanding dust as a filler in flexural deformation strength obtain a value of 0.069 MPa for sample 3 sapropel – wood fibre and 0.164 MPa (sample 3 sapropel – wood sanding dust) and 0.203 MPa (sample 3 sapropel – wood sanding dust – 'Aerosil'), while compressive strength crosswise shows 0.066 MPa for sample 3 – wood fibre 0.182 MPa for sample 3 sapropel – wood sanding dust – 'Aerosil', respectively. These results are relatively lower due to the lower intensity of the filler and binder bonding. The mixing of the binder with the filler is more complex, because for the binder it is more difficult to enter the filler structure as its particles are larger, longer (with each of different size). For all measurements, the values are higher using mix of sample 1 and sample 2 sapropel, as the reason could be higher sapropel adhesive capacity and lower amount of moisture.

In the study of sapropel and peat sawdust composite material [15], similar composites were created and results show that the type of filler and binder, as well as the preparation technology, change composite compressive and flexural strength. Accordingly to the indicated results, average compressive resistance is 0.03 MPa, but compressive resistance of peat-sawdust composite (activated peat binder) is 0.3 MPa.

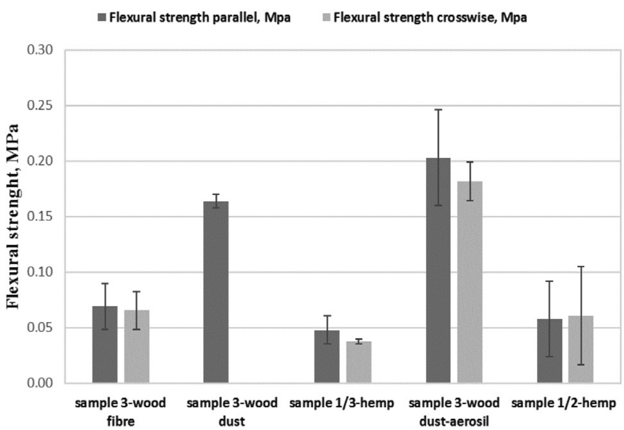

Figure 6. Flexural strengths parallel and crosswise of different composites.

Comparing the results of this work with the research into sapropel–concrete, the results of the current study show lower rates of wood fibre and hemp shives materials. During preparation 1 % NaOH solution was added. The obtained results of the studies showed that compressive strength of absolutely dry composite materials is 0.55 MPa, while that of air-dried – 0.56 MPa [11]. In the study about lime-hemp concrete, a variety of binders including metakaolin and dolomitic lime were compared. The obtained results show that compressive strength of different lime-hemp concrete materials ranges from 0.140 to 0.337 MPa, flexural strenght – from 0.021 to 0.059 MPa [21]. In the study on the composite material, which was created from agricultural by-products, it was concluded that the highest strength indicators were shown by durian peel and coconut-fiber composites, which range from 2.9 to 36 MPa [22]. In turn, the results of the study on the composite of sunflower stems and epoxy resin show compressive strength tests scores of 0.283 to 0.312 MPa. Flexural deformation strength results are from 0.06 to 0.09 MPa. High porosity is the reason of low mechanical strenght of the derived materials.

4. Conclusions

Using natural materials and local resources, such as sapropel, as well as industrial by-products such as birch wood sanding dust and fibre, and hemp shives it is possible to develop environmentally friendly composite materials for the construction industry, adjusting for the need for utilization. Granulometric composition of the particles, surface area and other characteristics of the material used as a filler have an effect on the binding with sapropel. Composite materials, which are made of birch wood sanding dust, 'Aerosil' and sample 2 and sample 3 sapropel, are characterized by relatively high mechanical strength, shape holding ability and easily amenable texture imprint. The composites sample 3 – wood sanding dust, sample 3 – wood sanding dust and 'Aerosil' during heating formed shrinkage cracks, thereby showing technological inferiority, as well as the need for evenly temperature raise and reduction of moisture in sapropel samples.

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Paper 5

SAPROPEĻA – KŪDRAS, SAPROPEĻA KOKSKAIDU SILTUMIZOLĀCIJAS PLĀKSNES UN TO ĪPAŠĪBAS

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Sapropeļa kūdras, sapropeļa kokskaidu siltumizolācijas plāksnes un to īpašības

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Kopsavilkums. **Siltumizolācijas materiāli, kuros par pildvielu tiktu izmantoti vietējie biomasas produkti, bet par saistvielu kalpotu dabiskas izcelsmes saistvielas, piemēram, sapropelis, uzskatāmi par inovatīviem un to pielietošana sekmētu ekoloģiskās būvniecības nozares attīstību. Šādu risinājumu izstrāde ir aktuāla, jo Latvijā ir ievērojami sapropeļa resursi, kuru izmantošanu kavē to nepietiekama izpēte un ekoloģiskās būvniecības nozares intensīva attīstība. Pētījuma mērķis ir iegūt sapropeļa-koksnes, kūdras-koksnes siltumizolācijas plāksnes, noteikt optimālās plātnes sastāva attiecības un raksturot iegūto plātņu īpašības. Veikto pētījumu rezultātā tika noteiktas siltumizolācijas materiālu paraugu mehāniskās, siltumvadītspējas un skaņas izolācijas īpašības un izvērtētas iespējas tos izmantot ekoloģiskajā būvniecībā, kā arī veikts salīdzinājums ar šobrīd tirgū esošajiem produktiem.**

Atslēgas vārdi: **kūdra, sapropelis, sapropeļa izmantošanas iespējas, ekoloģiski būvmateriāli, siltumizolācijas materiāli, vietējie resursi, ilgtspējīga izmantošana.**

I. Ievads

Ievērojama daļa sabiedrības resursu ir jāizmanto mājokļa uzturēšanai un apsildei, tāpēc īpaši svarīgi ir efektīvu un videi draudzīgu siltumizolācijas materiālu izstrāde, izmantojot vietējos resursus. Ekoloģiskās būvniecības materiālu attīstība un to pieaugošais izmantošanas īpatsvars būvniecībā kļūst arvien plašāks tāpēc, ka tas dod iespēju ekonomēt resursus ražošanas laikā un nerada piesārņojumu apkārtējā vidē. Šādi materiāli ir pilnībā pārstrādājami, turklāt sadalās relatīvi ātri pēc to ekspluatācijas. Siltumizolācijas materiāli, kuros par pildvielu tiktu izmantoti koksnes atkritumi (skaidas), bet par saistvielu kalpotu dabiskas izcelsmes saistvielas, piemēram, sapropelis, uzskatāmi par inovatīviem, un to pielietošana sekmētu būvniecības nozares konkurētspēju. Šādu risinājumu izstrāde ir aktuāla, jo Latvijā ir ievērojami sapropeļa resursi, kuru izmantošanu kavē to nepietiekama izpēte. Sapropeļa krājumi Latvijā ezeros sasniedz 700 – 800 milj.m^3[1], bet purvos zem kūdras slāņa 1,5 miljardi m^3[2]. Tajā pašā laikā sapropeļa ieguve var sekmēt degradētu un aizaugušu ezeru atjaunošanu, uzlabot saldūdens resursu kvalitāti, palīdzēt attīstīt dažādas saimniecības nozares, piemēram, zivsaimniecību, hidroenerģētiku, lauku tūrismu.

Sapropelis ir organogēns nogulumiezis (recekļveidīga dažādu nokrāsu masa), kas ir veidojies no ūdens augiem un dzīvnieku, galvenokārt planktona, atliekām stāvošos vai vāji cauri tekošos ūdens baseinos [3]. Atkarībā no organisko vielu daudzuma, tās masas veidojošajiem organismiem, sapropeļa minerālās daļas masas un sastāva, sapropelis tiek iedalīts 3 tipos: biogēnais, klastiskais un jauktais. Par vērtīgāko ar plašām izmantošanas iespējām pieņem biogēno sapropeli, kuru iedala organogēnajā un kramainajā sapropelī. Biogēna sapropeļa organisko vielu daudzums nav mazāks par 70%, un tā organiskās masas veidotāji var būt zaļaļģes, zilaļģes, kramaļģes, ūdens dzīvnieki un kūdras veidotājaugi [4].

Latvijā ezeros apmēram 80% gadījumu organiskās vielas saturs sapropeļa sausnā ir lielāks par 60% [5], kas norāda uz to, ka sapropeļa resursi Latvijā ir augstvērtīgi un ar plašām izmantošanas iespējām.

Biogēnam sapropelim ir konstatētas līmvielas īpašības, kuras raksturo – salīmējoša un hidrofobizējoša spēja. Šim sapropelim ir labs plastiskums, viskozitāte, adhēzijas īpašības un adsorbcijas spējas [6], kā arī saistīgums. Lielāko ieguldījumu sapropeļa līmējošo īpašību izveidei sniedz slāpekli saturošas vielas, tajā skaitā brīvās aminoskābes un humusvielas. Tāpēc sapropelis var būt izmantojams kā saistvielas piedeva kokmateriālu atkritumiem, linu apstrādes, papīra–kartona ražošanas rūpniecības neizmantotajiem atkritumiem [7], kokšķiedru plātņu izgatavošanai, kuras paredzētas celtniecības materiālu izstrādei. Sapropelis izmantots arī cementa un citu saistvielu aizstāšanai, iegūstot sapropeļbetonu, kas ir celtniecības materiāls, kuram par saistvielu ir ņemts organiskais sapropelis, bet par pildvielu zāģu skaidas un grants [8], [9]. Tiem var pievienot arī veldzētus kaļķus, smilti, lai palielinātu mehānisko izturību. Sapropeļa saistvielas īpašības izmantojamas, izgatavojot celtniecībai noderīgus materiālus, gan karstā veidā (līmspiedē paaugstinātā temperatūrā un spiedienā), gan arī izgatavojot tos aukstā veidā - blietēšanas paņēmieni [8].

Neskatoties uz pētījumu rezultātiem, kas tika veikti 20. gadsimta 60., 70. gados un pierādīja sapropeļa izmantošanas augsto potenciālu, šis pētījumu un praktiskas izmantošanas virziens neattīstījās. Mūsdienās aktualizējoties jautājumiem par tautsaimniecība, kas izmanto vietējos dabiskas izcelsmes resursus, sapropeļa izpētes virziens būvmateriālu izmantošanā kļūst aktuāls.

Videi draudzīgas būvniecības pamatā ir izstrādāti šādi principi:

1) konstrukcijās un apdarē jāizmanto dabiski materiāli, materiāli pēc ēkas vai tās daļas nokalpošanas otrreizēji jāizmanto;
2) būvmateriālu pārstrāde ļauj iegūt jaunus produktus, nenodarot kaitējumu dabai;
3) materiālu ekonomija – materiāliem jāsniedz energoresursu ekonomijas iespējas, jāizmanto atjaunojami resursi, kur tiek

iekļauta izejmateriālu ieguve, ražošana, iepakojums, uzstādīšana, lietošana un pārstrāde (utilizācija). Svarīgi ir pieminēt to, ka materiāli neizdala kaitīgus ķīmiskos savienojumus, ir ilgi ekspluatējami [10], [11], [12]. Materiāliem ir jāsniedz visas dizaina funkcijas, jābūt vizuāli un estētiski pievilcīgiem un elpojošiem. Svarīgi ir izvelēties tādus būvmateriālus, kuriem ir labvēlīga iedarbība uz labsajūtu un veselību, mazs enerģijas patēriņš un nekaitīgs ražošanas process, reģenerēšanās un atkārtotas izmantošanas iespējas, materiāliem ir jābūt piemērotiem un ir jāizmanto decentralizēta ražošana [13], [14].

Svarīgi ir izvairīties no indīgu aizsarglīdzekļu un saistvielu izmantošanas, lai tas neradītu ekoloģisku kaitējumu, ja būvmateriāls nonāk apkārtējā vidē [13]. Ilglaicīga ekonomija un racionāla būvniecība ir iespējama, izmantojot dabiskos būvmateriālus un attīstot videi draudzīgas ražotnes. Vietējo materiālu izmantošana un konkrētai vietai raksturīgais būvniecības veids prasa minimālu transportu, un tādā veidā mājai nepieciešamo būvmateriālu ražošanai patērēto enerģiju samazinātu uz pusi [11], [12].

Viens no svarīgākajiem elementiem, kas ietaupa energoresursus mājoklī ir siltumizolācija. Tās galvenais uzdevums ir pasargāt dzīvojamās platības no siltuma zudumiem vai arī no sasilšanas, piemēram, pagrabu. Siltumizolācijas materiālus izgatavo plātņu, paklāju un lokšņu veidā. Visefektīvākais siltumizolācijas materiāls ir gaiss, kurš atrodas tieši miera stāvoklī. Ir svarīgi siltumizolācijas materiālu lietošanas laikā pasargāt no samitrināšanās, jo mitrums paaugstina siltumvadītspēju, kā arī pazemina mehānisko izturība [15].

Siltumizolācijas materiālus ir iespējams izgatavot no organiskām un arī no neorganiskām vielām. Organiskos siltumizolācijas materiālus gatavo no koksnes atkritumiem, kūdras, vilnas, salmiem, koksnes šķiedrām [16], [17]. Plašāk no organiskajiem siltumizolācijas materiāliem lieto fibrolītu, kokskaidu un kokšķiedru plātnes. Neorganiskie materiāli ir azbests, stiklšķiedras un minerāli [15]. Atkarībā no materiāla izcelsmes vietas to var iedalīt trīs grupās – minerālu, sintētiskie un atjaunojamie. Dažos gadījumos produkti var saturēt maisījumu komponentes, piemēram, kaņepju un kaļķa, fibrolīta – koka, vilnas un cementa sajaukumu [11].

Latvijā viens no dabiskajiem materiāliem, kuru var pielietot siltumizolācijas materiālu ražošanā, ir kūdra, jo kūdra ir salīdzinoši lēts un viegli pieejams materiāls [18].

Pētījumu rezultāti par sapropeļa izmantošanu būvniecībā liecina, ka sapropelis ir konkurētspējīgs siltumizolācijas materiālu izveides komponents. Sapropeļbetons ir izmantojams gan siltuma izolācijai (rūpnīcas ēku, saldētavu sienu un pārsegumu, kā arī ierīču un cauruļvadu, gan arī slodzi nenesošu sienu un šķērssienu veidošanai [19]. Gan sapropeļbetons, gan arī kūdras plātnes ir no pilnībā videi draudzīgiem materiāliem veidots, tāpēc sapropeļa un kūdras siltumizolācijas materiālu izveide ir cieši saistīta ar ekoloģisko būvmateriālu nozari.

Siltumizolācijas materiālu kritērijus vai funkcijas un kvalitātes īpašības nosaka un regulē likumdošana, un tiem ir izstrādāti starptautiski piemērojami standarti. Šie kritēriji ir izstrādāti, arī balstoties uz vides prasībām, lielā mērā ņemot vērā dzīves cikla ilgumu. Vācijā ir izstrādāta Eiropas kvalitātes zīme *„Natureplus”*, kas nosaka būvniecības materiālu standartus, kas atbilst materiāla tehniskajiem parametriem un iekļauj arī ekoloģiskā materiāla kvalitātes zīmi. *„Naturplus”* kvalitātes zīme ir piešķirta tādiem siltumizolācijas materiāliem kā linu, kaņepju, aitu vilnas, korķu un citu izejvielu materiāliem [16], [20].

Pētījuma mērķis ir noskaidrot iespējas iegūt sapropeļa-koksnes, kūdras-koksnes siltumizolācijas plāksnes, noteikt optimālās plātnes sastāva attiecības un raksturot iegūto plātņu mehāniskās, siltumvadītspējas un skaņas izolācijas īpašības, kā arī to izmantošanas iespēju izvērtējumu ekoloģisko būvmateriālu nozarē.

II. MATERIĀLI UN METODES

Materiāli

Kūdras-kokskaidu kompozītmateriālu izveidē laboratorijā tika izvēlēta Baložu kūdras lauka kūdra ar 73 % mitruma. Darbā izmantotās kokskaidas ir 0-1,5 cm garas priedes koka skaidas [21]. Sapropelis tika iegūts Pilveļu ezerā, kas ir eitrofs ezers, kurš atrodas Latgales augstienē, Rāznas pauguraine. Sapropeļa virsējais 30 cm biezais slānis tika iegūts ar kameras tipa mīksto iežu urbi. Materiālu izgatavošanā tika izmantots kūdrains sapropelis ar pelnu saturu 11% un organisko vielu saturu – 89%, karbonātu saturu – 0,45%. Izejas sapropeļa mitrums ir 92% un blīvums ir 1,11g/cm^2 [22].

Kompozītmateriālu izgatavošana

Aktivētās kūdras masa ar saistvielas īpašībām tika iegūta, kūdru apstrādājot mehāniski – termisko ložu planetārajās dzirnavās RETSCH PM 400. Aktivēto kūdras masu sagatavoja, izmantojot 300 g kūdras un ievietojot malšanas traukā kopā ar 8 malšanas bumbām un malšanu veicot 30 min ar 300 apgriezieniem minūtē. Sapropelis pirms siltumizolācijas materiālu iegūšanas netika ne mehāniski, ne termiski apstrādāts, bet uzreiz sajaukts kopā ar skaidām. Sapropeļa un koksnes skaidu sajaukšana (izejvielu masas attiecības 1:3) tika veikta manuāli līdz vienmērīgas masas iegūšanai. Pēc tam iegūtā masa tika ievietota veidnē (30×30 cm ar regulējamu augstumu) un noblīvēta pie 0,03 MPa spiediena 3 stundas, lai nodrošinātu blīvāku kompozītmateriāla struktūru, paaugstinātu tā mehānisko izturību, samazinātu galaprodukta rukumu, kā arī rukuma plaisu veidošanos. Sapropeļa-kūdras kompozītmateriāla plāksnes 24 h tika žāvētas 25 °C un 24 h 105 °C.

Kompozītmateriālu testēšana

Kompozītmateriālu testēšanai tika sagatavoti gatavā materiāla paraugi ar atšķirīgu mitruma daudzumu: 0, 5, 10, 15%. Salizturības pārbaude tika veikta, plāksnes izturot pie -18 °C 4 stundas, tad 4 stundas pie +20 °C līdz pilnīgai sasilšanai un tad atkārtoti atdzesējot. Siltumvadītspējas un mehāniskās pārbaudes tika veiktas pēc 5, 10 un 25 saldēšanas-atkušanas cikliem. Kompozītmateriālu paraugiem tika noteiktas mehāniskās, siltumizolācijas un akustiskās īpašības, kā arī veikta izgatavoto materiālu degamības testēšana.

Siltumizolācijas īpašības

Siltumvadītspēja tika noteikta sausām (0%) un mitrām plātnēm (15%), kā arī pēc saldēšanas atkušanas ietekmju izpētes (5, 10, 25 cikli), iegūstot sakarību starp siltumvadītspējas koeficientu un izstrādājuma mitrumu pakāpi. Saldēšanas–atkušanas ietekmju izpēte tika veikta klimata kamerā (Environmental Chamber JHT Series, Model No. YHT-100 z/07-394B. [23]. Sagatavojot materiālus mehāniskajām pārbaudēm klimata kamerā saldēšanas–atkušanas apstākļi: temperatūras amplitūda no +20 °C līdz -18 °C, ilgums 8 stundas. Mitrums klimata kamerā pie pozitīvas temperatūras sasniedza 95%.

Siltumizolācija tika mērīta, izmantojot LaserComp FOX 600 siltumizolācijas mērītāju. Tehniskā informācija nosaka, ka paraugu noteikšanas precizitāte ir 0,025mm. Tests tika veikts ar paraugu biezuma automātisko noteikšanu (parametru intervāls: biezums – 203 mm, platums – 610 mm). Ierīcei ir divas horizontālās plātnes, kuras nodrošina nepieciešamo temperatūru no -15°C līdz +85°C. Abās ierīces devēju plātnēs ir iestrādāti jutīgi sensori siltumplūsmas mērīšanai, un tie atrodas plātņu vidū. Ierīces vadītspējas diapazons ir no 0,001 līdz 0,35 W/mK [24].

Papildus iepriekš minētajām metodēm, tika noteikts kompozītmateriāla siltumapmaiņas procesa ātrums. Lai iegūtu rezultātus starp plātnēm, tika ievietots termometrs, kas nosaka materiāla virmas temperatūras pieaugumu atkarībā no laika. Tas tika veikts, termometru ievietojot starp kompozītmateriāliem, tiem veicot saldēšanas ciklus saldētavā. Process tika vadīts, izmantojot programmatūru Sarmalink_61_offline.

Materiāla mehānisko īpašību testēšana

Lai salīdzinātu kūdras–koksnes plātnes un sapropeļa–koksnes plātnes mehānisko izturību savā starpā un ar citiem siltumizolācijas materiāliem, tiem tika veiktas mehāniskās pārbaudes, tos slogojot speciāli paredzētā iekārtā. Mehāniskās pārbaudes tika veiktas paraugiem, kuriem veikta saldēšanas ciklēšana 5, 10, 25, 54 un 69 reizes un dažāds mitruma saturs: 0, 5, 15%. Mehāniskās pārbaudes tika veiktas uz 5985 Floor Model Universal Testing System iekārtas, kas paredzēta materiālu stiprības noteikšanai statiskā slogojumā, mērījumu precizitāte ir +/- 0.5%, mērījumi tiek nolasīti datorā, kurš ir tieši savienots ar ierīci (Savietojams ar Bluehill ® Software). Būtisku iespaidu uz mehānisko pārbaužu rezultātiem atstāj slogošanas ātrums, testos izmantotais slogošanas ātrums bija robežās no 0,0005 līdz 1016 mm/min. Iekārtas slodzes devēja spēks ir 250kN. Vertikālā testa telpa ir 1430 mm, bet augstums ir 1930 mm [25].

Paraugu mehāniskā pārbaude spiedē tika īstenota paralēli paraugu formēšanas virzienam, kas tika izvēlēts saistībā ar paraugu struktūras īpatnībām, īpaši ņemot vērā mehāniskai pārbaudei domātu paraugu sagatavošanas specifiku (paraugu šķērsgriezumā pildvielas lielākoties atrodas horizontālā plaknē).

Skaņas izolācijas īpašības

Materiāliem tika veikta arī skaņas izolācijas pārbaude. Iekārtas standarts ir ar numuru LVS EN ISO 10534-2:2002 un nosaukumu – „Akustika - Skaņas absorbcijas koeficienta un pilnās pretestības noteikšana pilnās pretestības caurulēs", izmantojot pārejas funkcijas metodi [26]. Tiek izmantota 4 mikrofonu metode akustiskā caurulē (Brüel&Kjær. Impedance/Transmission Loss Measurement Tubes. Type 4206. The Four-microphone Method with PULSE Acoustic Material Testings oftware – Type 7758.) [27].

Skaņas izolācija ir pārvades zudums jeb skaņas redukcijas indekss R (dB), ir grīdas, sienas, durvju vai kāda cita šķēršļa, kas ierobežo skaņas kustību, efektivitātes mērvienība. Skaņas pārvades zuduma mērvienība ir decibels (dB). Jo augstāks ir sienas skaņas pārvades zudums, jo labāk tā ierobežo nevēlamu skaņu iekļūšanu [28].

Iekārta darbojas pēc principa, ka tās vidū tiek ievietots paraugs starp 2 ģipša plātnēm, bet caurules galā ir sūklis, kas absorbē skaņu, lai tā neatbalsotos. Parauga diametrs, kas tika ievietots akustiskajā caurulē ir 98 – 99 mm, bet biezums 45 – 50 mm.

Kūdras–kokskaidu un sapropeļa kokskaidu un priedes koka pašaizdegšanās rezultātu salīdzinājums

Lai spriestu par kompozītmateriālu degšanas raksturlielumiem, tika veiktas vienkāršas degšanas pārbaudes. Tika noteikta temperatūra, pie kuras sākas paraugu pašaizdegšanās. Degšanas eksperimentiem tika izmantota mufeļkrāsns SNOL. Porcelāna tīģeļos tika ielikti paraugi (kūdras–kokskaidas, sapropelis–kokskaidas, kokskaidas) un ievietoti mufelī, uzstādot vienmērīgu T°C pieaugumu līdz 500°C. No katra materiāla mufelī tika ielikti 3 paraugi, karsēšanas procedūru atkārtojot 3 reizes.

III. Rezultāti un diskusija

Kompozītmateriālus veido vienā gadījumā aktivētā kūdra (saistviela) un kokskaidas (pildviela), bet sapropeļa–kokskaidu plātnēs, kā saistvielas tiek izmantots neapstrādāts sapropelis, bet pildvielas – kokskaidas. Kūdras–kokskaidu plātnes izgatavošanai tika izmantota [18] izstrādāta metode, bet sapropeļa–kokskaidu plātnes izgatavošanas metode ir oriģināla.

Iegūtās plātnes ir vieglas, porainas un viegli drūpošas. Sapropeļa–kokskaidu plātne ir drupenāka par kūdras–kokskaidu plātni. Sapropeļa–kokskaidu plātnei krāsa ir zaļgana, gaiši brūna, bet kūdras–koksnes kompozītmateriāla krāsa ir tumši brūna. Izveidoto plātņu augstums ir 4,5 – 5,5 cm, bet platums 29,3 – 30,1 cm. Iegūto plātņu vidējais blīvums ir 234,3 kg/m^3. Minēto parametru vērtības ir atkarīgas no plātnes formēšanas apstākļiem. Plātnēm ir sīkporaina uzbūve ar viendabīgu šķiedru struktūru ar vaļējām un savā starpā savienotām porām. Plātņu izgatavošanas procesā nav nepieciešams speciāls apģērbs vai citi īpaši aizsardzības līdzekļi – jo izejvielas nav veselībai kaitīgas un izgatavošanas procesā neveidojas kaitīgi izgarojumi. Ņemot vērā plātņu iegūšanas apstākļus, izmantotā sapropeļa, kūdras un kokskaidu īpašību variabilitāti, ir iespēja iegūt minētos kompozītmateriālus ar plašu īpašību intervālu.

Tika pētītas iegūto kompozītmateriālu mehāniskās īpašības: noturība pret lieces (1.tabula) un spiedes īpašībām (2.tabula). Laboratorijas apstākļos izveidotajiem paraugiem tika veiktas mehāniskās pārbaudes spiedes pretestības un lieces pretestības noteikšanai.

Mehāniskā stiprība siltumizolācijas kompozītmateriāliem tika pārbaudīta, tos pirms tam testējot pēc sala izturības pārbaudes nosacījumiem, pamatojoties uz N. Brakša pētījumiem par sapropeļbetonu [9]. Salizturības pārbaude ir būtiska, lai pārbaudītu izstrādāto materiālu ekspluatācijas iespējas Latvijas klimatiskajos apstākļos. Atšķirībā no N. Brakša pētījumiem, kad paraugi tieši pirms mehāniskajām pārbaudēm bija pilnībā jāiegremdē ūdenī, šajā pētījumā netika veikta šāda manipulācija. Salizturības testēšana tika veikta pilnībā izžāvētam paraugam, kā arī ar mitrumu piesātinātam (15%), kā arī pēc saldēšanas – atkušanas cikliem (5x, 10x, 25x).

Iegūtie rezultāti sniedz ieskatu par Latvijā pieejamās kūdras un sapropeļa augsti tehnoloģiskās izmantošanas iespējām, tai skaitā būvniecībā, siltumizolācijas materiālos, kā kompozītmateriālos saistvielas veidā. Aktivētas kūdras kā saistvielas iegūšana ļauj izmantot iespēju to aktīvi transportēt un uzglabāt ilgākā laika posmā.

1.TABULA

LIECES MEHĀNISKĀ STIPRĪBA ATKARĪBĀ NO MITRUMA PIESĀTINĀJUMA UN SALDĒŠANAS CIKLU SKAITA

Testētās plātnes veids	Kūdra–koksne		Sapropelis–koksne	
	Slodze liecē, N	Lieces stiprība, Mpa	Slodze liecē, N	Lieces stiprība, Mpa
sauss (0 %)	112	0,153	11	0,015
mitrs (15 %)	125	0,164	18	0,021
gaisa sauss (5%)	111	0,284	n.a.	n.a.
5X	232	0,351	20	0,028
10X	269	0,386	20	0,027
25X	341	0,409	20	0,026

Pēc norādīto reižu skaita (X) - sasalšanas-atkušanas ciklu skaits.

Izmantotā tehnoloģija [18], salīdzinot ar plaši izmantotām kūdras un sapropeļa siltumizolācijas materiālu izveides tehnoloģijām, prasa mazāku enerģijas patēriņu, jo pirmkārt tiek izmantoti vietējie resursi, bet materiāla saistvielas izveidošanas laiks un patērētā enerģija ir daudz mazāka. Svarīgi ir pieminēt žāvēšanas laiku, kas tiek pielietots daudz mazākā mērā, un tas liecina par šādas tehnoloģijas zemāku energoietilpību.

Izejvielu un gala produktu pārstrādājamība atbilst ierobežotu pasaules resursu lietderīgās izmantošanas tendencēm. Tieši runājot par sapropeļa izmantošanu siltumizolācijas materiālos, mērķis ir panākt sapropeļa lietošanu ar mazāku enerģijas pievienošanu pārstrādes laikā, salīdzinot ar kūdras–kokskaidu plātnēm, pievienojot sārmu un tādējādi iegūstot augtākus rezultātus mehāniskajās pārbaudēs.

Rezultāti norāda, ka materiāls ir salizturīgs, jo sasaldējot un atkausējot paraugus, to mehāniskā stiprība, kā apliecina pārbaudes rezultāti uz lieci, nav būtiski samazinājušies. No mitruma daudzuma materiālos mainās plātņu spiedes pretestība. Sapropeļa–kokskaidu vidējā lieces pretestība ir 0,02 MPa, bet kūdras–kokskaidu vidējā spiedes pretestība ir 0,3 MPa.

Lieces rezultātiem pie izvēlētā paraugu mitruma režīma mehāniskās stiprības izmaiņas nav būtiskas. Pēc literatūras datiem, mehānisko pārbaužu lieces rezultātiem atkarībā no mitruma daudzuma paraugā vajadzētu vienmērīgi samazināties, taču iegūtie rezultāti to neparāda. Šādi gatavotiem kompozītmateriāliem to mehāniskās īpašības nepasliktinās uzņemot gaisā esošo mitrumu, kā arī pēc saldēšanas–atkušanas cikliem, kas paaugstina to potenciālu izmantošanai būvniecībā. Ievērojami mazāka mehāniskā izturība ir sapropeļa–kokskaidu plātnēm, kas ir atkarīgs ne tikai no materiāla, bet arī tā sagatavošanas, jo sapropelis atšķirībā no kūdras netika apstrādāts, taču šādu manipulāciju veicot arī ar sapropeli, tā mehāniskā izturība varētu pieaugt. Jāatzīmē, ka tika izmantots sapropelis ar ļoti augstu mitrumu (92%), kuru samazinot varētu iegūt labākas kompozītmateriāla mehāniskās īpašības.

2.TABULA

SPIEDES STIPRĪBA ATKARĪBĀ NO PARAUGA MITRUMA PIESĀTINĀJUMA UN SALDĒŠANAS-ATKUŠANAS CIKLU SKAITA

Testētās plātnes veids	Kūdra–koksne		Sapropelis–koksne	
	Slodze spiedē pie 10% defor-mācijas, N	Kūdras–kokskaidu kompozīta stiprība spiedē pie 10 % lineārām deformā-cijām, MPa	Slodze spiedē pie 10% deformā-cijas, N	Sapropeļa–kokskaidu kompozīta stiprība spiedē pie 10 % lineārām deformācijām, MPa
sauss (0 %)	112	0,153	11	0,015
mitrs (15 %)	125	0,164	18	0,021
gaisa sauss (5%)	111	0,284	n.a.	n.a.
5X	232	0,351	20	0,028
10X	269	0,386	20	0,027
25X	341	0,409	20	0,026

Pēc norādīto reižu skaita (X) - sasalšanas-atkušanas ciklu skaits.

Rezultāti norāda uz to, ka materiāls ir sala izturīgs. Atkarībā no mitruma daudzuma mainās plātņu spiedes pretestība. Sapropeļa–kokskaidu vidējā spiedes pretestība ir 0,06 MPa, bet kūdras–kokskaidu vidējā spiedes pretestība ir 0,13 MPa. Spiedes pretestības rezultāti norāda uz to, ka kompozītmateriālu stiprība ir pietiekama, lai ar tiem veiktu montāžas darbus, līmējošus savienojumus.

No iegūtajiem rezultātiem var secināt, ka nejaušās spiediena izmaiņas var manāmi ietekmēt izgatavojamo paraugu izturību, tādēc šim apstāklim jāvelta īpaša uzmanība.

Spiedes rezultātu variabilitāti pie izvēlētā paraugu mitruma režīma un saldēšanas ciklu skaita varētu izraisīt kompozītmateriālu izgatavošana un to sagriešana, lai noteiktu mehānisko stiprību. Izstrādāto kompozītmateriālu salizturību ietekmē to izgatavošanas process, kurā ir jāpanāk homogēnāka saistvielas un pildvielas samaisīšana. Samazināt rezultātu izkliedi un paaugstināt mehānisko stiprību varētu, pārejot no roku maisīšanas tehnoloģijas uz mehānisku samaisīšanu.

Tā kā viena no nozīmīgām jebkura būvmateriāla īpašībām ir to spēja izolēt skaņu, tad bakalaura darba ietvaros tika veikta izstrādāto materiālu skaņas izolācijas īpašību izpēte (3. tabula).

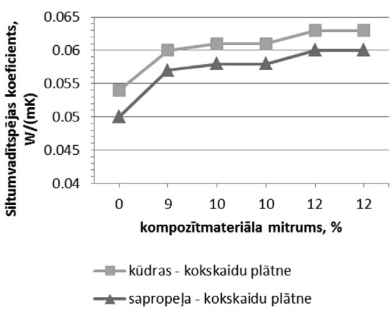
3.TABULA

SKAŅAS IZOLĀCIJAS TESTU REZULTĀTI, IZMANTOJOT 4 MIKROFONU METODI

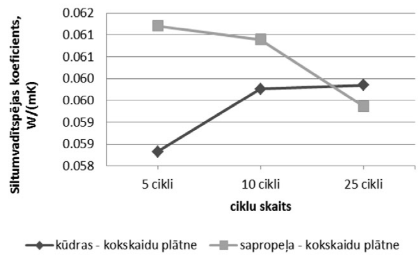
Testētā plātne	Skaņas izolācija, dB
Kūdras –koksne	30
Kūdras –koksne	32
Sapropelis - koksne	32
Sapropelis - koksne	31

Viena no būtiskākajām prasībām ēku būvniecībā ir skaņas izolācija. Pārlieku liels troksnis rada lielu stresa risku un traucē sarunāties, kā arī tiek uztverts kā vides piesārņojums [29].

Iegūtie skaņas izolācijas rezultāti liecina par kompozītmateriāla ļoti labām izolācijas īpašībām. Salīdzinot ar citiem ekoloģiskajiem siltumizolācijas materiāliem, piemēram, linu šķiedru siltumizolācijas materiālu, rezultāti ir sliktāki, un tie atšķiras par 14 vienībām. Linu šķiedru materiālam skaņas absorbcijas rezultāts pēc literatūras datiem ir 45 dB, bet linu – vilnas siltumizolācijas materiāls aiztur 40 dB skaņas absorbciju [30]. Veicot jaunus pētījumus, rezultātus ir iespējams uzlabot.



1. att. Kūdras kokskaidu un sapropeļa – kokskaidu siltumvadītspējas koeficients atkarībā no mitruma piesātinājuma kompozītmateriālā.



2. att. Kūdras – kokskaidu plātnes un sapropeļa – kokskaidu plātnes siltumizolācijas koeficients atkarībā no parauga saldēšanas ciklu skaita.

Ņemot vērā skaņas izolācijas īpašības, var secināt to, ka smagāks materiāls ir labāks skaņas izolācijas sfērā. Kā labākos pieejamos skaņas absorbcijas materiālus Latvijā min kokšķiedru universālā pielietojuma plātnes, minerālās vates blīvākos paraugus un korķa izstrādājumus [31].

Siltumvadītspēja ir materiāla spēja caurvadīt siltumu no tā vienas virsmas līdz otrai, ja starp tām ir temperatūru starpība, un to raksturo siltumvadītspējas koeficients. Jo mazāks ir šis koeficients, jo kvalitatīvāks ir siltumizolējošais materiāls. Siltumizolāciju lielā mērā ietekmē tilpummasa, mitrums [15] un porainība.

Sapropeļa–kūdras kompozītmateriāla un kūdras–kokskaidu kompozītmateriāla plātnēm tika veikta siltumvadītspējas pārbaude, mainot plātnes mitruma rādītājus un saldēšanas ciklu skaitu katrai plātnei.

Tika mērīta siltumvadītspēja gan paraugiem, kuriem ir dažāds mitrums (1.attēls), gan paraugiem, kuriem ir dažāds saldēšanas ciklu skaits (2.attēls).

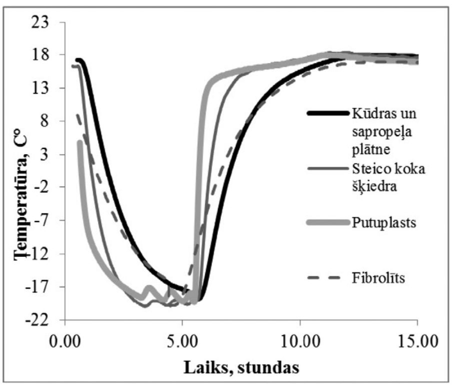
Pēc rezultātiem var spriest, ka kūdras–kokskaidu materiāls un sapropeļa– kokskaidu materiāls ir ar līdzīgiem rādītājiem, tādējādi šiem siltumizolācijas materiāliem ir līdzīgs potenciāls un izmantošanas iespējas.

Kūdras kokskaidu un sapropeļa kokskaidu izveidotajām plātnēm ir raksturīga sīkporaina uzbūve ar viendabīgu šķiedru struktūru ar vaļējām un savā starpā savienotām porām. Ir novērojams tas, ka uz materiāla siltumvadītspēju būtiska ietekme ir mitruma daudzumam. Vidējais sapropeļa–kokskaidu siltumvadītspējas koeficients ir 0,067 W/(mK), bet kūdras–kokskaidu vidējā vērtība ir 0,060 W/(mK). Kūdras–kokskaidu plātnei veicot saldēšanas ciklus, tās siltumvadītspēja nedaudz palielinās, taču sapropeļa–kokskaidu plātnes koeficients samazinās un kļūst labāks. To varētu izskaidrot ar saldēšanas procesa izraisītu plātnes žūšanas procesu un materiālā esošā mitruma zudumu, kā rezultātā kompozītmateriāla poras ūdens tvaiku vietā tiek aizpildītas ar gaisu, kas ir labāks izolējošais materiāls. Kūdras–kokskaidu plāksnēs mitrums sasniedz koksnes šķiedru piesātināšanas punktu, tālāk materiāla mehāniskās īpašības nepasliktinās un briešana, siltumvadītspēja sasniedz maksimālo vērtību un tālāk nepieaug [32]. Pēc pirmajiem rezultātiem, kas ir veikti ar sapropeļa–kokskaidu plātnēm, var spriest, ka to izmantošana

Latvijas apstākļiem ir ieteicama, jo saldēšanas cikli nepasliktina materiāla īpašības.

Papildus siltumvadītspējas koeficienta mērījumiem un saldēšanas cikliem, tika noteikts siltumvadītspējas koeficienta rezultāts plātnei ar mitruma daudzumu 59%, kas bija 0,101 W/(mK). Lai gan tik augsta dabīga materiāla samitrināšanās nenotiek, šie rezultāti norāda uz augsto mitruma ietekmi uz siltumvadītspēju, kas nosaka tās vienlīdzīgas prasības pret visiem izolējošajiem materiāliem, nodrošinot to izolētību no mitruma.

Literatūrā ir atrodami dati par eksperimentiem, kas ir veikti ar sapropeļa – salmu plātnēm, kas pēc sastāva ir ļoti līdzīgs sapropeļa–kokskaidu plātnei. Salīdzinot ar sapropeļa–kokskaidu plātni, siltumvadītspējas koeficients ir mazāks, tas ir 0,55 W/(mK). Darbā ir uzsvērts, ka mainot, sapropeļa un salmu attiecību, ir iespējams panākt labākus rezultātus siltumvadītspējas koeficientam [33]. 4. tabulā minēto kompozītmateriālu īpašību kopums tika vērtēts, ņemot vērā izmantoto izejvielu (organiska, neorganiska), siltumvadāmības koeficientu, bioloģisko noturību, mitruma ietekmi un ekoloģiskās drošības pakāpi. Izvērtējot siltumizolācijas materiālu siltumvadāmības koeficientus, ir skaidri redzams, ka materiāli, kuros tiek izmantotas dabiskas šķiedras, ir ar zemāku siltumvadāmības koeficientu. Taču pielietojot šādus materiālus būvniecībā, atkarībā no izmantošanas veida un saskares iespējas, ir jānovērtē arī to mehāniskās īpašības, produkta dzīves ilgumu vai nav alerģiju izraisošs.



3. att. Testēto materiālu siltumapmaiņas procesa ātrums.

Eksperimenta rezultāti ar temperatūras izmaiņu kumulatīvo efektu parāda, ka no salīdzinātajiem materiāliem, kūdras–kokskaidu plātne un sapropeļa–kokskaidu plātne uzrāda labākos rezultātus (3. attēls). Respektīvi, kompozītmateriāls vislēnāk atdziest, sasniedzot -20°C 3,8 h laikā, un tas arī vienmērīgāk uzņem siltumu, sasniedzot +18°C. Līdz ar to var spriest, ka materiālam ir vienmērīgāks siltumapmaiņas process un ka to izmantojot konstrukcijās, tam ir izteiktākas termoregulācijas īpašības. Materiāls kļūst augstvērtīgāks tieši pasīvo māju celtniecības izmantošanā, jo regulē iekšējo ēkas klimatu [39]. Pēc iegūtās informācijas iekšējās virsmas temperatūras svārstības ietekmē materiālu dažādā spēja uzņemt (akumulēt) siltumu un pēc tam to atdot. Vislabākie siltumietilpības rādītāji ir dabīgam kokam. Ļoti būtisks rādītājs ir tas, cik ātri ārsiena atdod saglabāto siltumu, tas ir, kāds ir tās atdzišanas ātrums. Ja atdzišana notiek ļoti strauji, tad palielinās izmaksas par apkuri, jo, lai uzturētu nemainīgu nepieciešamo iekšējo gaisa temperatūru, biežāk jāieslēdz apkures sistēmu [40]. Pateicoties tam, vasaras karstajās dienās telpās tiek nodrošināts patīkams vēsums, bet ziemas periodā – mājīgs siltums.

Tika veikts izstrādāto materiālu degšanas riska novērtējums (5. tabula).

5.TABULA

KŪDRAS – KOKSKAIDU UN SAPROPEĻA KOKSKAIDU UN PRIEDES KOKA PAŠAIZDEGŠANĀS ĪPAŠĪBU SALĪDZINĀJUMS

Parauga veids	T °C	T°C, vid. aritmēt.
Kūdras - kokskaidu plātne	345	333
	330	
	325	
Sapropeļa - kokskaidu plātne	290	296
	295	
	302	
Priedes koka skaidas	345	345
	340	
	350	

Uz degšanas pārbaudes iegūto datu pamata ir iespējams secināt to, ka kūdras kokskaidu plātnes pašaizdegšanās temperatūra ir augstāka, nekā sapropeļu–kokskaidu plātnes pašaizdegšanās temperatūra. Tas izskaidrojams ar to, ka paraugi atšķiras pēc blīvuma un šķiedru izkārtojuma paraugos. Respektīvi, kūdras kokskaidu plātnes šķiedru izkārtojums ir blīvāks un starp tām ir mazāk gaisa, taču sapropeļa–kokskaidu plātne ir trauslāka un ar ievērojami zemāku mehānisko izturību. Izmantojot šādu izgatavošanas metodi, šķiedrainā struktūra, kas rodas paraugā, ir ar lielāku daudzumu gaisa, un tas samazinu temperatūru, kurā paraugam sākas pašaizdegšanās (ir lielāka oksidētāja – gaisa skābekļa daudzumu klātbūtne).

4.TABULA

DAŽĀDU SILTUMIZOLĀCIJAS MATERIĀLU RĀDĪTĀJU SALĪDZINĀŠANAS TABULA [9], [34], [35], [36], [37], [38]

Rādītāji	Izejviela	Siltumvadāmība, W/m³	Bioloģiskā noturība	Mitruma ietekme	Ekoloģiskā drošība
Ekovate	Celulozes šķiedra, dabas minerāli (borāti)	0,038 – 0,041	Novērš sēnīšu attīstīšanos	Neietekmē	Absolūti nekaitīga
Stikla šķiedra	Smilts, kaļķakmens, soda	0,047 – 0,052	Nav datu	Nosēžas	Nav datu
„Geokars" siltumizolācijas materiāls	Kūdra, kokskaidas	0,047 – 0,08	Nav datu	Neietekmē	Absolūti nekaitīgs
Minerālvates plāksnes	Metalurģijas sārņi, kalnu ieži, saistošs – fenola spirts vai bitumens	0,047 – 0,084	Noturīga pret sēnīšu iedarbību	Nav datu	Ekspluatācijas laikā izraisa kaitīgas vielas
Sapropeļbetons	Sapropelis, zāģu skaidas, smilts, grants, māli,	0,035	Noturīgs pret sēnīšu iedarbību	Samazinās mehāniskā izturība un siltumvadītspēja	Absolūti nekaitīgs
Sapropeļa - kokskaidu plātne	**Sapropelis, kokskaidas**	**0,067**	**Nav datu**	**samazinās mehāniskā izturība un siltumvadītspēja**	**Absolūti nekaitīga**
Kūdras - kokskaidu plātne	**Kūdra, zāģu skaidas**	**0,06**	**Nav datu**	**samazinās mehāniskā izturība un siltumvadītspēja**	**Absolūti nekaitīga**
Aitas vilna	85% ir dabīgā vilna un 15% poliesteris	0,039	Nav datu	Neietekmē	Nav datu
Fibrolīts	koka ēveļskaidas, cements un ūdens	0,068	Noturīgs	Neietekmē	Dabai nekaitīgs materiāls
Perlīts	vulkāniskas izcelsmes stiklveida ieži	0,045 - 0,05	Nav datu	Nav datu	Nav datu
Stiprināti kaņepes spaļi	neapstrādāti un mineralizēti kaņepes spaļi	0,048	Augsta	Nav datu	Nav datu
„Steicoprotect" koka šķiedras	kokmateriālu atgriezumi	0,040	Nav datu	Nav datu	Nav datu
Arbolīts	koksnes sveķainās šķiedrās un minerālas saistvielas (cementa vaimagnija oksīds)	0,09 - 0,10	Augsta	Neietekmē	Nav datu
Uzpūsts korķis	korķozola mizas	0,032 - 0,045	Augsta	Nav datu	Nav datu
Lins	auga īsās šķiedras, bora sāls, nātrija silikāts	0,037- 0,065	Nav datu	Nav datu	Nav datu
Kaņepju - kaļķa kompozītmate-riāls	Kaņepju spaļi, saistviela	0,0713	Nav datu	Nav datu	Nav datu
Fibrolīts	koka ēveļskaidas, cements un ūdens	0,068	Noturīgs	Neietekmē	Dabai nekaitīgs materiāls

Svarīgi ir pieminēt to, ka koksne ir anizotrops materiāls un tās fizikālās, kā arī mehāniskās īpašības ir ciešā sakarā ar to, kāds ir šķiedru virziens, kuras izmanto [32]. Pēc pārbaudēm var spriest, ka iegūtie materiāli ir ieskaitāmi degošu materiālu grupā, jo, iedarbojoties aizdedzināšanas avotam uz kompozītmateriālu, tas aizdegas, gruzd vai pārogļojas. Pēc aizdedzināšanas avota iedarbības izbeigšanās tas turpina degt, gruzdēt vai pārogļoties. Lai uzlabotu kompozītmateriāla aizsardzību pret uguni un paaugstinātu ugunsdrošību, ir jāveic nepieciešamie ugunsdrošības pasākumi, kā arī jānodrošina materiāla izolētība, piemēram, izmantojot ģipškartona loksnes. Siltumizolācijas plātnes uz koksnes pamata ir iespējams apstrādāt ar antipirēnu, padarot to par grūti degošu vai nedegošu siltumizolācijas materiālu [41], un šis pats risinājums ir izmantojams arī izstrādātajām kūdras–kokskaidu un sapropeļa–kokskaidu plāksnēm, piemēram, pievienojot borskābes piedevas vai citus maztoksiskus antipirētiķus.

Koksnes materiālus apstrādājot ar pretuguns aizsardzības līdzekļiem, tajos samazinās tādi rādītāji, kā liesmas izplatība, degšanas jauda, uguns reakcija. Pastāv divu veidu pretuguns aizsardzības veidi – koksnes piesūcināšana un apdare. Koksnes piesūcināšana ir koksnes virspusēja apstrāde ar darba šķīdumu, to apsmidzinot [42]. Lai pilnveidotu materiālu izmantošanas iespēju, tie ir jāapstrādā ar dažādiem līdzekļiem, kas uzlabo ugunsdrošības rādītāju un bioloģisko noturību, jo tas palielina kompozītmateriālu ilgmūžību un izmantošanas iespējas.

IV. Secinājumi

Izmantojot vietējās izejvielas (kūdru, sapropeli, koksnes skaidas), ir iespējams izstrādāt videi draudzīgus siltumizolācijas materiālus izmantošanai būvniecībā. Izmantojot sapropeli kā līmvielu, pirmo reizi iegūts sapropeļa–kokskaidu siltumizolācijas kompozītmateriāls. Kūdras–kokskaidu un sapropeļa–kokskaidu kompozītmateriāla mehāniskās, skaņas izolācijas un siltumizolācijas rādītāji ir augsti un salīdzināmi ar tirgū piedāvātajiem siltumizolācijas materiāliem. Pētītos kūdras–kokskaidu un sapropeļa–kokskaidu kompozītmateriālus ir iespējams izmantot ekoloģiskajā būvniecībā kā siltumizolācijas materiālu, kā arī, paaugstinot mehānisko izturību, par ēku struktūras elementiem. Iegūtie materiāli teicami nodrošina gāzu apmaiņu (ir "elpojoši"), to sastāvā esošā kūdra un sapropelis spēj absorbēt nepatīkamas smakas un ēkā veidot antibakteriālu vidi. Pētījumā iegūtie rezultāti pierāda, ka sapropeļa–kokskaidu plātnes ir perspektīvas izmantošanai Latvijas apstākļos, jo ir ar augstu salizturību un noturību pret izmaiņām sasalšanas-atkušanas ciklos.

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Vaira Obuka, Aleksandrs Korjakins, Raitis Brencis, Ilmārs Preikšs, Oskars Purmalis, Karina Stankeviča, Māris Kļaviņš. Sapropel/Peat-Wood Chip Insulation Materials and Their Properties

We live in the world, where the population rapidly increases, and local municipalities and governments should think about possibilities of providing sustainable development. The building of new constructions demands many resources. At this time when people pay more attention to ecological building and saving energy resources, the research on local resources and their potential use is very topical, especially, when thinking not only of new buildings, but also of the renovation of existing constructions and heat insulation. Therefore, the sustainable use of local resources as thermal insulation materials is innovative.
In Latvia, there are quiet many peat and sapropel resources, which can be successfully used to create new innovative products. The aims of the research are to make heat insulation materials and to establish their optimal composition and properties. In this study, we made thermal insulation materials using activated peat, sapropel and wood chips and described their properties in comparison with the industrially produced materials.
We tested the optimal composition of products as well as their mechanical, heat insulation and acoustic properties. Results have shown that the obtained materials can be successfully used in constructions as heat insulation materials and elements of constructions. Materials have good thermal insulation capability and stability in our climatic conditions. Parameters of materials and their potential applications can be used to evaluate the development of ecological building and the use of local resources.

Вайра Обука, Александр Корякин, Райтис Бренцис, Илмарс Прейкш, Оскар Пурмалис, Карина Станкевича, Марис Клявиньш. Сапропель- и торфодревесностружечные теплоизоляционные плиты и их свойства

При современных темпах роста городского народонаселения строительная индустрия требует все больше минеральных ресурсов и энергии для создания жилья и инфрастуктуры. Одновременно приходится уделять внимание экологическому аспекту экономии ресурсов и энергии. В этом контексте, весьма актуальны возможности использования местных минеральных и биологических ресурсов при создании новых строительных материалов или улучшения свойств существующих (тепло- и звукоизоляции и др.).

Для Латвии, обладающей значительными ресурсами залежей торфа, сапропеля и высоким уровнем использования древесины в строительстве, весьма актуально создание на их основе новых инновационных материалов.

Полученные показатели механических, звукоизоляционных и теплоизоляционных свойств торфодревесностружечных и сапропельдревесностружечных композитных плит довольно высокие и сравнимы с представленными на рынке подобными материалами. Иследованные сапропель- и торфодревесностружечные композитные плиты возможно применить в экологическом градостроительстве как теплоизоляционный материал, а также с целью повышения механической устойчивости конструкций зданий. Полученные материалы хорошо обеспечивают газообмен в помещениях (стены «дышат»), сапропель и торф, входящие в состав этих плит абсорбируют неприятные запахи и образуют в помещениях антибактериальную среду.

Результаты исследований показывают, что использование сапропель- и торфодревесностружечных композитных плит в строительстве в условиях Латвии весьма перспективны, поскольку обладают повышенной морозоустойчивостью и устойчивы в периоды всего цикла промерзания и оттаивания.

Paper 6

BIODEGRADATION STUDIES OF SAPROPEL-BASED COMPOSITE MATERIALS

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Biodegradation studies of sapropel-based composite materials

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Biodegradation studies of sapropel-based composite materials

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Abstract. Traditional composite materials used for construction purposes currently face many questions regarding their sustainability – mainly because they do not come from renewable sources and due to the problems related to their end-of-life management. These challenges motivate companies and researchers to look at the natural fiber composite materials with increased interest. Usually natural fiber materials in construction are used together with mineral binders, but in this research new organic binder – sapropel (organic rich lake sediments) is used as a binder for natural fiber composite materials with various fillers. In previous research these composite materials have proven their applicability in construction industry due to their sufficient mechanical strength and low thermal conductivity. Thus, in this research evaluation of the biodegradability of composite materials were done, comparing them to natural fiber materials with mineral binders. As a methods respiration intensity of microorganisms in soil and enzyme activity of microorganisms were used. For studied materials biodegradability potential have been examined, depending on the filler properties and presence of mineral matter content in the obtained composite materials.

Key words: Sapropel, Composite materials, Biodegradation, Environmental applications

1. Introduction

One of the key questions regarding development of new construction materials is their sustainability - mainly because industrial construction materials do not come from renewable sources and due to the problems related to their end-of-life management [1;2]. Traditional natural fiber materials partially answer these challenges as they use mineral binders and natural fiber fillers. In this research a new kind of organic binder - sapropel (organic rich lake sediments) is used.

Sapropel-based composite materials can be considered to be a new natural fiber composite materials which are cost effective, recyclable and locally produced, as sapropel is a byproduct of lake recultivation processes and various filler materials, which are byproducts from such industries as agriculture and wood processing, can be used. Natural fiber composite materials should not only have properties required by the industry, but also be biodegradable after the end of their life cycle.

Sapropel can be used in the production of composite materials for building industry, interior functional design objects with both cold compaction techniques and hot–glue press at elevated temperature and pressure [3, 4]. In the previous research of sapropel-based materials prospective area of their application included creation of different composite materials: Sapropel – wood fiber, sapropel – wood sanding dust, sapropel – hemp shives [5], sapropel – wood-chips [6]. In these composite materials sapropel was used as a binder [5, 7, 8]. The research results showed that the use of sapropel as a binder and various byproducts as a filler allows the finished product to be included in the thermal insulation material category according to the technically qualitative indicators. In addition, the results of compressive and flexural strength resistance show that the strength of the composite materials is sufficient to be used in the industry.

Evaluation of biodegradability of various materials in soil is based mainly on the measuring evolved carbon dioxide as a function of time [9]. Microorganisms play an important role in maintaining nutrient cycles in soil (C, N, P, S) by recycling organic matter [10]. The activity of microorganisms depends on soil characteristics, climatic conditions and soil tillage technologies.

Conditions with different humidity were modelled in experiments. Biotechnology often uses so-called slurry systems [11, 12]. Slurry systems with high humidity and water content have a beneficial effect on the activity of biodegradable microorganisms due to the better transfer of substances.

Our study was aimed at comparative evaluating of the biodegradability of ten composite materials, which have been newly-developed from different types of sapropel and wood, hemp derived fillers. Enzyme and respiration activity of microorganisms in soil in the presence of composite materials was chosen as the evaluation criteria of biodegradability.

2. Materials and methods

2.1. Sapropel (binder for composite materials) sampling.

Sapropel sediments were sampled from three lakes in Latvia – Padelis (further: *carbonatic sapropel (CS))*, Veveru (further: *green algae sapropel (GAS))* and Pilvelu (further: *cyanobacteria sapropel (CBS))*, located in Rezekne District, Latgale Region. Loss on ignition (LOI) method was applied in order to estimate moisture content, content of carbonate matter and organic matter of sediments [13]. Moisture content of sapropel was determined after drying at 105°C, followed by organic matter estimation at 550°C for 4 h. The content of mineral substances was determined after heating at 900°C for 2 h.

2.1.1. Fillers for composite materials

Birch wood sanding dust (also known as wood dust) and fiber (also known as wood fibers), and hemp shives were selected as fillers for production of composite materials. Birch wood sanding dust and fiber are industrial by-products coming from JSC "Latvijas finieris" – a plywood manufacturing company. Birch wood fiber was up to 15 mm long and up to 0.1 mm thick (diameter). In addition, hemp shives ("Bialobrezeskie") were taken from "Zalers" Ltd. Hemp shive slices were up to 5.5 cm long and up to 0.6 cm thick.

2.1.2. Composite material preparation and curing

For the developed composite materials three types of raw sapropel have been used as a binder, i.e., green algae sapropel (GAS); cyanobacteria sapropel (CBS) and carbonatic sapropel (CS). Sapropel was mechanically treated by mixing together with electrical hand mixer until smooth and homogeneous material was formed. Mixing of sapropel-filler mass was done manually until homogeneous and smooth mixture was reached at the stage, where filler was fully covered with sapropel. Binder-filler mass ratio was 6:1. Metal molds with dimensions of 30×30 cm and with adjustable height were used for composite material production. The mixture of raw materials was laid in by layers in molds for more dense composite material structure, higher mechanical strength and for minimizing final product shrinkage. Sapropel-filler specimens were cured at the temperature of 80 – 105°C for 36 – 72 hours until the constant weight was reached.

For a reference of biodegradation tests a biocomposite materials with the same filler (hemp shives) were used. Mineral binders developed in previous studies were used for these materials - dolomitic lime consisting of 100% DL60 lime (Dolomite) and hydraulic lime consisting of 60% DL60 lime and 40% calcinated kaolin clay (Clay) [14]. Binder-filler mass ratio was 2:1. Block peat ("Laflora") was also used for composite materials biodegradation studies as a control material.

2.2. Evaluation of the biodegradability of the tested materials

In order to compare the potential biodegradability of the composite materials tested, an experimental scheme was developed: soil microbial enzyme activity and respiration were used as the main indicators [15]. Considering the need for microorganisms to adapt to the substrate, 7-day incubation period was included in the process requiring appropriate physicochemical conditions, growth factors (macro- and microelements, nutrients, vitamins). To accelerate the biodegradation process, the composite materials were placed in the soil amended with a substrate (molasses and a source of vitamins (plant extract)), as well as a consortium of soil-derived microorganisms with a high hydrolytic activity [16]. Altogether *10 composite materials where evaluated.*

Incubation of 0.25 mg specimen for evaluation of the biodegradability of the tested materials was performed in the sealed 100 mL vessels containing 10 g soil at 37 ± 2 °C for 7 days. The composition of the substrate added to the specimens was the following: 10 g clay loam soil, 2 mL mineral broth, 100 µL 30% molasses, 200 µL cabbage leaf extract, 100 µL inoculum (2.0x10^{10} CFU/mL) and 50 mL sterile distilled water [16]. The composition of mineral broth was the following, g/L: $MgSO_4$ – 0.2, $CaCl_2$ – 0.02, KH_2PO_4 – 1.0, K_2HPO_4 – 1.0, NH_4NO_3 – 1.0, $FeCl_3$ – 0.05). Specimens were prepared in three replicates. Soil moisture was 60% of the maximum water capacity. The physicochemical characteristics of clay loam soil are summarized in Table 1.

2.2.1. Respiration intensity of microorganisms

The microbial respiration was tested according to [15] with some modifications. The glass with 5 mL 0.05 M NaOH was placed in the sealed 100 mL vessel as described in 2.5. The respiration was estimated by back-titration of the unreacted NaOH using 0.05 HCl (adding 0.1% phenolphthalein indicator to the NaOH prior to titration). Two measurements of respiration have been made for each vessel with a sample, i.e., at the beginning of incubation and after 7 day of incubation period. Respiration assay was performed at 23 °C for 24h in the dark.

The intensity of the SIE was calculated by the formula [17]:

$$SIE = \frac{(A - B) \cdot 1.1 \cdot 60}{m \cdot h}$$

where,

A - titrated, control sample, mL;

B - titrated for the test sample, mL;

1.1 - coefficient (depends on molarity);

60 - coefficient (for conversion into hours);

m - sample weight, g;

h - trial time, min.

2.2.2. Enzyme activity of microorganisms: fluorescein diacetate hydrolysis

After 7 day incubation period, as described in 2.5., the fluorescein diacetate (FDA) hydrolytic activity of microorganisms was tested. 100 µL specimen was transferred to 1 mL tube containing 400 µL reaction mixture (4 mg FDA, 2 mL acetone, 48 mL 0.06M phosphate buffer, pH 7.6). The mixture was incubated for 60 min at + 37±2 °C [18, 19]. After incubation, 500 µL acetone was added to the specimens to stop the hydrolysis reaction. The optical density was measured at 490 nm using a microplate reader Infinite f50 (TECAN, Swirtzeland). Calibration curve was prepared using the thermally hydrolyzed FDA.

Table 1. Characteristics of the soil used

Parameter	Values	Parameter	Values
N, %	0.20	Electrical conductivity, mS/cm	0.162
C, %	2.06	Water capacity, %	149.47
PO_4^{3-}, μg/g	47.8	Na, mg/kg	14.3
P, μg/g	15.6	Mg, mg/kg	218.5
pH (1M KCl)	6.72	K, mg/kg	146.5
Redox potential, mV	-24.9mV	Ca, mg/kg	1802.6

The soil characteristics of the clay loam used in the experiment was determined (Table 1) using standard soil analysis methods. The Na, Mg, K, Ca content of the specimens was determined using a PerkinElmer AAnalyst 200 atomic absorption spectrometer. A non-electrode discharge lamp (Perkin Elmer) was used as a source, Na measurements were made at 589 nm wavelength, Mg at 285.2 nm, K measurements at 766.5 nm and Ca at 422.7 nm using flame atomization. N_2O, acetylene was used as the oxidizing gas. ANOVA (Anova: Single factor analysis) was used for statistical data processing.

3. Results and discussion

3.1. Composite materials (sapropel sampling)

Sapropel samples differed from one another in terms of moisture, organic matter and carbonates.

Table 2. Characteristics of the sapropel samples

Lake	Moisture,%	Organic matter,%	Carbonates,%
Padelis (carbonatic sapropel; CS)	85.97	15.27	35.57
Pilvelu (cyanobacteria sapropel; CBS)	94.99	84.51	1.26
Veveru (green algae sapropel; GAS)	97.66	86.25	1.18

Characteristics of the sapropel samples are shown in Table 2. For example, Lake Padelis sapropel sample contained 35.57% carbonates, moisture – 85.97%, and color – pale gray-pink. Lake Pilvelis sapropel sample was dark greenish brown with homogeneous and jelly-like structure. Lake Veveru sapropel sample moisture level was comparatively high, i.e. 97.66% and organic matter – 86.25%.

3.2. Evaluation of the biodegradability

Biodegradation experiments were performed by adding the composite materials to the soil amended with nutrients and a consortium of microorganisms with a high hydrolytic activity [16] in order to provide favorable conditions for degradation processes.

3.2.1. Soil microbial enzyme activity after incubation in the presence of composite materials

One of criteria for evaluating the biodegradability of the tested materials could be an increase of microbial enzyme activity, which responded to the presence of bioavailable nutrients. FDA hydrolysis involves the activity of various enzyme groups of microorganisms, i.e., hydrolases, proteases, esterases, lipases, etc. [20]. As shown in Fig.1, after 7-day incubation period all composite materials added to the soil stimulated FDA hydrolysis activity, comparing with the control set. After 7-day incubation period in the batch system, the lowest FDA hydrolysis activity was observed in the non-composite control (Fig. 1). All tested composite materials showed a stimulating effect on the enzyme activity of the microorganisms, with the highest mean value for [GAS-CS/Hemp shives], i.e., 2.01 ± 0.75 μM FDA $h^{-1}g$ dw^{-1} (Fig. 1). Comparison of the FDA hydrolysis activity showed a statistically significant ($p<0.05$) difference between control and composite materials, except CS/wood fibers. Greater FDA hydrolysis activity may indirectly indicate more intense biodegradation processes, as it depends on the availability of nutrients, the concentration of microorganisms, and their physical, chemical and environmental properties [20, 21].

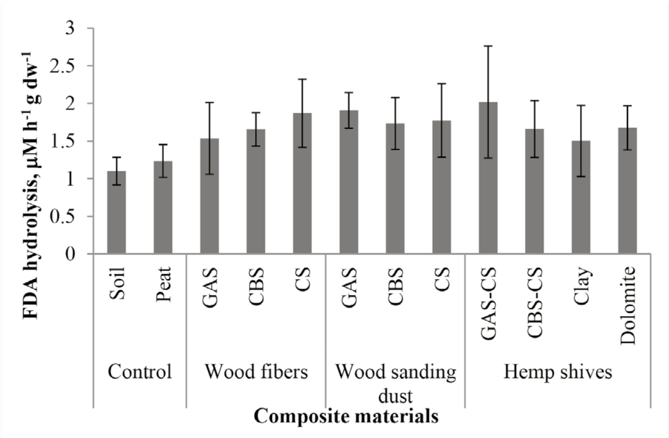

Figure 1. Fluorescein diacetate hydrolysis activity of microorganisms in a clay loam soil amended with nutrients, microbial consortium and composite materials. The ratio of a composite material to the substrate was 0.25:10.0. The substrate was prepared as described in Materials and Methods. FDA activity was measured after 7 day incubation period of a composite material with soil at 37 °C. GAS – green algae sapropel; CBS – cyanobacteria sapropel; CS – carbonatic sapropel. Control – the soil substrate without composite materials.

3.2.2. Respiration intensity of soil microorganisms in the presence of composite materials

The respiration intensity of microorganisms in the experimental batches was observed before and after 7 day incubation period at 37 °C. An increase of respiration intensity in the composite materials has been observed. The amended batches at the beginning of incubation showed statistically significant difference ($p<0.05$) and varied in the range from 31% to 70%, as compared to the control batch (Fig.2 A). The highest respiration intensity was in the soil containing CS/Wood fibers, while the lowest – CS/Wood sanding dust, i.e., 7.68 ± 0.35 and 5.92 ± 0.43 μg C-CO_2 h^{-1} g dw^{-1}, respectively (Fig.2 A). Among the types of composite materials, no statistically significant differences in respiration stimulating effect were found.

Figure 2B summarizes a second test carried out after 7 day incubation period, when readily available substrates have been used by microorganisms. The respiration intensity of microorganisms after 7 day incubation period was considerably lower than that at the beginning of the experiment. This can be explained by the fact that microorganisms have already degraded easily degradable substances. Subsequently, this data indicate the degradation state of comparatively hardly biodegradable substances (cellulose, hemicellulose, lignin) resulting in the original material fractionation in respect to polymer stability. No respiration was detected in the control soil. The highest respiration intensity was detected in CBS-CS/Hemp shives, while the lowest – in CBS/Wood sanding dust, i.e., 2.70 ±0.89 and 0.70 ±0.87 μg C-CO_2 h-1 g dw-1, respectively (Fig.2B).

The obtained data can be interpreted as the potential biodegradability of the tested composite materials under given test conditions. It shows that the materials used are biodegradable but with varying rate. It can be seen that it is mostly dependent on the used filler, the wood sanding dust has the highest biodegradability ratio as it shows the lowest respiration after 7 days, wood fibers and hemp shives have lower biodegradability as they have higher respiration after 7 days. Sapropel binder shows similar reparation as the reference lime binders, as the used sapropel is with high carbonate percentage. The used materials demonstrate that with varying ratio all of the materials are biodegradable and can be used to decrease the overall environmental impact of construction materials.

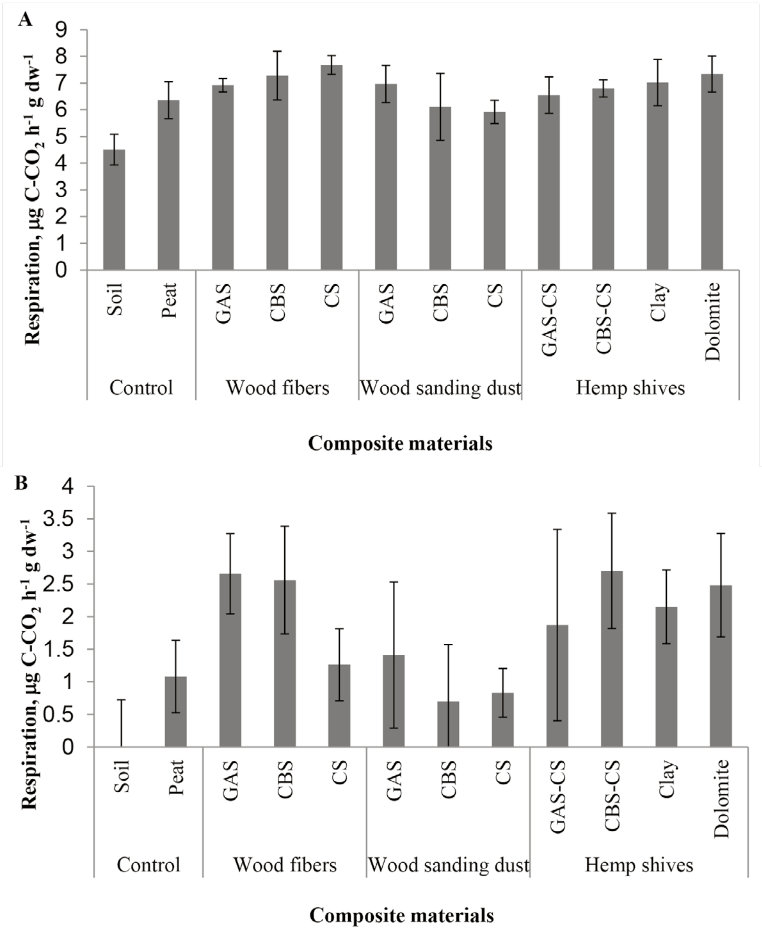

Figure 2. Respiration intensity of microorganisms in a clay loam soil amended with nutrients, microbial consortium and composite materials. The ratio of a composite material to the substrate was 0.25:10.0. The substrate was prepared as described in Materials and Methods. Respiration intensity was measured before incubation (A) and after 7 day incubation period (B) of a composite material with soil at 37 °C. GAS – green algae sapropel; CBS – cyanobacteria sapropel; CS – carbonatic sapropel. Control – the soil substrate without composite materials.

Previous studies of composite materials from peat and cellulose fibers [22] demonstrated reasonably good resistance in respect to destruction, as after a month of incubation their biodegradability reached 20-30%. Overall, in the experiment described above, the highest biodegradation intensity was in materials consisting of peat, 85% cellulose fiber and grape processing by-products. It is explained by the fact that the grape processing residues are an additional filler between the fibers, reducing the fiber content. However, the smallest biodegradation activity was shown in the mixture of peat and 100% cellulose fiber. In turn, the results of biological activity expressed in mg CO_2 per 100 g of substrate indicate the lowest activity in studied composites with increased mineral content [22]. Also our study demonstrate similar trend.

Patnaik and colleagues [23] have explored the biodegradation potential of thermal insulation and sound insulation materials, from wool waste and recycled polyester. Sheep wool showed the highest level of biodegradation over 50 days followed by sheep wool products and a control sample of cellulose fiber. At the same time, recycled polyester showed the lowest biodegradation level. Thus, it can be concluded that composite material, just as those developed in our study at the end of its life cycle, can be used on agricultural land as a nitrogen fixator for plants, thus reducing the fertilizer utilization rate [23].

4. Conclusions

Organic rich lake sediments (sapropel) – a byproduct of the lake cleaning – can be efficiently used to develop composite materials together with other production waste materials. Sapropel of different origin (green algae sapropel, cyanobacteria sapropel and carbonatic sapropel) at the development of composites serves as binder, but birch wood fiber, sanding dust, hemp shives as a filler material. The biodegradability of the obtained composites has been studied and major differences of the biodegradability potential have been found, mostly depending on the filler properties, but also on the presence of mineral matter content in the obtained composites. The obtained results demonstrate potential to use sapropel as a raw material for composites in combination with other waste materials with potential application as construction materials and design products, to extend the life of natural materials and achieve aims of reduction of waste streams.

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Paper 7

MICROBIOLOGICAL STABILITY OF BIO-BASED BUILDING MATERIALS

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Microbiological Stability of Bio-Based Building Materials

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ABSTRACT
The aim of this paper was to study the microbiological stability of bio-based composite building materials, which are made using organic-rich lake sediments (further – sapropel) with lime and magnesium cement as binders and hemp shives as filler. The microbial stability properties of the obtained composite materials were investigated and compared to similar composites. Because of their high organic content, these materials are prone to biodegradation; therefore, they were coated with ALINA LIFE TM organoclay coating, which helps to extend the product life, reducing the rate of biodegradation compared to the biocides used in industry. The effect of the coating on the resistance to decay by the *Aspergillus versicolor*, *Penicillium chrysogenum*, *Alternaria alternata*, *Cladosporium herbarum*, *Chaetomium* sp. and *Trichoderma asperellum* fungi was investigated under different conditions: relative humidity modes of 75% and 99% at 20°C for 45 days and four months. The results indicated that the composites made of sapropel and lime have similar microbial stability properties as lime and magnesium cement binder composite materials. ALINA LIFE TM organoclay coating showed advanced resistance to biodegradation; sapropel-lime composites have shown several good properties that make them suitable to be considered for use in the construction material industry.

Keywords: sapropel; lime-hemp materials; magnesium cement; microbial stability; biocides; organoclay additive

INTRODUCTION

There is a growing need to replace synthetic and fossil (mostly oil- and coal-based) materials with natural ones (Fava et al., 2015) to reduce the impact of exhaustion of non-renewable resources and the adverse influence of the greenhouse gas emissions. Considering the requirements for the application of materials in different industries, composite materials are especially valuable, combining different properties such as high compressive strength, flexibility and low weight. In order to advance the use of natural materials, the properties of these composites should not be inferior to synthetic ones. One of the approaches is to develop the natural material composites that combine binding and structure-forming properties in one product. Organogenic lake sediments (sapropel) are a good natural binder that can replace synthetic binders; sapropel is abundant in lakes in the northern hemisphere, being a waste material after the lake recultivation process.

Sapropel is a partially fine-grained renewable resource: it is an organic-rich lake sediment or sedimentary rock, and it appears in lacustrine environments of inland waters (Kurzo et al., 2004). With its high content of organic matter, sapropel can be used in agriculture and horticulture as a soil fertiliser and soil amendment (i.e. binder for granules). It also has the potential to be used in construction materials as a binder or adhesive substance (Balčiūnas et al., 2016; Obuka, et al., 2015). It is a valuable and available resource of natural origin, and it is estimated that in Latvia the reserves of sapropel in inland waters are around 700–800 million m^3; furthermore 1.5 billion m^3 underlie the peat layer – in total, over 2 billion m^3. Sapropel itself has a high ability to bind, as well as shape-holding capacity, adhesive properties and plasticity (Obuka et al., 2015). Therefore, in this research, it was used as a binder, as has been demonstrated in previous studies (Obuka et al., 2015, Obuka et al., 2017; Balčiūnas et al., 2016b). As its use as a binder does not require thermal processing, it has low embodied energy and low CO_2 emissions, making it very appropriate for use as an ecological insulation material with low environmental impact.

Different natural fibres can be used as structure-forming materials. In this research, hemp shives were used as filler materials in the development of composites. These filler materials are agricultural by-products that need to be recycled. One of the materials that incorporate hemp shives is hemp-lime self-bearing insulation material. It has a positive environmental impact that is directly related to the CO_2 emissions, as both components of the composite have sequestered CO_2: lime during hardening (carbonation) and hemp during growth (Shea et al., 2012). Sapropel, in its formation, has also absorbed CO_2 in the form of organic substances, thus being similar to hemp-lime materials.

In previous studies, sapropel composite materials with various fillers (e.g. wood fibre, hemp shives, or wood sanding dust) have shown the compressive strength from 0.15 to 0.73 MPa, with a density ranging from 200 to 600 kg/m^3, and thermal conductivity from 0.063 to 0.080 W/m×K. These properties are similar to other bio-based building materials, such as hemp-lime concrete (Sinka et al., 2015) or magnesium-hemp concrete (Sinka et al., 2018), thus proving the potential of sapropel composite as a self-bearing insulation material used in construction.

One of the major problems in relation to the development of bio-based building materials is their microbial stability with respect to fungi and other microorganisms. The main cause of microbial growth is excess moisture and dampness from inadequate ventilation or leaking roofs; the concerns regarding this growth are worsening appearance (which leads to material replacement or reinstatement) and loss of mechanical properties, as well as sick building syndrome, which is caused by spores and metabolites of microorganisms and seriously impacts human health. These problems show that the reasons for protection are not simply economical but related to the health issues of the environment at home and in the workplace (Falkiewicz-Dulik et al., 2015; Klamer et al., 2004).

In a study that investigated the biodegradability of sapropel composite materials depending on the filler used, it was concluded that sapropel composites are biodegradable at the end of their life cycle (Obuka et al., 2019). This biodegradability leads to concerns about the microbiological stability of sapropel composites when they are used as construction materials in buildings. Thus, in this study the microbiological resistance of these materials was tested under different humidity and temperature conditions as well as compared to other bio-based building materials: commercially available (such as wood fibre cement boards and hemp-lime composites), experimental (magnesium-hemp composites) and filler only (hemp and flax shives).

Producing the materials with microbiological resistance would be economically beneficial because improving indoor environments could lower the health care costs and increase the worker productivity, resulting in an estimated savings of \$30 billion to \$150 billion annually (Dean & Doris, 2014). It is safe to say that this field of research is important, and the benefits are not only more durable materials, but human health in general.

The indoor concentration of microorganisms depends on various factors, such as the number of bacteria and fungi in the air, ventilation systems (natural, mechanical or mixed), building conservation conditions and indoor climate. The main factor influencing the growth of moulds is the moisture level; it is also influenced by temperature and the properties of the building materials. The optimal relative humidity for human health is 40–60%, at room temperature. The critical level for fungal growth was to be above 75% moisture. Excessive indoor humidity can be caused by such factors as natural disasters, construction failures, improper maintenance of buildings, as well as the initial moisture levels in the materials used in building construction (Apine et al., 2015).

One of the ways to improve the microbiological resistance is to use biocides; in this study, two different biocides were used as additives to composite material mass. The first was ACTICIDE FD (THOR Ltd.), which contains a combination of active substances CIT (chloromethylisothiazolinone, also known as 5-chloro-2-methyl-2H-isothiazol-3-one) and MIT (methylisothiazolinone also 2-methyl-2H-isothiazol-3-one) and is effective against *Aspergillus* spp., *Cladosporium* spp., *Penicillium funiculosum* and others. The second was BACTERICIDE (Elvi Ltd.), containing quaternary ammonium compounds as active substances. However, it must be noted that, according to the EU legislation, the use of active substances in biocides must be lowered several times; as of 1st of May 2020, MIT is classified as allergenic from concentrations as low as 0.0015% (15 ppm), according to the European commission's 13th ATP to CLP (*Commision Regulation (EU) 2018/1480*, 2018).

Biocide leaching from bio-based materials can be considered a problem, as it can lead to decreased efficacy of microbial protection and causes environmental pollution (Paijens et al., 2020). Therefore, it is important to consider and also to test alternatives to traditional biocides that are available in the industry. The chosen alternative to traditional biocides is organoclay technology, which is novel, environmentally friendly, non-leaching and easy to use. As an alternative, montmorillonite mineral material can be used: it is specifically surface treated to change a hydrophilic surface into a hydrophobic, as a result changing the structure and functionality of the mineral. The organoclays are a new type of additive for finishing materials and paints that prevent the negative effects of the external environment on materials, thereby prolonging their longevity and reducing the use of biocides to protect materials (Kostjukova et al., 2017). Organoclay additive material was used as an alternative to composite material mass protection for the sapropel composites and other bio-based building materials in this research.

MATERIALS AND METHODS

Materials

Sapropel

The sapropel sediments were sampled from Lake Pikstere, located in Jekabpils District, Selonia, Latvia. The properties of the sapropel used have been determined in previous research using various methods (Obuka et al., 2017). The sapropel samples differ from each other in terms of organic matter, moisture and carbonate, as well as the ash content. The properties of the sapropel that was used are the following: sapropel type – green algae; moisture – 96.45%; organic matter content in dry matter – 82.67%; ash content of dry matter – 17.33%; pH (water extract) – 6.89; electric conductivity – 124.75 mS/cm^2; non-H density – 1.028 g/m^3; H density – 1.069 g/m^3; and colour – greenish brown.

Mineral binders

In this research, four different binders were used – formulated hydraulic lime, hydraulic lime, magnesium phosphate and magnesium oxychloride cement. The sample designation can be seen in Table 2. Formulated hydraulic lime (FHL) binder consists of 60% hydrated lime CL90 (produced by Lhoist Poland Ltd.) and 40% metakaolin that was a by-product of porous glass production (by Stiklaporas Ltd. in Lithuania). The hydraulic lime (HL) binder used in hemp-lime construction in Latvia consists of 70% hydrated lime, 20% hydraulic lime and 10% additives. Hydraulic lime is used as a stand-alone binder and as a binder with sapropel, at a ratio by mass of 1:1.

Magnesium phosphate cement (MPC) consists of 55% (by mass) dead-burned magnesium oxide M-76 burned at 1700 ºC (Integra Ltd, Slovakia) and 45% mono-potassium phosphate 0–52–35 (N-P-K proportion) with P_2O_5 content at least 52.1% (Praton SA Ltd). Magnesium oxychloride cement (MOC) consists of caustic magnesium oxide CCM RKMH-F burned at 800 ºC (RHI AG Ltd, Austria) and magnesium chloride hexahydrate $MgCl_2 \cdot 6H_2O$ (Germany) dissolved in water (brine 1:1).

Table 1. Designation of materials and methods used

Designation	
Sample types	
Sapropel-lime-hemp composite	SLHC
Magnesium oxychloride cement	MOC
Formulated hydraulic lime	FHL
Hydraulic lime	HL
Magnesium phosphate cement	MPC
Hemp shives	HS
Flax shives	FS
Wood wool	WW
Wood fibre cement board	WC
Sample designations	
ALINA additive	A
Biocide additive	B
Fungi mixture	F
Control without additive	K

Sample preparation

Mixtures of the samples can be seen in Table 2. Sample preparation and the properties of hemp shives are described in previous research (Obuka et al., 2017); only the sample dimensions differ. For the first stage of the experiment, the samples were prepared in 70×70×70 mm cube moulds, wood wool (WW) was cut with a similar surface area. For the second stage, the samples were prepared in 40 mm diameter and 10 mm high cylindrical forms, with wood fibre cement board (WF) and WW cut with similar surface area; for the second stage, additional samples with lowered mineral binder amount were also produced, using 50% and 20% of the binder amount of the first stage with the same amount of shives, producing the samples with less binder coverage and microbiological protection.

Microbiological stability tests

Two experiments were conducted to determine the microbiological stability. In both experiment stages, the material samples were artificially inoculated with six fungal strains:

1. *Aspergillus versicolor* MSCL 1346;
2. *Penicillium chrysogenum* MSCL 281;
3. *Alternaria alternata* MSCL 280;
4. *Cladosporium herbarum* MSCL 258;
5. *Chaetomium* sp. MSCL 851;
6. *Trichoderma asperellum* MSCL 309.

Aspergillus versicolor and *Penicillium chrysogenum* belong to primary colonisers, *Alternaria alternata* and *Cladosporium herbarum* to secondary, and *Chaetomium* sp. and *Trichoderma asperellum* to tertiary colonisers. Primary colonisers can develop at a relative humidity <80%, secondary at 80–90%, and tertiary at a relative humidity >90% (Stefanowski et al., 2017).

For the experiments, the fungi were grown in Petri dishes, and a suspension of mycelial fragments and spores was prepared from each fungus in sterile distilled water (autoclaved at 121 ºC for 15 min) to obtain OD_{545} 0.16. All six fungal suspensions were mixed in equal amounts. The analysed samples of materials were inoculated with 3 ml or 5 ml of the mixed fungal suspension (depending on the size of the sample).

When the fungal growth was observed, the fungi were identified by macroscopic and microscopic (Leica DM 2000, Leica Microsystems) features, at least to the generic level. The intensity of fungal growth was assessed based on the scale (shown in Table 3) according to the ASTM C1338–96 *Standard test method for determining the fungi resistance of insulation materials and facings* (Klamer et al., 2004).

After visual evaluation, 1.0 ± 0.5 g material samples were removed from the composite material where fungal overgrowth was observed. The samples were divided into smaller fractions with a knife, scissors or tweezers, and placed in plastic tubes. Afterwards, they were poured into 1 ml of sterile distilled water (autoclaved at 121 ºC for 15 min), then shaken vigorously for 5 min. The sample suspension (0.1 mL) was then plated on Malt Extract Agar medium (Oxoid) and the samples incubated at room temperature (20 ± 2 °C) for 5–7 days. The fungal genera were determined with microscopic and macroscopic methods (Klamer et al., 2004).

Incubation conditions

In the first stage of the experiment, the analysed material samples were incubated in two relative humidity modes –75% and 99% RH – at a temperature of 20 °C: 75% RH was found to be the typical operating conditions of bio-based building materials measured during the in-situ tests (Sinka et al., 2018), while 99% RH represents elevated moisture that can occur during drying or improper building

Table 2. Mixtures of the samples

Type	Hemp shives	Water for shives	Sapropel	Hydraulic lime binder	Formulated hydraulic lime binder	Magnesium phosphate cement	Magnesium oxide	$MgCl_2$ brine 1:1	Water for binder
SLHC	1	-	2.5	2.5	-	-	-	-	-
MOC	1	1.25	-	-	-	-	2	1.33	-
FHL	1	1.25	-	-	2.5	-	-	-	1.25
HL	1	1.25	-	2.5	-	-	-	-	1.25
MPC	1	1.25	-	-	-	2.7	-	-	0.90

Table 3. Evaluation of fungal growth on materials (average values)

Evaluation/ Intensity of growth	Characteristics	Colour scale
0	No growth detected microscopically	
1	Microscopically detected growth	
2	Microscopically detected growth covering the whole surface	
3	Macroscopic (visible to naked eye) growth present	
4	Macroscopic growth covering >80% surface	

maintenance. The moisture levels and temperature were monitored with digital sensors. In order to ensure 75% RH, a sodium chloride salt solution was kept in the chamber with the samples. In turn, to ensure 99% RH, the samples were kept in separate sealed boxes with sensors inside, and 3 ml of sterile water was poured on the samples when a decrease in RH level was detected. The visual evaluation of composite materials was performed after 4 months of incubation.

In the second stage of the experiment, the samples were kept only at an RH of 99% and a temperature of 20 ± 2°C; the visual assessment was performed after 45 days. In order to ensure 99% RH, the samples were poured with 3 ml of sterile water twice a week, thus maintaining a humid environment simulating rain condition.

Additional antimicrobial protection

For the first stage of the experiment, ACTICIDE FD – a combination of CIT and MIT – was used for additional biological protection tests. It was added to the composite materials in the amount of 1% of the total mass. It is effective against *Aspergillus* spp., *Cladosporium* spp., *Penicillium funiculosum* and others (Thor, 2020).

In the second stage of the experiment, the BACTERICIDE biocide was used as an active substance containing quaternary ammonium compounds. It was added to the composite materials in the amount of 1% of the total mass.

In both the experiments, the *ALINA Ltd.* product ALINA LIFE TM organoclay coating was used for additional biological protection. It was added to the composite materials in the amount of 4% of the total mass.

a) b)

Fig.1. Control samples of wood wool covered with *Trichoderma* (A) and MPC composite covered with *Penicillium* and *Aspergillus* (B)

RESULTS

The first stage of the experiment

Out of the 75% RH material samples, only MPC and WW showed an overgrowth (Figure 1); no fungal overgrowth was observed on other samples. Under such humidity conditions, only fungi that are in the category of primary colonisers can grow and they have low activity, which results in small overgrowth.

At 99% RH, MPC showed intensity of growth level 4, wood wool showed intensity of growth level 3, and both showed macroscopic fouling with fungi (Fig. 1); the remaining specimens showed intensity of growth level 1 or an increase in microscopically detected fungi. The low microbiological stability of wood wool can be explained by a low pH level of 4.28. Although magnesium phosphate cement has a high pH level of 10.45 that develops with time as the cement hardens (Jia et al., 2019), it has low microbiological stability, which is related to the monopotassium phosphate that is used as a hardener for the binder. The monopotassium phosphate water solution has a pH lower than 7 and can also be used as a concentrated mineral fertiliser (Hegedűs et al., 2017; Shen et al., 2017); thus, the undissolved part of the hardener can serve as a nutrient for fungal growth.

The fungal species found in the samples of the materials are summarised in Table 4, where it can be seen that the main fungi that developed in the samples were those that were inoculated with the suspension, but others – such as *Verticillium*, *Simplicillium*, *Mucor* and *Aspergillus niger* – were also found.

As the first stage of the experiment did not show enough fungal growth to be able to fully compare the different materials, it was necessary to perform the second stage of the experiment. In the first stage, humidity was increased only when a decrease in air RH was detected in the samples with humidity sensors. Although microscopic fungal growth was observed in most of the samples, it can be concluded that such humidity conditions were not sufficient to produce the fungal growth large enough to be compared by visual inspection. Therefore, in the second round of experiments, the control of humidity conditions was significantly increased by adding 3 ml of sterile water twice a week, and the binder amounts for mineral binders were decreased to 50% and 20% of those used in the first stage.

The second stage of the experiment

From analysing the changes in the microbiological stability of composites depending on the concentration of the binder (Fig. 2), it can be concluded that a decrease in the amount of mineral binder decreased the microbiological stability. For MOC, FHL, and HL biocomposites at 100% concentration, the fouling assessment was 0–1.5, at 50% concentration it was 1–3, and at 20% it was 2.5–4 (Fig. 2).

The decrease in microbiological stability correlated with the lowering of pH in the specimens. The lime-based binder biocomposites (FHL and HL) showed higher microbiological stability than the MOC biocomposites, since on the 100% binder specimens fouling was not observed, while on MOC the fouling corresponded to the levels 1–2. At 50% and 20% specimens, this difference disappeared. This can be attributed to the pH level, which for the lime-based specimens was around 12 at 100% but for the MOC was 9.76, while the reduction of binder in 50% and 20% specimens

Table 4. Detected fungi at the first stage of the experiment

Type	Inoc.	C	A	B	pH
MOC	F	*Penicillium, Aspergillus, Cladosporium herbarum*	*Penicillium, Aspergillus*	0	9.76
	K	*Aspergillus, Scopulariopsis*	*Chaetomium*	0	
FHL	F	0	*Simplicillium*	*Verticillium*	11.99
	K	0	0	0	
MPC	F	*Aspergillus, Penicillium*	-	-	10.45
	K	0	-	-	
WW	F	*Trichoderma*	-	-	4.28
	K	*Aspergillus niger, Trichoderma*	-	-	
SLHC	F	*Aspergillus*	*Scopulariopsis*	0	12.18
	K	*Aspergillus, Chaetomium*	0	0	12.16

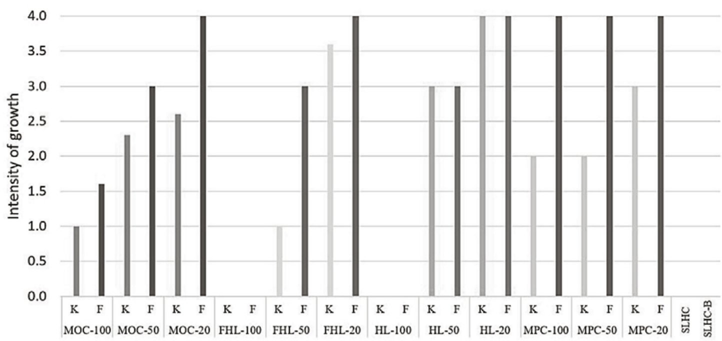

Fig. 2. The second stage of the experiment: fouling depending on binder.

resulted in a similar pH and microbiological stability (Table 5).

The decrease in microbiological stability in the MPC biocomposites was less pronounced, as the intensity of growth at 100% concentration was 2–4, while at 20% it was 3–4. Such an increased intensity of growth in MPC was similar to the results of the first stage of the experiment and can be explained by the impact of the hardener, potassium phosphate. Although the growth was found on local spots, it was evaluated as level 4; this can be seen as a drawback of the visual assessment method and scale used as, for example, there was no distinction between the HL-20 (Fig. 5) and MPC-20 samples (Fig. 6).

A comparison of the control (K) and fungal inoculated (F) samples (Figure 2) showed that the artificially inoculated samples had an increase of between 20% and 50%. Table 5 shows the diversity of fungal colonies in the samples, as determined by microscopic examination of the fungi. It can be seen from the table that the fungi found in the inoculated samples, mainly *Aspergillus versicolor*, *Penicillium chrysogenum* and *Cladosporium herbarum*, were almost absent in the control samples.

The comparison of the control samples and the samples with improved microbial stability by organoclay additive or biocide coating (Table 5) showed that both types of coating generally improved the microbial stability. The organoclay-added samples showed 13.8% lower overgrowth and those with the biocide product had 9.1% lower. However, this effect was not the same for all formulations. The organoclay additive in HL binder showed no improvement; neither did biocide for the MOC and FHL binders.

The microbiological stability of the biocomposite aggregate hemp shives (HS) was low – the intensity of fungal growth was 3.2–4 (Fig. 3). Some literature sources tend to attribute the antibacterial properties to the hemp shives (Ali, Almagboul, Khogali, & Gergeir, 2012), but the experiments showed fungi fouling on them. However, when compared with the aggregate of similar origin, flax shives (FS), it can be observed that the flax shives were completely covered with fouling (Fig. 3) and fungal growth started much earlier than for the hemp shives. Thus, hemp shives have somewhat better microbiological resistance than flax shives, but with the methods used in this research, they cannot be distinguished as both had macroscopic growth covering >80% of the surface and no evaluation according to the speed of fungal growth has been made, which limits a full interpretation of the research results.

The microbial resistance (Fig. 3) of the reference building materials – wood wool (WW) and wood fibreboard (WF) – was also experimentally tested. The fastest growth of *Trichoderma* on wood wool was due to the low pH 3.63 (Table 4), similar to the first stage of the experiment (Fig. 1). However, the WF samples showed very high microbial resistance and a high pH of 11.8. Only a small amount of *Paecilomyces* was detected in most samples (Table 5).

In the second stage of the experiment, it was discovered that the fungi belonging to the species of *Paecilomyces* and *Stachybotrys* were the most common on the materials included in the research. In some cases, *Penicillium, Acremonium, Cladosporium, Aspergillus, Trichoderma* and *Mucor* were also observed, indicating that the substrates

a) b)

c) d)

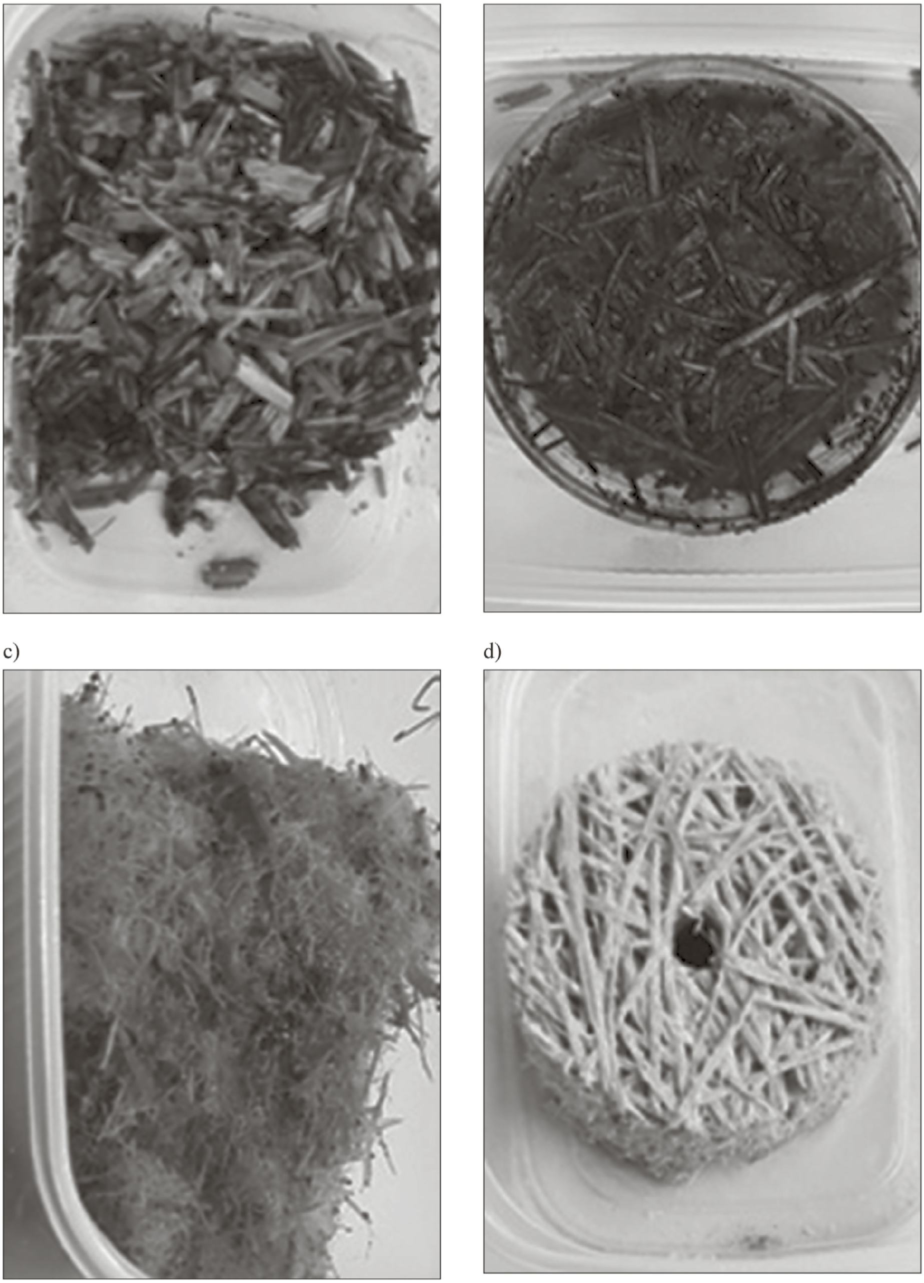

Fig. 3. Materials after microbiological stability tests: A) hemp shives; B) flax shives, C) wood wool; D) wood fibre cement board.

contained sufficient amounts of moisture and nutrients for the fungal development. Most of these fungi feed by cellulose; therefore, they can be found on cellulose-based materials (Bech-Andersen, 2004; Klamer et al., 2004).

Stachybotrys also feeds by lignin and for this reason, it is often found on wood and its products (Vance et al., 2016), and it is also known as black mould (Ding et al., 2018). Since hemp shives contain high levels of lignin and cellulose, this type of fungi can be found on a large number of specimens (Fig. 4–7). The mycotoxins produced by these fungi cause allergic reactions, and they are often associated with various health problems caused by inappropriate indoor microclimate (Hossain et al., 2004).

The environmental reaction (pH) plays an important role in the spread of fungi and bacteria in building materials and was measured in both the first and second stages of the experiment. The composite materials with pH levels up to 8 are more susceptible to colonisation by microorganisms than alkaline cement materials, which have a pH of about 12–14 and are therefore relatively insensitive to colonisation in the early state of the composite. However, over time, the carbonation process lowers the pH of cementitious alkaline materials to about 9, allowing the microorganisms to develop on the materials. Some

Table 5. Assessment of fungal colonies growth in the second stage of experiment

Type	Inoc.	C	A	B	pH
MOC-100	K	1	0	2	9.76
	F	1.6	1	1	
MOC-50	K	2,3	1	1	9.55
	F	3	1	3	
MOC-20	K	2.6	2.3	3	9.55
	F	4	3	4	
FHL-100	K	0	0	0	11.99
	F	0	0	0	
FHL-50	K	1	0	1	9.24
	F	3	3	3	
FHL-20	K	3.6	1	3	9.17
	F	4	4	4	
HL-100	K	0	0	0	12.40
	F	0	0	0	
HL-50	K	3	3	0	8.68
	F	3	3	1.5	
HL-20	K	4	4	4	8.61
	F	4	4	3	
MPC-100	K	2	2	2	10.49
	F	4	4	3	
MPC-50	K	2	2	3.5	10.47
	F	4	3	4	
MPC-20	K	3	3	3	10.32
	F	4	1	1	
HS	K	3.8	4	1	8.50
	F	4	4	4	
FS	K	4			7.25
	F	4			
WW	K	3			3.63
	F	3			
WF	K	1			11.80
	F	0			
SLHC	K	0	0	0	11.99
	F	0	0	0	
SLHC – B	K	0	0	0	12.1
	F	0	0	0	

a) b) c)

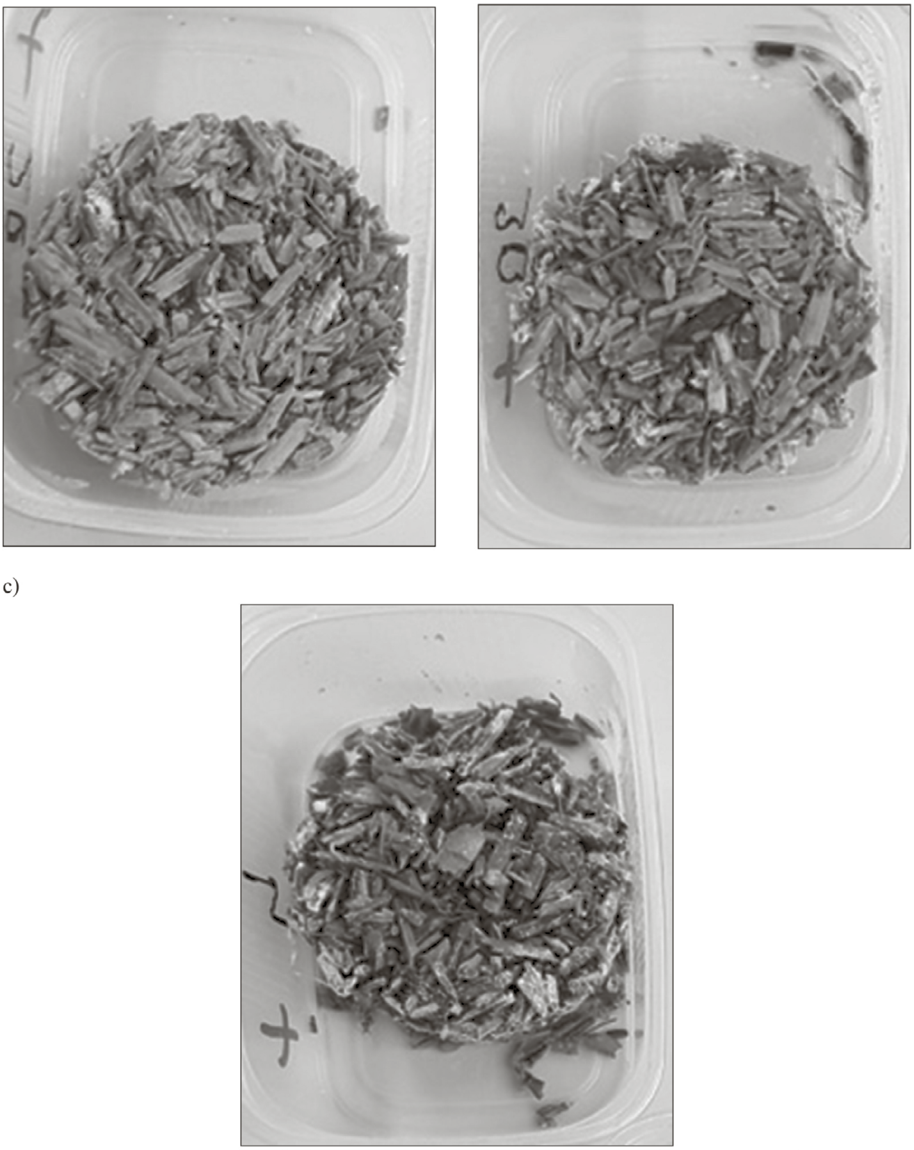

Fig. 4. Magnesium oxychloride biocomposites with varying binder amount: A) MOC-100, B) MOC-50, C) MOC-20

studies have examined the accelerated carbonate contamination of mortars and show that their bioavailability is significantly increased. Thus, such composites can be a significant source of indoor air pollution (Verdier et al., 2014).

DISCUSSION

Composite materials are especially valuable, as they reflect the requirements for the application of materials in different industries, by combining

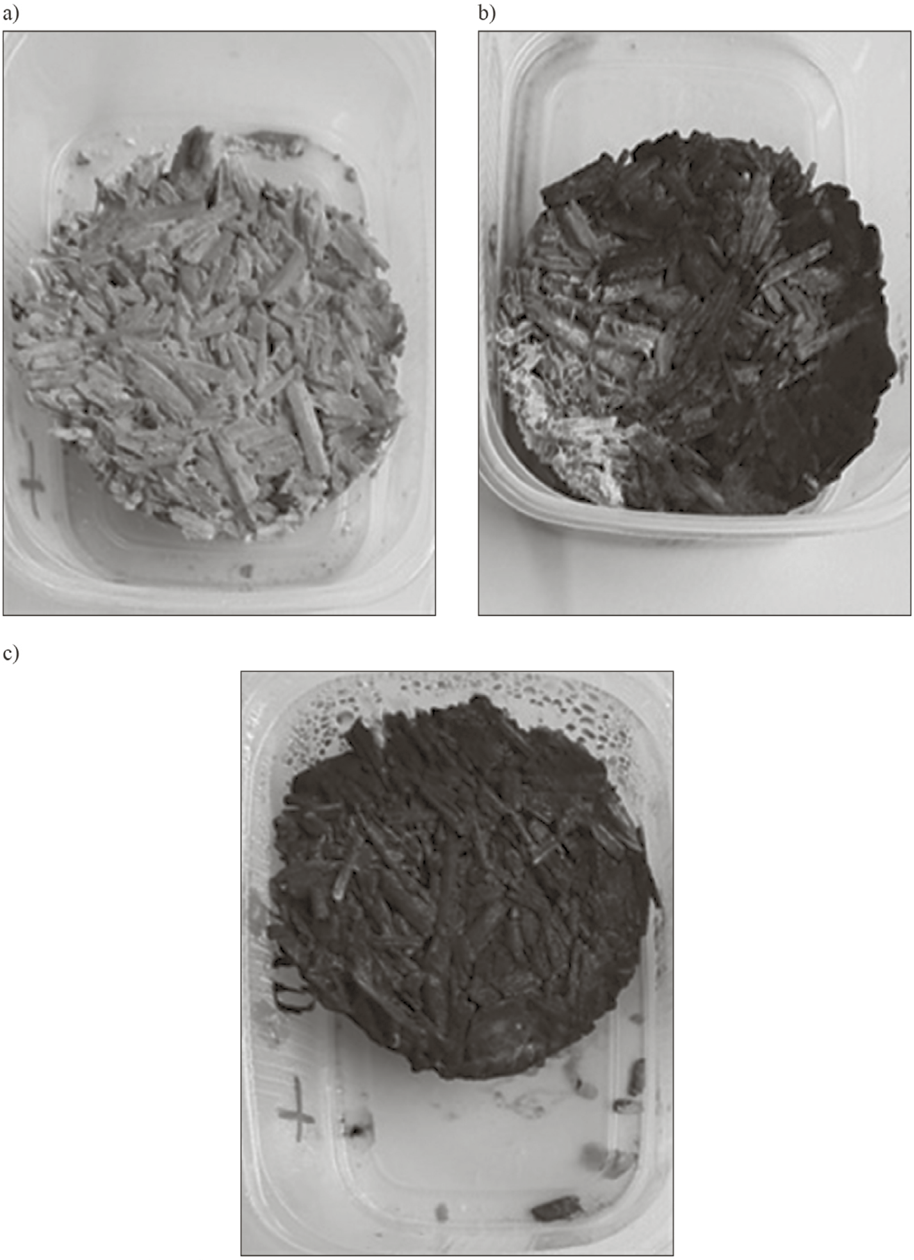

Fig. 5. Hydraulic lime biocomposites with varying binder amount: A) HL-100; B) HL-50; C) HL-20

various properties such as carbon neutrality and renewable raw material source. However, they need to gain microbial resistance and suitable strength properties to further develop their uses in the market. In order to develop the use of natural materials, the properties of these composites

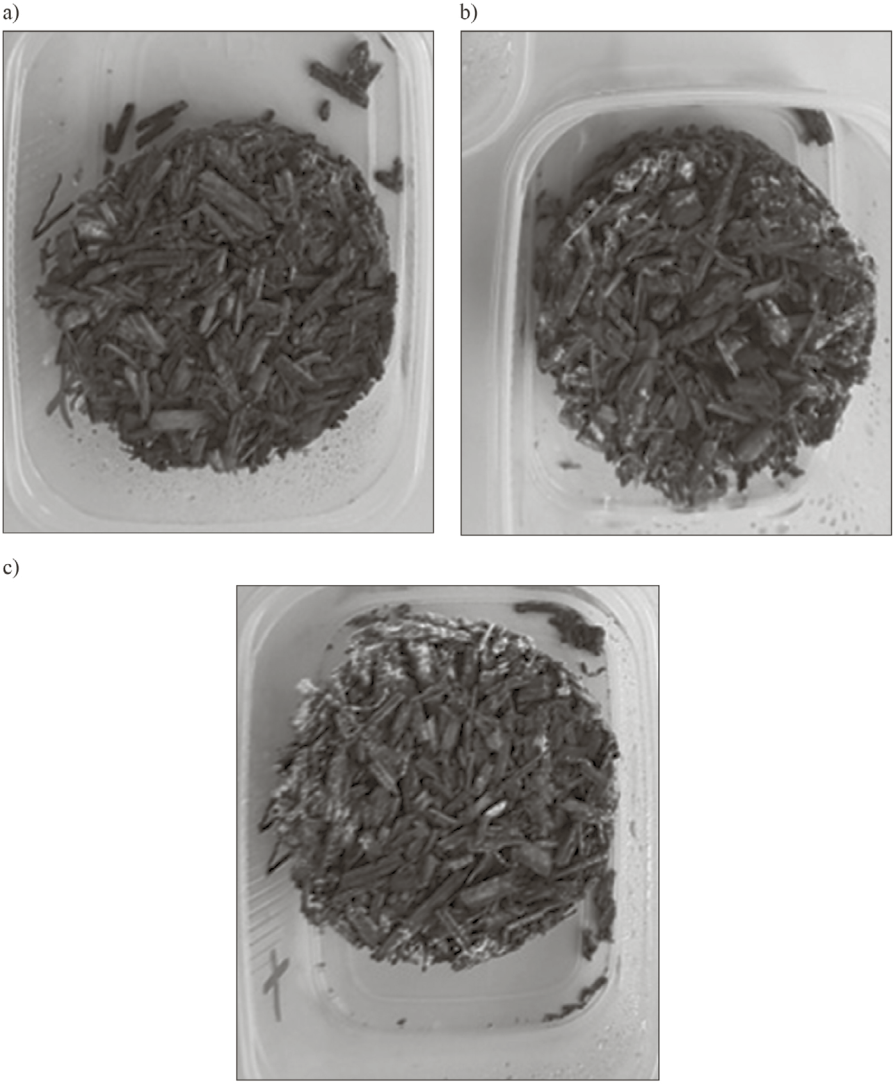

Fig. 6. Magnesium phosphate biocomposites with varying binder amount: A) MPC-100; B) MPC-50; C) MPC-20

should not be inferior to the artificial ones. This study, which is a continuation of previous studies on the microbiological stability of materials, uses a new binder – organogenic lake sediments (sapropel) – that shows its effectiveness in comparison with the building materials currently used in the industry. Sapropel is a good natural binder that can replace synthetic and mineral binders and is a waste material after the lake recultivation process that should be reused in high value-added products. With its high substance of organic matter, it can be used in construction materials as a binder or adhesive substance (Balčiūnas et al., 2016; Obuka et al., 2015). Sapropel is a valuable and available resource of natural origin.

The same humidity conditions, i.e. 99% RH, were used in both test stages, but they were created in different ways. In the first stage, the humidity level was monitored by sensors and, when it dropped below 99%, it was manually increased

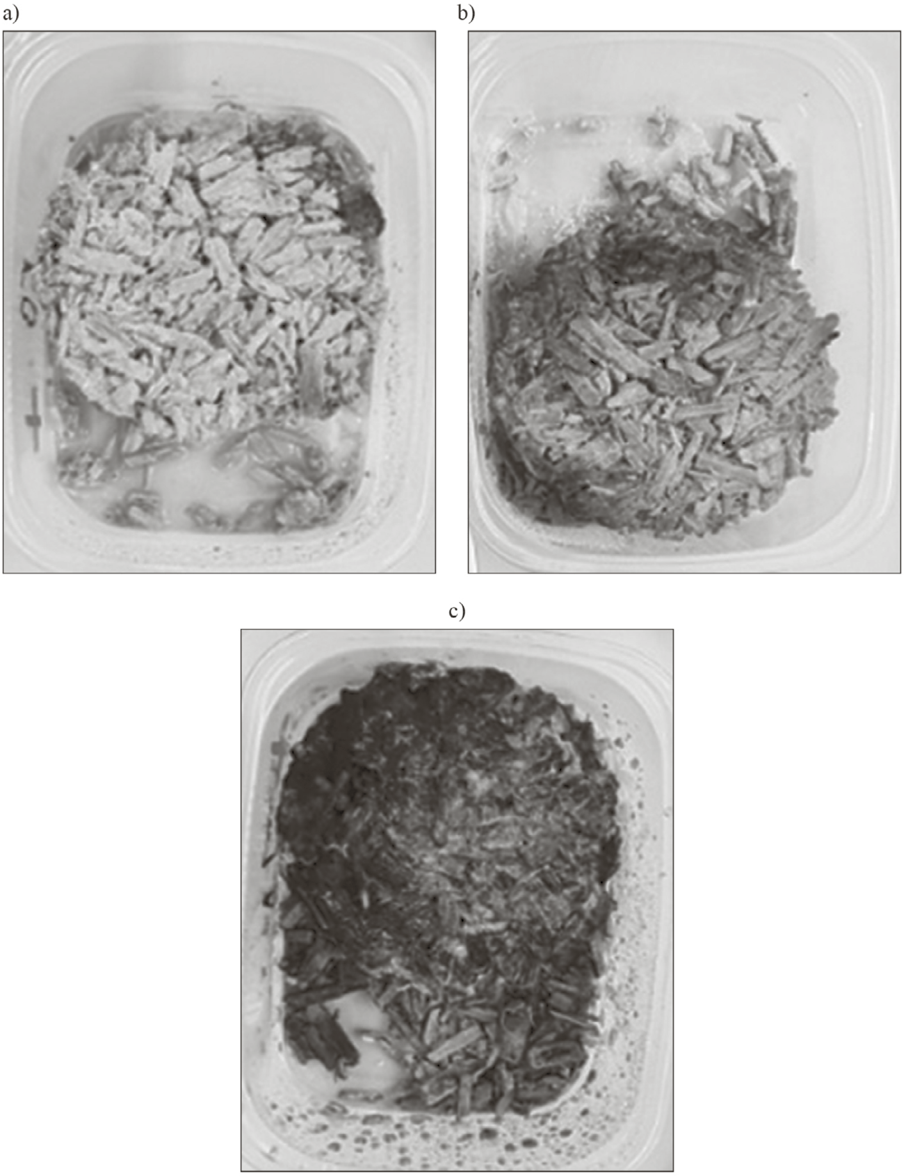

Fig. 7. Formulated hydraulic lime biocomposites with varying binder amount: A) FHL-100; B) FHL-50; C) FHL-20

by adding 3 ml of water to the samples. In the second stage, the humidity level was maintained by sprinkling the samples twice a week with 3 ml of sterile water, so that the samples were significantly wetter in this part of the test. Although microscopic fungal growth was observed in most of the samples of the first stage, it can be concluded that such humidity conditions were not sufficient to produce the fungal growth large enough to be compared by visual inspection. On

Table 6. Detected fungi and other organisms on samples

Type	Inoc.	C	A	B
MOC-100	K	*Paecilomyces*	*0*	*Paecilomyces*
	F	*Paecilomyces*	*Paecilomyces*	*Paecilomyces*
MOC-50	K	*Paecilomyces*	*Paecilomyces*	*Paecilomyces*
	F	*Paecilomyces, Scopulariopsis*	*Paecilomyces*	*Paecilomyces, Aspergillus, Cladosporium*
MOC-20	K	*Paecilomyces*	*Paecilomyces*	*Paecilomyces*
	F	*Cladosporium, Paecilomyces, Scopulariopsis*	*Aspergillus, Paecilomyces, Scopulariopsis*	*Paecilomyces, Scopulariopsis*
FHL-100	K	0	0	0
	F	0	0	0
FHL-50	K	0	0	0
	F	*Scopulariopsis, Cladosporium, Aspergillus, Paecilomyces*	0	*Scopulariopsis*
FHL-20	K	*Acremonium, Paecilomyces*	*Paecilomyces*	*Scopulariopsis, Paecilomyces*
	F	*Cladosporium, Scopulariopsis*	*Paecilomyces, Scopulariopsis, Stachybotrys*	*Paecilomyces, Scopulariopsis, Cladosporium*
HL-100	K	*0*	0	0
	F	*0*	0	0
HL-50	K	*0*	0	0
	F	*Aspergillus, Cladosporium, Paecilomyces*	*Paecilomyces, Chaetomium*	*Paecilomyces*
HL-20	K	*Scopulariopsis, Paecilomyces*	*Paecilomyces*	*Paecilomyces*
	F	*Paecilomyces, Chaetomium, Penicillium, Trichoderma, Cladosporium, Coprinus comatus, Scopulariopsis, Stachybotrys*	*Paecilomyces, Coprinus comatus, Scopulariopsis*	*Paecilomyces, Scopulariopsis*
MPC-100	K	*Scopulariopsis*	*Paecilomyces*	*Paecilomyces, Scopulariopsis*
	F	*Paecilomyces, Scopulariopsis,* Actinobacteria, *Readeriella*	*Paecilomyces, Scopulariopsis*	*Paecilomyces*
MPC-50	K	*Paecilomyces, Scopulariopsis*	*Paecilomyces*	*Paecilomyces*
	F	*Readeriella, Paecilomyces, Scopulariopsis*	*Readeriella, Paecilomyces*	*Readeriella, Paecilomyces*
MPC-20	K	*Paecilomyces, Scopulariopsis*	*Paecilomyces*	*Paecilomyces*
	F	*Paecilomyces, Scopulariopsis, nematodes, Readeriella*	*nematodes, Paecilomyces, Mucor, Trichoderma*	*Paecilomyces*
HS	K	*Coprinus comatus, Paecilomyces, Geotrichum*	0	*Chaetomium*
	F	*Mucor, Cladosporium, Chaetomium, Coprinus comatus, Stachybotrys*	*Mucor, Stachybotrys, Coprinus comatus*	*Mucor, Cladosporium, Chaetomium, Stachybotrys, Alternaria*
FS	K	*Scopulariopsis, Acremonium, Coprinus comatus, Paecilomyces*	-	-
	F	Nematodes, *Paramecium, Paecilomyces, Coprinus comatus, Alternaria*	-	-
WW	K	*Paecilomyces,*	-	-
	F	*Trichoderma*	-	-
WF	K	*Paecilomyces*	-	-
	F	-	-	-
SLHC	K	0	0	0
	F	0	0	0
SLHC – B	K	0	0	0
	F	0	0	0

the other hand, in the second part, increasing the moisture level resulted in a significantly higher level of fungal growth, which fully allowed the samples to be visually compared with each other. This variation in the results suggests that there was a difference in the conditions under which the sample was kept, because although the RH was 99% in both test stages, the regularly moistened samples were more favourable for fungal growth. Such elevated humidity is useful to assess the differences between various materials, but it should be noted that it represents very aggressive environmental conditions – the exposure to precipitation moisture – in which the tested materials would not be used. Therefore, the test results cannot be interpreted as material inability to resist biodegradation, but only to be used for comparison with each other and with other commercially available materials. Other researchers found that using high RH (93%) and increasing the temperature to 30ºC yielded the conditions favourable for mould growth and for the comparison of different materials (Laborel-Préneron et al., 2018).

Comparing the materials, it can be seen that the biocomposites of sapropel, lime and magnesium oxychloride cement binders have an equally high level of protection against biodegradation because at a medium level of binder they do not show fungal growth even under high humidity conditions. This result is equivalent to the results of a commercially used building material with biomass filler – wood fibreboard – and is even better than the result of wood wool, which shows growth even with reduced air humidity. This leads to the conclusion that these materials have the potential to be used as construction materials under the conditions where they are protected from the effects of external moisture. Magnesium phosphate biocomposites show lower microbial resistance, so their use in construction is possible only in combination with additional additives that would provide the protection against fungal exposure.

The organoclay-coated samples showed 13.8% lower overgrowth and biocide products showed 9.1% lower overgrowth. The observed improvement is not significant, but at the same time, it demonstrates that adding supportive coating with appropriate biocides or their alternatives can prolong the life of natural composite materials. However, this effect was not the same for all formulations.

Considering that the organoclay additive in HL binder showed no improvement, it could be due to a pH level decrease that leads to more active microbial growth, or it may be that the concentration of organoclay additives needs to be increased or that there is organoclay incompatibility with the HL binder. When using organoclay as a biocide alternative, it needs to be considered that it is not possible to substitute biocides in a ratio of 1:1. Current testing demonstrates that the biocides could be substituted with organoclay additive in a ratio of 1:4, which leads to the discussion of cost-effectiveness of the used alternatives available in the industry. The finding that the biocide ACTICIDE FD BACTERICIDE with MOC and FHL binders showed no improvement leads to the consideration that either the concentrations are too low or there is biocide incompatibility with MOC and FHL binder formulations.

The visual assessment method can be used effectively, but only in combination with microscopic methods. Studies often estimate the distribution of fungi on a plot as a percentage or points (Table 5) and assume that if the percentage is high, the surface of the composite will be discoloured. However, even if nothing can be seen with the naked eye, the whole sample can be completely covered with mould, which was also proven in this study (in the first stage of the experiment); therefore, microscopic methods were also used in this study. Using only visual expert judgment in a study can give poor insight into the microbiological resistance and stability of the analysed composite materials. It may also be that a fungus with a strong effect on the material can give a low percentage share; strong, but heterogeneous, well-developed growth would yield a low percentage (Johansson et al., 2014)

Fungi vary in their water requirements and represent different groups in the successional colonisation order (Johansson, 2014). Fungi are a series of micro-fungi belonging to various systematic categories. In their natural cycle, they act as decomposers and their spores are found in the air and on various types of surfaces. Under appropriate conditions, spores germinate, and hyphae grow to form mycelium. This process can occur in parts of the building structure and on internal surfaces, with the risk of adversely affecting the indoor environment and human health. The development of such fungi entails significant costs due to the need for renovation, so both economic reasons and health protection are important grounds for reducing the mould risk of buildings. The conditions for fungi growth include appropriate nutrient availability, temperature, pH and humidity. In general, the availability of water in the material is considered to be the decisive condition for the growth of the fungi.

Ultimately the best way to determine the susceptibility of materials to fungi is to physically test the subject material. One of the aims of this study was to evaluate the susceptibility of the materials used to mould growth under varying conditions and methods of inoculation, using the visual assessment and microscopic methods, and the set aim has been fulfilled. Because the materials used in the study are of natural origin and contain wood and fibre plant materials, processing is required to ensure the antimicrobial activity and protection (Stefanowski et al., 2017).

CONCLUSIONS

The following conclusions can be drawn from both stages of the experiment and the analysis of their results:

1. Lime-based binder biobased composite material shows the highest microbiological stability. This is attributed to the pH level, which for the lime-based specimens is around pH 12 at high binder concentrations. However, as the amount of binder decreases, the pH level and microbiological stability of biocomposites also decreases and they become more similar to biocomposites of other binders.
2. Magnesium oxychloride cement biobased composite material show slightly lower microbiological stability at high binder content, as their pH is around 10, but as the binder decreases, the pH does not fall as fast as lime binder biocomposites; thus, at lower binder amounts, the lime-based and magnesium oxychloride cement biocomposites have similar microbiological stability.
3. Magnesium phosphate cement biobased composite material have the lowest microbiological stability among mineral binders because, although the pH of the binder increases above 10 during curing, it does occur over time and the monopotassium phosphate water solution that is used as a hardener for the binder has a pH lower than 7; it can also be used as a concentrated mineral fertiliser; thus, the undissolved part of the hardener can serve as a nutrient for fungal growth.
4. Bio-based composite material, where sapropel was used as a binder, shows one of the highest microbiological stability results. In addition, fungi and other organisms were not detected on the samples.
5. The tested sapropel, lime and magnesium oxychloride cement biobased composite materials have a higher microbiological resistance than the commercially used wood wool insulation; therefore, they have the potential to be used in construction under similar conditions, i.e. in structures protected from external moisture.
6. Using visual expert conclusions, as in this study, can give a modest insight into the microbiological resistance and stability of the studied composite materials. It may also be that a fungus with a robust effect on the material can give a low growth percentage share.
7. The organoclay-added samples showed 13.8% lower overgrowth and those with the biocide product had 9.1% lower; however, incompatibility was observed with formulated hydraulic lime (20%), magnesium oxychloride cement (20%), hydraulic lime (20%) and magnesium phosphate cement (100%) binders.

Acknowledgments

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Paper 8

GRANULATION OF FLY ASH AND BIOCHAR WITH ORGANIC LAKE SEDIMENTS – A WAY TO SUSTAINABLE UTILIZATION OF WASTE FROM BIOENERGY PRODUCTION

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Research paper

Granulation of fly ash and biochar with organic lake sediments – A way to sustainable utilization of waste from bioenergy production

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ABSTRACT

The main waste generated during the thermochemical processes of biomass burning used for bioenergy production in cogeneration plants are ash and biochar which can be used as fertilizers in forestry and agriculture. However, several difficulties are attributed to possibilities of practical exploitation of ash and biochar due to the transporting, handling and mode of application. Granulation of energy generation waste has been shown in some circumstances as a cost-effective and environmentally friendly method. Production of granules (pellets) from wood ash and biochar leads to improved recycling and logistics of waste as well as helps to control and avoid undesirable environmental effects such as leaching of nutrient excess.

The aim of this study was to prepare granules from wood fly ash and biochar mixed with organic-rich freshwater lake sediments (sapropel) used as a natural binder and a source of organic matter for enrichment of derived granules to be applicable as a soil improver. Characterization of raw materials and derived granules included range of physical and chemical analysis. Applied granulation technology involved homogenization of components following by extrusion and drum granulation, and the process was developed for prospective production of soil improvers. It was estimated that the most optimal mass ratio of raw materials applicable for the process of granulation is 67:100 (fly ash to sapropel) and 30:100 (biochar to sapropel) resulting in production of granules 3–8 mm in diameter. Among the characteristic parameters of granules apparent density, bulk density, compressive strength, total element content and element content by fractions was assessed.

1. Introduction

Targets set by the climate and energy policies of the European Union encourage the member states to increase the use of renewable energy resources in production of heat and power [1–3]. Use of biomass (woody energy crops, forestry residues, agricultural residues and others) to produce heat and electric power is sharply increasing in the Baltic States [4].

Besides the cogeneration of power and heat indispensable for industrial and household needs, the main waste generated during the thermochemical processes of biomass burning are ash and biochar which on the one hand can be used as a raw material, but on the other hand can induce environmental risks if managed improperly [5]. Ashes are a waste of biomass combustion and usually consist from bottom and fly ash if particle precipitator systems are used to prevent emissions of particulate matter [6]. Another waste material in case of cogeneration power plants, biochar or charcoal, is obtained in a process of slow pyrolysis (carbonization) – decomposition of organic matter, for example, wood, induced by heating in inert atmosphere (anaerobic conditions) at temperature 300–800 °C [7–9]. Currently the cogeneration power plants have to pay for utilization of waste (residual) products, therefore, new solutions have to be invented to initiate sustainable use of these residuals.

A number of studies have revealed that ash and biochar generated from wood can be used as fertilizers in forestry [10,11] and agriculture [12,13], in particular to obtain nutrient input of nutrients K and P into soil [5]. However, several difficulties are attributed to possibilities of practical exploitation of ash and biochar due to the transporting, handling and mode of application [5,13,14]. If compared to soil, fly ash and biochar are lighter and less dense which leads to their movement to the upper layers of soil resulting in accumulation in top-soils. Subsequently, release of finer particles of biochar into the atmosphere can be

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caused promoted by wind or water flows [15]. This potential problem can be prevented by adding a binder and changing the physical state of dusty powders to granules or pellets of ash and biochar [16]. In general, methods applied for use and processing of ash and biochar are similar to those applied for chemical fertilizers [5]. Among them, granulation of waste generated from the thermochemical transformation of biomass has been shown in some circumstances as a cost-effective and environmentally friendly method [13]. As a binder in the process of granulation various synthetic or natural substances can be applied. Several studies have described use of hydroxypropyl methylcellulose [16], polylactic acid [17], starch alkaline lignin and inorganic binders such as $Ca(OH)_2$ and NaOH [18], as well as ground-granulated blast furnace slag, coal fly ash and metakaolin [19].

Potential use of organic rich freshwater sediments (such as sapropel) as a binder for sapropel concrete [20], sapropel/clay composites [21], sapropel/hemp shives [22] and lime/hemp/paper production waste [23] have been studied since middle of the last century. Sapropel (also called as gyttja or dy) is an alternative of a natural binder as it has adhesive properties with high ability to bind as well as a shape holding ability and plasticity [20]. The most intensive formation and accumulation of sapropel is characteristic to the temperate zones of Asia and Europe, and the continent of America in the Great Lakes' region [24,25]. Sapropel is accumulating in waterbodies as a result of natural development of lakes from oligotrophic to eutrophic with final overgrowth with higher vegetation if recultivation is not performed. In most of the studied lakes rich in organic sediments the depth of sapropel is 2.0–4.5 m, but the depth of open water < 1 m [24–27]. Thus, the ecosystems of such lakes are of poor environmental quality. In this case, sapropel extraction is considered as a major tool to reduce the internal loading of nutrients and renaturalize lakes to better ecological status. Therefore, in this respect sapropel can be considered as a waste product remaining from recultivation of lakes. In Latvia, municipal programs of landscape improvement and exploitation of nature resources indicate sediment extraction from lakes, ponds and estuaries exposed to overgrowth as a method that improves regional ecological status [28–31]. From such point of view synergic effect will be obtained if sapropel can be utilized purposefully. Total amount of sapropel that is possible to extract from lakes of Latvia is estimated not less than 700 to 800 million m^3 [27]; therefore, sapropel sediments have a great potential to be used in various fields of economics, currently mainly in agriculture as a fertilizer, as well as in building industry as a binder or adhesive substance but not exclusively [23,32–34]. Formation of sapropel takes place in anaerobic conditions and such GHG as methane is released; however, no surplus GHG will be released if sapropel will be used otherwise. Limitations of sapropel use exist due to its high water content (80% and more), but if used for granulation with such extra dry powders as ash or biochar, high content of sapropel's moisture can be considered as an advantage. Thus, environmentally friendly soil amendment in form of granules can be elaborated by combining sapropel and wood fly ash or biochar.

If compared to raw waste of combustion (ash, biochar) which usually is a dusty powder with poor wettability [35], the porous structures such as granules are expected to have better water sorption properties and resistivity to wind erosion. Waste of wood combustion itself is hydrophobic, and instead of absorbing water it forms droplets with surface covered with char particles [36]. Problem of utilization, handling and transportation applies also to other powder-type substances, for example, bulk dried distillers grains with solubles (DDGS) that is a major co-product of the dry-grind process, produced millions of metric tons a year, remain to have a challenge in its reuse due to issues concerning caking, poor flowability and segregation [37]. Thus, dusty powders in form of granules, pellets, tablets or capsules (assessing which is technically more applicable form) provide easier storage, transportation and handling of the product; as well as practical application of granulated material leads to reduced health hazards [5]. Another positive point that can be mentioned is that granulated waste of wood combustion have lower risk of spontaneous self-combustion [38,39]. Granules as a final product need to have sufficient mechanical strength to withstand handling of retaining their initial form. Mechanical strength of granules can be enhanced by increasing amount of binder in composition. Required strength of granules to be applied as a soil amendment is 2 MPa [16]. In general, derivation of granules or pellets from wood fly ash and biochar leads to improved recycling and logistics of waste materials produced during the bioenergy production as well as helps to control and avoid undesirable environmental effects such as leaching of nutrient excess [40,41].

The aim of this study was to find a sustainable way for utilization of waste from bioenergy production by making granules from wood fly ash and biochar mixed with sapropel used as a natural binder and a source of organic matter for enrichment of derived granules to be applicable as a soil improver.

2. Materials and methods

2.1. Sampling and description of raw materials

Energy generation waste used – fly ash and biochar. Samples of wood combustion fly ash and wood pyrolysis biochar were obtained from commercial power plants located in Lithuania and Latvia in September, 2016. Sample collection was performed based on the clear sampling procedure which was developed according to literature [42]. About 2 kg of ash or biochar were collected three times a day during one week and these subsamples were mixed thoroughly. Subsequently, seven consolidated samples (each 500 g) of ashes were obtained during one week at every combustion power plant. Samples were collected in plastic buckets with hermetic lids and delivered to the laboratory where they were stored in a dry place at room temperature. Derived fly ash and biochar samples differed due various fuel used at the energy production plant and various thermochemical process and temperature applied (Table 1).

To estimate characteristic parameters such as dry matter, volatile matter, fixed carbon and ashes of energy generation waste analyses according to standards of ASTM International were applied [43,44]. Gravimetric water (moisture) and dry matter content was detected as a loss in weight after drying of samples at 105 °C for 2 h in a drying oven (Plus II Oven, Labassco). Content of volatile matter was determined as a loss in weight at 950 °C under specified conditions in a muffle furnace (Omron). Ash content was determined as a residue after burning to constant weight at 750 °C for 6 h in a muffle furnace. To estimate bulk density (ρ_b) measurements in a graduated cylinder were done [45]. Solid density (ρ_s) was estimated using pycnometer method [46]. Material porosity (φ) was calculated as one minus division of bulk and solid density [47].

Lake sediments used as a binder. Specific freshwater lake sediments

Table 1
Short specification of energy generation waste used for granulation.

Type of waste (sample abbreviation)	Fuel used for bioenergy production	Cogeneration power plant	Thermo-chemical process applied (t, °C)
Fly ash (Ash-FA)	Coniferous softwood chips	'Oil Investment Projects' Ltd., Lithuania	Combustion (950)
Biochar (Char-BJ)	Non-coniferous softwood chips	'Jekapbils Cogeneration Station' Ltd., Latvia	Pyrolysis (800)
Biochar (Char-BT)	Non-coniferous hardwood chips	'Taurene Cogeneration Station' Ltd., Latvia	Pyrolysis (600)

– sapropel (gyttja) – with characteristic high content of organic compounds formed from remains of water plants and animals were used as a binder of natural origin for granulation of fly ash and biochar. Sapropel was obtained at three freshwater lakes in Latvia and Lithuania – Lake Midulis (Lithuania), Lake Piksteres and Lake Pilvelis (Latvia); samples were labeled as Sapro-MD, Sapro-PK and Sapro-PL, respectively. Lake sediment coring was carried out in autumn, 2016, using a 10 cm diameter Russian-type peat sampler with a 1.0 m long camera after a certain procedure [48].

Loss-on-ignition method for sapropel samples was applied in order to estimate content of moisture, organic matter, ash and carbonates. Moisture of sapropel was determined after drying at 105 °C for 12 h. Content of organic matter, ash and carbonates was analyzed by ashing samples sequentially at 550 °C for 4 h and at 900 °C for 2 h [49]. Bulk density for raw and homogenized sapropel were calculated and expressed as kg/m^3 [50]. Specific parameters of sapropel such as class and type were detected according to the sapropel classification [26].

2.2. Preparation of raw materials

Before granulation, energy generation waste (wood fly ash and biochar) was screened using a sieve of mesh size 1500 μm. Mass ratio assessment was performed to detect particle size distribution of raw energy generation waste. XRD analysis using Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) and a LynxEye detector was applied to determine principal constituents of fly ash and biochar.

Homogenization of sapropel prior being used as a binder is very important because its properties such as viscosity, size and morphology of particles changes significantly after homogenization. Optical microscopy images of sapropel suspension before homogenization revealed big agglomerations and microorganisms (> 50 μm), while after homogenization of sapropel mainly de-agglomerated matter remained. Homogenization of sapropel was prepared using a high-speed multi-disc mixer-disperser described in literature [51]. In preliminary studies this technology was used for preparation of such mixtures as a coal-water slurry [52], as well as a porous ceramic and concrete material [53]. With the motor of this high-speed multi-disc mixer-disperser the rotor shaft rotates up to 6000 rev/min. Thus, in the zone of influence of the working elements, if a liquid medium is used, such phenomena as impact, transonic fluctuations and cavitation occur at the same time. In comparison with various commercially available rotor-stator homogenizers which operate mainly in batch mode, use of the high-speed multi-disc mixer-disperser allows to process a slurry in-line which is significant for commercial applications. Mixing of suspension of energy generation waste and sapropel as a binder was performed using an anchor type mixer (Clatronic, KM3350).

2.3. Process of granulation

Granules from energy generation waste and lake sediments were derived by applying two methods commonly used for production of granulated fertilizers, i.e., extrusion and drum granulation (Fig. 1).

Three pairs of used raw materials were processed for granulation: Ash-FA mixed with Sapro-MD, Char-BJ mixed with Sapro-PK, Char-BT mixed with Sapro-PL, and after drum rotation granulation following granules were derived: AshGran, CharGran1 and CharGran2 respectively. During the process of extrusion following granules were derived: AshExtr, CharExtr1 and CharExtr2, respectively. Addition of binder provide bonding of particles of energy generation waste bonded and improve densification character of derived granules [18]. Granules were prepared using laboratory scale granulator without a spray option that was previously tested to obtain small batches of clay granules [54]. Fly ash (Ash-FA) with homogenized bulk binder Sapro-MD, and biochar (Char-BJ, Char-BT) together with bulk binders Sapro-PK, Sapro-PL, respectively, were homogeneously mixed using an anchor type mixer at rotation speed 50 rev/min. Sapropel was gradually added during the process of mixing which was carried out for up to 2 min. Proportions of substances were adjusted during the experimental process of mixing the components to gain the best consistency of the mixture that result in stable formation of equally sized granules.

For preparation of granules using the drum rotation granulator the mixture of energy generation waste with the binder was transferred into the granulator to fill not more than ¼ of the drum volume, and agglomeration was carried out during 3 min. The matter in the drums is rotating by a centrifugal force, and the granules are formed along the edge of the rotating cylinder, where diameter of the cylinder is 30 cm and rotation speed 50 rev/min. Increase in rotation speed and prolongation of rotation period causes higher density of granules and explicit spherical shape. Diameter of derived granules may vary from 3-5 mm to 8 mm. Another benefit of drum granulation is that it does not require an extra addition of raw material.

For extrusion, homogenized mixtures of energy generation waste and binder were extruded through 9 mm conical nozzles. Length of the granule depends on time of separation which in this case was every 2 seconds resulting in 9 mm long granules; the shape of the granules is cylindrical. Derived wet granules were instantly powdered with fly ash or biochar, respectively, to prevent sticking caused by water migration to the surface of granules during the process of granulation. Afterwards, granules were rounded using the drum granulator during 100 s at rotation 50 rev/min. If necessary, fly ash or biochar was added during the process. This technological mode is beneficial since it provides decrease of moisture content of granules and increase the density, therefore, ensuring faster drying process afterwards. At the final phase of the process of granulation, granules were dried in a drying oven (Plus II Oven, Labassco) for 48 h at 50 °C.

2.4. Testing of derived granules

Granules were tested to investigate their physical and chemical properties. Moisture content was determined by moisture analyzer (Kern, MRS120-3), by 7 parallel measurements at 105 °C. Moisture absorption was determined according to the standard GOST 12730.3-78. Surface area of granules was determined by the program Quantachrome QuadraWin – Data Acquisition and Reduction for QuadraSorb CA, version 5.11 2000-12 (QuadraSorb). Mechanical tests were performed on Zwick Z100 ROELL universal testing machine, according to the standard method [55]. The total test volume of granules was 0.5 L. The samples were tested for compressive strength at a rate of 5 mm/min, until stress at 10% deformation was recorded. For granules determination of density of the substance, material bulk density and bulk density according to the standard method [55] was implemented. Water absorption was detected according to the standard method [56]. Detection of density for each type of granules were performed for 12 parallel measurements. Other tests were conducted for 5–7 parallel measurements or repetitions.

Microscopy images were derived using a light microscope Keyence VHX-2000 (Keyence Corp) equipped with 54 Mpix camera and lens VH-Z20R/Z20W (for × 20–200 times magnification).

One of important parameters detectable for granulated products is a load-keeping ability caused by a self-weight during storing. Granulated products must contain less than 10% of broken granules from the whole volume. The compressive strength also was measured at 10% threshold for compression [57]. Using the formula (1) it was possible to calculate maximum material column with 10% of crashed granules:

$$H = (F\times 101971.62)/D, \tag{1}$$

where H – material column (m), F – compression stress (MPa), D – material bulk density (kg/m^3), 101971.62 – conversion coefficient (1 MPa = 10^6 N/m^2 = 101971.62 kg/m^2).

To assess total element content in energy generation waste and samples of binder as well as derived granules samples were mineralized

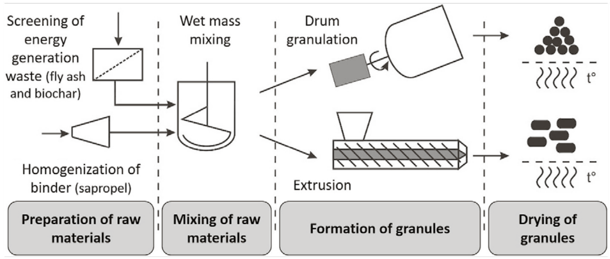

Fig. 1. Scheme of applied granulation process.

by wet digestion using *Aqua regia* (1:3, concentrated HNO_3 and HCl, both analytically pure, Sigma Aldrich). Theoretical concentration of elements in derived granules was also calculated taking into account content of moisture and mixed proportions of raw materials. Furthermore, estimation of element bioavailability was done by applying modified 3-step sequential extraction analysis [58,59] for derived granules that allowed to obtain three fractions as follows: 1) fraction of water soluble (easily available) compounds (after dissolving a sample in heated up deionized water); 2) fraction of weak acid soluble compounds (after dissolving the remains from the first step in 0.11 M CH_3COOH; 3) residual fraction (after dissolving the remains from the second step in *Aqua regia*). Each analytical solution was made in triplicate and, at each step, blank samples were prepared in the same manner. Concentration of elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sr, Ti, Tl, V and Zn) in solutions was measured using ICP-OES (iCAP 7000, Thermo Scientific) and expressed as mg/kg of sample dry matter. Quality of the analytical measurements was ensured by the analysis of certified reference material IAEA-336 Lichen (IAEA) containing reference values on wide spectra of major and minor elements.

3. Results and discussion

3.1. Characterization of raw materials

Fly ash and biochar. Mass ratio assessment of particle size distribution revealed that in fly ash sample Ash-FA and biochar samples most abundant were particles smaller than 0.25 mm (39–43%), following by particles of size 0.25–1 mm (36–39%), while particles 1–2 mm and larger than 4 mm constituted only 14–18% and 3–4%, respectively. XRD analysis revealed that the greatest part (finest fraction) of energy generation waste consists of several crystalline phases such as portlandite, lime, quartz, calcite, periclase, microcline, hydroxyapatite and merwinite.

Moisture content of fly ash and biochar was less than 4%. The ash content was higher for fly ash (> 60%) and significantly lower for biochar samples (< 20%). Content of volatile matter and fixed carbon oppositely was detected higher for biochar samples. Values of pH and electrical conductivity were detected similar to all dry powders. Higher bulk and solid density was detected for fly ash than for biochar samples, but porosity was quite lower for fly ash than for biochar but not with a great difference (Table 2).

Lake sediments used as a binder. All samples of sapropel belonged to organogenic class of sapropel with content of organic matter more than 80% and with ash content less than 20% (Table 3).

According to previous studies, positive correlation between sapropel moisture and organic matter content in dry matter was observed due to the colloidal structure and the ability of sapropel organic matter to bind water [60], as the result, organogenic sapropel in fresh condition always contains more than 90% of moisture. pH values of organogenic sapropel are close to neutral as it has insignificant amounts of ash and carbonates of dry matter (less than 30%). The bulk density of fresh sapropel samples indicated in Table 3 increases with the content of vascular plant remains [24].

De-agglomeration after sapropel homogenization was confirmed by the analysis of particle size distribution (Fig. 2). Homogenized Sapro-MD contained mostly particles of size 1–30 μm, while for homogenized Sapro-PL and Sapro-PK average particle size was 70–400 μm. This fact could be explained by the presence of ductile non-disintegrated plant fragments and sand-like mineral particles.

Taking into account data of micrographs and particle size distribution, it was detected that two of three samples of binder (i.e., Sapro-MD and Sapro-PK) were characterized by practically equal granulometric parameters of two typical fractions – fine and coarse. Modal parameters of fine fraction were very similar (13–15 μm) for all three sapropel samples. After dispersion of sapropel samples, they were characterized dually: mode of fine fraction for all samples was practically equal, but mode of coarse fraction differed among the samples (Table 4). Sapro-MD in comparison with other samples of binder was characterized by better properties of grindability because after homogenization and dispersion the course fraction was reduced to the minimum, thus, the best result of homogenization was gained. Regarding the samples Sapro-PL and Sapro-PK, obtained results of homogenization were not achieved as fully as for Sapro-MD, and that possibly can be attributed to specific composition of organic components which during the homogenization may form chain-type structures.

3.2. Physical characterization of derived granules

In, earlier studies [61], amount and viscosity of a binder has been recognized as an important parameter in controlling behavior of granulation. If an organic binder is used to make the mixture, it plays a key role in the granulation process. Finally, content of the binder has significant effects on mechanical properties of derived granules.

The binder was used in current study was homogenized sapropel with average moisture content 92%, 97% and 94% for Sapro-MD, Sapro-PK and Sapro-PL samples, respectively. Content of organic matter which ensure binding of energy generation waste in granules after drying are 81%, 83% and 89% for Sapro-MD, Sapro-PK and Sapro-PL samples, respectively (as indicated previously in Table 3). If organic rich lake sediments (sapropel) are used for granulation, it is easier to control utilized amount of the binder due to known sapropel's water content, and, furthermore, moisture content can be detected at every step of the process of granulation. By controlling the water amount at the mixing stage it is possible to ensure uniform distribution of sapropel. Fig. 3 illustrates moisture content of all used raw materials and intermediate products at certain stage of the processing.

Table 2
Properties of energy generation waste samples.

Sample abbrev.	Content of parameter[a], %				pH	EC[b], S/m	Density, kg/m^3		Porosity (φ), m/m^3
	DM	VM	C_{fix}	Ash			Bulk (ρ_b)	Solid (ρ_s)	
Ash-FA	98.49	8.82	27.53	62.14	12.57	1.36	370	2430	0.84
Char-BJ	96.49	31.21	51.31	13.97	12.41	0.96	210	1970	0.89
Char-BT	98.57	30.65	48.57	19.34	12.63	1.54	190	1850	0.90

[a] DM – dry mass, VM – volatile matter, C_{fix} – fixed carbon.
[b] EC – electrical conductivity.

After a number of trials of granulation (for both processes, drum granulation and extrusion), it was established that very narrow range of the binder/waste ratio is eligible for production of granules, i.e., Ash-FA with Sapro-MD at mass ratio 67:100 and Char-BJ or Char-BT with Sapro-PK or Sapro-PL, respectively, at mass ratio 30:100. Taking into account the mass ratio of sapropel to fly ash or biochar and content of organic matter in each type of sapropel, the amount of added organic binder in the mixture was equal to 12.9 wt%, 11.3 wt% and 22.3 wt% for mixtures Sapro-MD with Ash-FA, Sapro-PK with Char-BJ and Sapro-PL with Char-BT, respectively. To assess the optimal binder content, the bisection method was applied. Initially taken mass ratio was 100:100 (dry waste to binder), and amount of binder was decreased for a half, but for each next iteration diapason with exceeded binder was chosen. For example, the experiments using fly ash and sapropel resulted as follows: 100:100 – too wet, 50:100 – too dry, 75:100 – too wet, 62.5:100 – too dry, 68.75:100 – satisfactory, but over-wetted. Taking into account these data, 67.0% of fly ash into granulation mass was an empirically chosen value that suited very well for granulation of raw materials. The process was repeated using biochar and sapropel. Unsatisfactory granulation results were not presented in this paper.

Morphology analysis revealed structure differences among the types of granules. Granules derived by the drum granulation has explicit porous structure in the middle of a granule while their surface layers are denser (Fig. 4). Extruded granules has cylindrical shape and steady porous structure (Fig. 5). Only some scientific studies can be found regarding investigation of inner and outer porosity/density of granules; similar findings in comparison to our date are mentioned, but not thoroughly investigated by other scientists [62,63], thus leaving an area for further research.

All granules made by the drum granulation are characterized by near-spherical shape, with smooth surface, and the process of granulation process went fast and evenly. It was experimentally approved, and it well correlated with known data. To obtain granules or pellets both, drum granulation and extrusion techniques, have been widely applied for decades. However, for each particular pair of dry powder and binder as a final application for formation of granules more suitable is only one of the granulation methods [64]. Our study included comparison of both techniques to estimate the best solution applicable for industrial production of granules. Taking into account the conditions applied for granulation, the size of produced granules was in range of 3–8 mm, but it should be noted that applied mass ratio of waste and binder in the mixture is optimal for that particular granulation equipment. It is estimated experimentally that for each couple of chosen dry powder and binder, the process window for the nucleation growth exists; therefore, it can be considered as an '*optimal condition*' for granulation at certain circumstances [64].

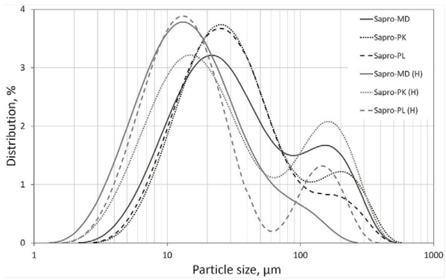

Fig. 2. Particle size distribution of raw and homogenized (H) samples of binder.

According to the theory of granulation [53,54], the process of drum granulation and the parameters of produced granules are strongly dependent on the setup parameters of granulation (such as rotation speed, drum diameter etc.). However, for commercial production scaling-up of the technology will be necessary. Granules produced by the extrusion are less sensitive to scaling-up of the production technology [65].

Detected parameters such as size and volume values, bulk density, apparent density, compressive strength etc. for produced granules are summarized in Table 5 and illustrated in Fig. 6.

Comparison of granules produced by extrusion and drum granulation revealed that the main different parameter between these methods is density. Greater compressive strength can be attributed to granules with higher value of density. It was calculated that height of material column (height of the storage of granules) is quite variable – extruded granules could be safely stored at bulk conditions or in big-bags stacked one over another in height up to about 80 m, or with safety coefficient 3 up to 27 m, but granules made by drum granulation up to 100 m and 34 m, respectively, which is enough for commercial application to

Table 3
Properties of sapropel used as a natural binder for granulation.

Lake, location	Sample abbrev.	Type of sapropel	Content of parameter[a], %			pH	EC[b], mS/m	Bulk density, kg/m^3	
			M	OM	Ash			Raw	H[c]
Midulis, Lithuania	Sapro-MD	Peaty	91.98	81.34	18.66	7.58	9.64	1042	1066
Piksteres, Latvia	Sapro-PK	Green algae	96.45	82.67	17.33	6.89	12.48	1028	1069
Pilvelis, Latvia	Sapro-PL	Cyanobacteria	93.48	88.46	11.54	6.43	8.83	1025	1017

[a] M – moisture, OM – organic matter.
[b] EC – electrical conductivity.
[c] H – homogenized.

Table 4
Characteristic parameters of particle size before and after dispersion of sapropel samples.

Sample abbrev.	Raw or homo-genized (H)	Mean particle size, μm			Modal particle diameter, μm		Reduction of coarse fraction > 100 μm, %
		Fine fraction (d_{m1})	Coarse fraction (d_{m2})	Total (d_m)	Fine fraction (d_1)	Coarse fraction (d_2)	
Sapro-MD	Raw	29.7	183.7	64.8	22.0	153	21.1
	H	18.2	106.4	25.0	12.8	110	3.6
Sapro-PL	Raw	32.6	200.0	49.2	13.0	145	11.8
	H	15.9	157.7	36.0	25.0	165	12.7
Sapro-PK	Raw	34.3	232.7	63.6	15.0	163	24.2
	H	20.4	178.1	66.0	25.0	200	17.3

ensure storage of granules without their collapse. Material column is strongly dependent on the compressive strength, while safety coefficients allow to assess the height of destruction of granules in a column at such influences as vibration, falling, compression etc. As higher the value of the safety coefficient is, as greater amount of criteria is included in the calculation of the material column. In order to allow granules to be dosed, packaged, transferred and used for their intended purposes, e.g., as a granulated fertilizer, their mechanical strength is significant. As finer the granules are, as harder it is to transport, store and operate them.

If granules are thought to be applied as a fertilizer in agriculture, it is very significant to assess their mechanical properties which indicate feasibility to prepack, dose, transport and practical use of the granules. As crumbly or brittle granules are, as it becomes more complicated to transport, store and utilize them. It was detected that volume of extruded granules is up to 5 times greater than volume of granules from drums, while content of moisture oppositely is lower for extruded granules.

Water absorption differed between ash/sapropel and biochar/sapropel granules as for biochar-based mixture it was higher for granules derived by the drum granulation, while for ash-based mixture oppositely significantly higher for extruded granules (Fig. 6a). Values of specific surface area are higher for extruded granules as well as for biochar-based granules due to more porous structure (Fig. 6b).

Relationship between the compressive strength and some other parameters of derived granules (Fig. 6f–h) revealed that by increasing of apparent density the compressive strength is increasing for granules derived by the extrusion. The tendency for granules derived from the drum granulation is opposite, i.e., by increasing of apparent density the compressive strength is reducing. However, further studies are needed to explain this phenomenon.

3.3. Chemical composition of raw materials and granules

Total concentration of elements in raw materials revealed that on average fly ash have higher element content than biochar especially regarding such elements as Mn, Al, Fe, Na, Ti, Cu, Cd, Tl, Pb, Se, Co (Fig. 7a). However, some elements, e.g., Zn, Ba, Sr, Li, Ni, Mo, V, Sb can be found in biochar at higher concentration.

Differences of element concentrations in sapropel samples on average are not variable; only regarding trace elements it was determined that Sapro-MD is more rich in Co, Li, Cr, V than other sapropel samples (Fig. 7b). Such elements as Cd, Tl, Se, Mo, Be were detectable at very low concentration or below detection limit in sapropel. Nevertheless, taking into account proportions and moisture content of raw materials, impact of elements constituting sapropel is negligible to elemental composition of granules in comparison with composition of energy generation waste. Thus, prior application in agriculture attention should be paid more on concentration of possibly harmful for environment elements that are present in fly ash and biochar.

Total concentration of elements in derived granules revealed that theoretical calculated values are quite higher (up to 20%) than real concentration after quantitative analysis. Therefore, calculated values are presented in this paper as a worst case sample eligible for risk assessment. On average, as it was expected higher total concentration of elements was detected in granules made from fly ash and sapropel than in biochar/sapropel granules. Despite the presence of potentially harmful elements (e.g., Al, Cd, Pb, Cr, Ni), in granules they were mostly detected at low concentration (Fig. 7c). Furthermore, assessment of element bioavailability revealed that the greatest part of elements is bound in residual fraction which indicate their negligible solubility and bioavailability in environment. Among the elements that can be found in water or weak acid soluble fractions and, thus, can be assessed as bioavailable in environment are Ca, K, Mg, Mn, Na, Ba, Sr, Co, Li, Mo, V (Fig. 8).

Although ash/sapropel granules had comparatively higher total element concentration, it can be observed that element bioavailability in lower (Fig. 8a) in comparison with biochar/sapropel granules (Fig. 8b). In case of application of granules in agriculture it is important that bioavailability is high for those elements particularly necessary for plant development, i.e., essential macronutrients – N, P, K, Ca, Mg and essential micronutrients – Mn, Fe, Cu, Zn, Co, Ni and Mo.

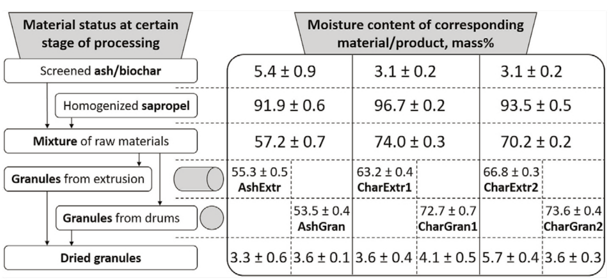

Fig. 3. Moisture content of raw materials and intermediate products at every stage of process during the granulation.

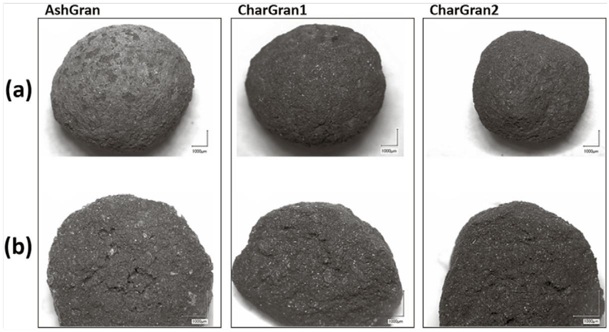

Fig. 4. Granules made by the drum granulation at ×20 times magnification: a) common view, b) cross section.

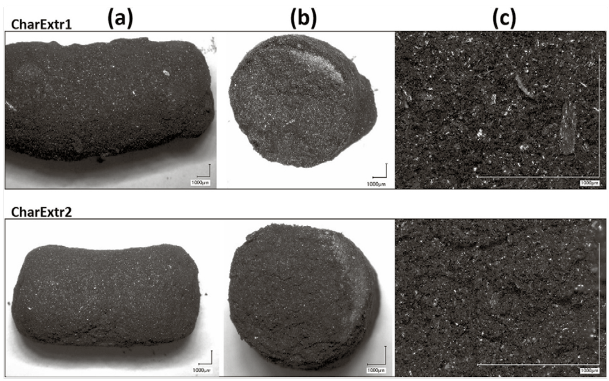

Fig. 5. Optical images of granules made by from biochar by extrusion: a) common view and b) cross section both at ×20 times magnification, c) cross section at ×200 times magnification.

Table 5
Descriptive parameters of granules.

Parameter	Extruded granules			Granules from drums		
	AshExtr	CharExtr1	CharExtr2	AshGran	CharGran1	CharGran2
Diameter, cm	0.8	1.0	0.8	0.8	0.8	0.9
Height, cm	2.1	2.3	1.9			
Volume, cm^3	1.1	1.9	1.1	0.4	0.4	0.4
Material column, m	82	68	60	32	83	103
Material column with safety coefficient 3, m	27	23	20	11	28	34
Material column with safety coefficient 10, m	8	7	6	3	8	10

Results indicated that from essential elements Ca, K, Mg, Mn, Co and Mo are present in granules in form of compounds with high or medium bioavailability, while availability of P, Fe, Cu, Zn and Ni for plants can be estimated as quite low. Thus, applicability of granules for use in agriculture should be assessed considering soil composition and properties. It should be taken into account that quite high content of Na in granules and assessed its high bioavailability is unfavorable for plants, therefore, use of granules in salinized soils could not provide positive effect to soil sustainability. Regarding such essential elements for plants as N and P, it was estimated that total content of P content in granules is quite high (up to 5.9 g/kg) but it is mainly bound in residual fraction (80–95%) and only small amount could be available for plants from weak acid fraction (5–20%). Regarding N, its content in energy generation waste and subsequently in derived granules is quite variable – from 94 mg/kg to 895 mg/kg. It might be important to enrich granules with a source of N and P, however, further investigation is needed. Another important basic element is carbon, and organic carbon content was detected in fly ash and biochar revealing that they may contain at

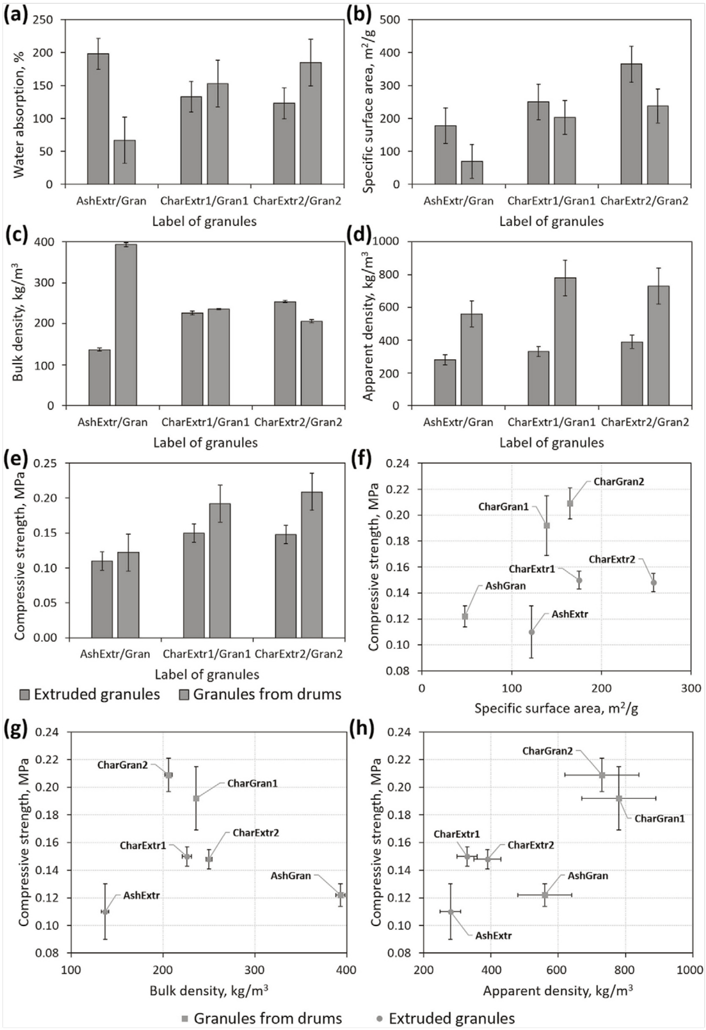

Fig. 6. Descriptive parameters of granules depending on the method of granulation: a) water uptake, b) specific surface area, c) bulk density, d) apparent density, e) compressive strength; and relationship between compressive strength and f) specific surface area, g) bulk density and h) apparent density.

least 49% of organic carbon and subsequently a little lower amount of it can be found in granules that is favorable for soil microflora.

4. Conclusions

If organic-rich freshwater lake sediments (sapropel) are used as a binder together with energy generation waste, prior the process of granulation it is compulsory to perform homogenization of ingredients itself to gain maximum homogeneity of composition of derived granules. The most optimal mass ratio of raw materials applicable for the process of granulation is 67:100 (fly ash to sapropel) and 30:100 (biochar to sapropel) resulting in production of granules (3–8 mm in diameter) applicable for use in agriculture.

Application of rotary drum granulation allows to derive granules

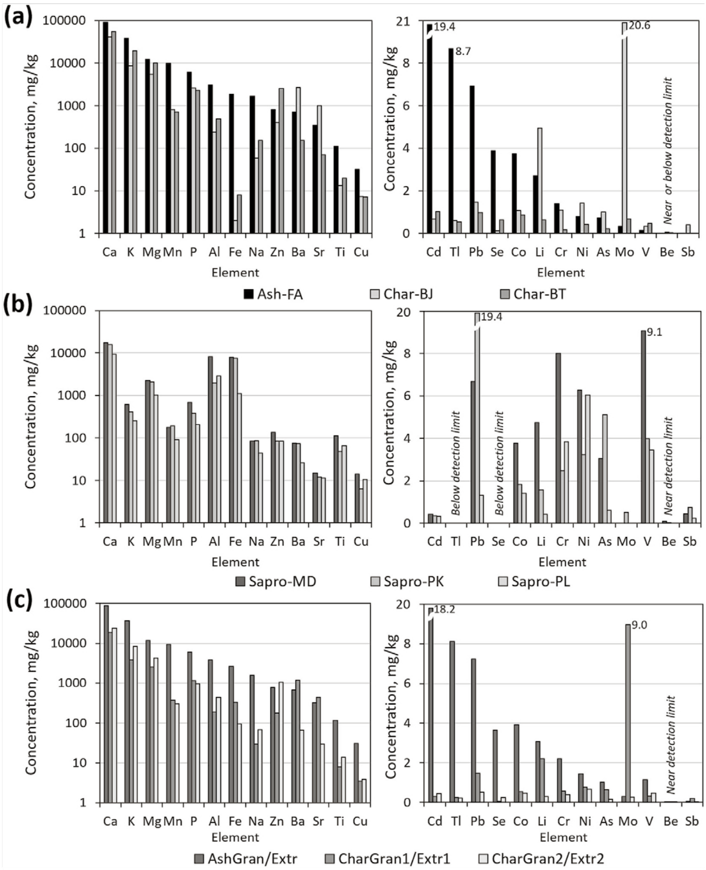

Fig. 7. Concentration of metallic elements, metalloids and phosphorus in raw materials a) energy generation waste, b) binder and c) derived granules.

characterized with increased mechanical strength by 10–25% and bulk and apparent density by 25–50% higher in comparison with granules derived by process of extrusion. Resulting water absorption of granules mainly depends on the properties of used sapropel, therefore, it is quite variable and may reach almost 200% in case of ash/sapropel extruded granules and a bit lower (153–185%) from drum-derived granules using biochar/sapropel mixture. Biochar/sapropel granules obtained in the process of extrusion together with a higher density have increased strength parameters, however, for extruded granules by increasing the density, compressive strength decreases. In comparison to drum granulation method, extrusion creates granules with lower moisture content, thus reducing the cost of energy needed for the drying process of granules. Furthermore, residual heat from combined power plants can be used for drying of granular material thereby intending more sustainable exploitation of cogeneration.

Analysis of chemical composition revealed that ash/sapropel granules are richer in elements than biochar/sapropel granules, but bioavailability of elements is comparatively higher for biochar/sapropel granules. However, enrichment of granules with such essential elements for plants as N and P could significantly elevate possibilities of use of granules in agriculture.

In general, utilization of bioenergy production waste together with organic-rich lake sediments is one of the ways forward sustainable reuse of waste materials as well as it leads to protect freshwater lakes from overgrowing due to sapropel removal from lakes. Granules derived from fly ash or biochar together with sapropel might be a future product applied in agriculture in case of run out of natural resources, e.g., shortage of peat deposits.

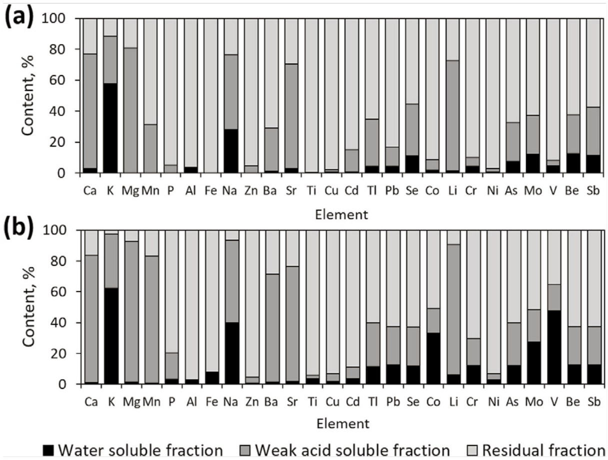

Fig. 8. Distribution of metallic elements, metalloids and phosphorus in a) ash/sapropel granules, b) biochar/sapropel granules by fractions regarding bioavailability of elements.

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