RIGA TECHNICAL UNIVERSITY

WATER RESEARCH & BIOTECHNOLOGY

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BIOENERGY TECHNOLOGIES AND BIOTECHNOLOGIES

Book of Abstracts

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Dear Colleagues and Friends,

As part of the 64th International Scientific Conference of Riga Technical University section “Bioenergy Technologies and Biotechnologies”, it is my great pleasure and anticipation to introduce this collection of abstracts, showcasing the latest advancements and research findings in the fields of bioresources, wastewater treatment, environmental engineering, and biotechnologies.

In today’s world, where the pursuit of sustainable solutions is paramount, environmental engineering and biotechnologies have emerged as crucial pillars in our quest for a cleaner, greener future. These innovative approaches offer not only opportunities for energy generation but also promise significant benefits for resource recovery, wastewater treatment, and environmental conservation.

Together, let us harness the power of bioenergy technologies and biotechnologies to drive positive change for our planet and future generations.

Assoc. Prof. Linda Mezule
Director of Water Systems and Biotechnology Institute

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RESOURCE RECOVERY ROUTES FOR SEWAGE SLUDGE IN LATVIAN WWTPS

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INTRODUCTION

An important part of the global transition to a circular economy is the re-examining of the current methods of waste management. Wastewater treatment plants (WWTPs) generate sewage sludge as a by-product of the treatment process. Shifting the understanding of sewage sludge from waste to resource is essential for the development of new, resource-efficient approaches to sludge management [1]. Currently, in most European countries, including Latvia, sludge is recognized for its organic matter and nutrient content and is reused as a feedstock for composting or anaerobic digestion, with the final application being a fertilizer or soil improver [2]. Still, new innovative approaches for sludge management are needed to recover the chemical value embedded in the sludge. Thinking of sludge as a source of organic compounds such as carbohydrates, proteins and lipids reveals new possibilities for sludge treatment, including the production of biofuels and biochar [3]–[5]. Within this study, a thorough assessment of the chemical content of Latvian municipal sewage sludge was performed and the possible routes of resource recovery were determined for each type of sludge based on its properties and the technological setup at the WWTP.

METHODS

Data on the amount of sludge produced in Latvia in 2022 was obtained from the national environmental database 2-Water [6] or provided by the WWTP operators. Chemical characterisation of sewage sludge was performed on primary, secondary and digested sludge samples from 13 Latvian WWTPs collected between January and March 2022.

RESULTS

In 2022, the sewage sludge waste stream in Latvia reached 20.0 thousand tonnes (dry weight). This includes 13672 t of dewatered secondary sludge from WWTPs all across Latvia (Table 1). Additionally, the country's largest WWTP produced 6376 t dewatered anaerobically digested sludge by using primary (7665 t) and secondary sludge (5110 t) as a feedstock for anaerobic digestion. This WWTP is the only one in Latvia that produces primary sludge, and also the only one with an on-site anaerobic digester. Here, the entire national supply of primary sludge, along with the majority of the produced secondary sludge, is used for biogas production. The resulting digested sludge is temporarily stored in open-air fields until it is deemed safe for further utilization. In the smaller Latvian cities, secondary sludge is the main by-product of wastewater treatment, 20 % of it is applied on agricultural lands, 8 % is composted, 22 % is in temporary storage under the legislated waiting period, while the remaining sludge is used in other ways (including anaerobic digestion outside of the WWTPs).

Table 1. Sewage sludge generation and utilization in Latvia (2022 data)

	Tonnes, dry weight	**Utilization**
Primary sludge	7665	100 % to anaerobic digestion
Secondary sludge	13672	22 % in temporary storage 8 % composted 20 % agricultural use 51 % used in other ways
Digested sludge	6376	100 % in temporary storage

Table 2. Current uses and future options for sewage sludge management in Latvia

	Current uses	**Future options**
Primary sludge	Feedstock for anaerobic digestion	Cellulose recovery; biochar, bioethanol and biodiesel production
Secondary sludge	Composting; land application; feedstock for anaerobic digestion	Protein extraction; biochar, bioethanol and biodiesel production
Digested sludge	Composting; land application	Biochar production; phosphorus recovery

Chemical analysis showed that proteins are found in abundance in all sludge types – 23.9 % in primary sludge, 18.5 % in secondary sludge and 8.0 % in digested sludge. The best source of carbohydrates was primary sludge (10.0 %), including 7.1 % cellulose. Lipid levels were similar in all types of sludge – 9.1 %, 9.8 % and 8.6 % in primary, secondary and digested sludge, respectively. The organic fraction was 77.4 %, 78.6 % and 66.1 % of dry weight for primary, secondary and digested sludge, respectively.

DISCUSSION & CONCLUSIONS

Currently, the final destination of nearly all of the sewage sludge produced in Latvia is land application as a fertilizer or soil improver. Based on the chemical characterisation results, it is clear that primary sludge is a great source of cellulose. Furthermore, it is evident that cellulose should be recovered before it enters the biological (secondary) treatment to avoid the loss of this material via biodegradation (Table 2). In the majority of Latvian WWTPs, secondary sludge is the main waste stream. Secondary sludge is a suitable material for protein extraction, enabling the production of protein-based fertilizers [7]. Primary and secondary sludge could also be suitable for the production of bioethanol or biodiesel due to the moderate amount of carbohydrates and lipids, respectively [8], [9]. After the proposed resource recovery actions, the remaining organic fraction of primary and secondary sludge could be used for biochar production [5]. Carbohydrates and lipids are also the main substrates for anaerobic digestion, meaning that in WWTPs with anaerobic digesters, it is in their best interests to preserve these macromolecules and avoid their recovery from primary or secondary sludge. Due to the process of biogas production, digested sludge has a lower content of macromolecules than other types of sludge, making it more suitable for applications such as biochar production from the organic fraction or phosphorus recovery from the inorganic fraction. This type of dual resource recovery approach would utilize the sludge biomass to the fullest extent. Additionally, a techno-economic analysis could be beneficial for the WWTPs to determine whether the introduction of an anaerobic digester would yield more valuable products than the processing of secondary sludge by other methods. The chemical content of sewage sludge reveals the possibilities of applying a resource recovery approach. The various routes of implementing resource recovery highly depend on the current technological setup at the WWTP. This research put forward novel proposals that are specifically relevant to Latvian WWTPs but could also be applicable at any WWTP with an activated sludge process, anaerobic digesters, and sludge of similar quality.

ACKNOWLEDGEMENTS

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THE ISSUE OF ODOUR EMISSIONS FROM WASTE TREATMENTS AND THEIR IMPACT ASSESSMENT

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INTRODUCTION

The perception of odours is an issue that emerges when an individual is exposed to an air concentration of a substance that is higher than the so-called "odour threshold" concentration, i.e. the minimum concentration of that substance that can be perceived by the sense of smell. Though rarely associated with irreversible health effects, odours affect the well-being of people, inducing negative psychological responses that may also cause reversible physical symptoms like nausea, headache and shortness of breath [1]–[3]. In addition, odour nuisance may cause adverse socio-economic effects in areas with important odour emission sources, like the depreciation of properties and terrains or the closure of companies responsible for odour emissions and the consequent loss of jobs.

Most industrial activities are equipped with air pollution control technologies that are usually effective against odour emissions. Other activities involving biological processes, like mechanical-biological waste and wastewater treatments, biorefineries or zootechnical activities [4]–[6], are usually less controlled and characterised by the absence of channelled systems for the release of exhausted air. This makes such activities potential sources of malodorous compounds.

Contrarily to air pollutants, regulations on odour impact are absent in several countries worldwide [7] and may largely differ among countries when adopted [8]. Besides provisions on the processes and the techniques to adopt to minimise odour emissions, odour regulations or guidelines may define the modalities to monitor and model odour emissions and concentrations, both at the source level and in the surroundings. Dynamic olfactometry is the most adopted analytical methodology in Western countries to determine the odour concentration of an air sample [9]. Given the level of subjectivity of odour perception, dynamic olfactometry is based on the statistical outcomes of a panel of people exposed to progressively diluted concentrations of a real air sample in a laboratory. Thus, it is not a real-time assessment of the situation in the field. Alternative instrumental and fastest

techniques exist (e.g., electronic noses and gas chromatography), but they always require calibration with dynamic olfactometry [10].
The present contribution is an overview of the regulatory schemes adopted in Italy on odour impact assessment and a critical analysis of the challenges involved in odour dispersion modelling.

METHODS

The overview is based on the regional guidelines on odour impact assessment in force in Italy and on the scientific literature on this topic. The guidelines contain provisions on the evaluation of odour concentrations at the source level and around biological treatment plants and farms. Regarding odour dispersion modelling, the reference procedure to simulate emission sources and carry out dispersion simulations is described. In addition, the odour concentration limits and the assessment criteria are reviewed and presented. Furthermore, examples from the available literature on applying modelling techniques to odour impact assessment are discussed. Finally, practical situations are proposed where the definition of the emission source is challenging and likely to affect the reliability of the simulation results.

RESULTS

The overview of the Italian guidelines for odour impact assessment presented the monitoring protocol, the main provisions to prevent odour emissions and improve odour dispersion, and the odour concentration limits that an activity subject to environmental impact assessment must guarantee. The overview on the application of dispersion modelling highlighted that all the literature studies focussed on conventional emission sources such as stacks (point sources) and biofilters or heaps of waste/biomass (area sources). There is a lack of studies involving other types of sources whose parameterisation is debatable, such as volumetric sources. This is the case, for instance, of warehouses containing decomposing material and characterised by vertical openings along the perimeter. Although such situations are widespread, no modelling protocol has yet been published in the literature. The simulation of such peculiar sources can be carried out by a combination of odour sampling and meteorological monitoring, adopting the following protocol:

1) measure the mean indoor odour concentration;
2) consider the periods when gates, doors or windows are open, the opening area, and the wind speed and direction in the proximity of the plant;
3) multiply the mean odour concentration by the opening area and the time-varying wind speed when the wind forms an angle between 0° and 180° with the plane of the opening. This way, time-varying odour emission rates can be estimated.

DISCUSSION & CONCLUSIONS

In the first part, this contribution describes the main elements of an odour impact assessment, which is expected to play an important role in the future due to the need to adopt renewable energy strategies, including the production of biofuels from biomass conversion. The complex approach that involves source characterisation, modelling techniques and comparison with limit values is explained. Examples taken from the Italian guidelines are presented, including provisions on emission control, especially for wastewater treatment plants. Despite the improvement in computing capabilities, dispersion modelling still lacks a conceptual framework to simulate complex (though common) situations. The present contribution proposes a protocol to simulate complex situations like the emission of odours from warehouses containing decomposing waste or biomass. This protocol may be useful to modellers, environmental consultants and assessors to improve the reliability of dispersion simulations and the results of odour impact assessment studies.

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ASSISTED BIO-DRYING OF WASTE AS A PRE-TREATMENT OF ENERGY RECOVERY OPTIONS

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INTRODUCTION

The 1992 United Nations Convention on Biological Diversity (CBD) defines biotechnology as "any technological application that uses biological systems, living organisms, or derivatives thereof, to make or modify products or processes for specific uses" [1]. Thus, in the sector of municipal solid waste (MSW), we can find cases where biotechnology plays a strategic role [2].

This is the case of composting, a natural process involving the biological degradation of organic wastes, such as green waste, food waste, etc., under aerobic conditions [3]. It allows a significant reduction in waste streams and generates a valuable end product for agriculture and gardening.

In the MSW sector, a less-known aerobic process based on a biotechnological approach is bio-drying [4]. It consists of an aerobic bioconversion treatment of the residual municipal solid waste (RMSW); that is, the waste is not source-separated. The final product(s) are intended for use as solid recovered fuel. Bio-drying is an aerobic biological mechanical pre-treatment that exploits the exothermic properties of biological reactions (obtained thanks to the insufflation of air within the mass of waste) to produce the heat necessary to modify the water content of the waste, thus increasing the calorific value of the waste itself (referring to the residual mass). The aim of the process is to eliminate part of the water contained in the RMSW to produce a material with better energy characteristics. The loss of water is obtained at the expense of a portion of the energy contained in the waste; in fact, the heat derives from the biochemical oxidation of a part of the volatile solids (VS) present in the putrescible fraction of the RMSW. The bio-drying process does not require the addition of water and also requires lower airflow rates compared to bio-stabilization (that is, a pre-treatment before landfilling). The contact time, which is linked to the development period of the biological process, is equal to 1–2 weeks. The bio-dried product obtained is generally processed (this stage depends on the initial composition of the RMSW) to produce a "high

quality" fuel, which can be used in thermoelectric power plants, cement factories or gasification/pyrolysis plants. The bio-dried material can, in fact, be easily post-treated to separate glass, metals and inert materials still remaining in the RMSW (to be sent for recycling, in particular with regard to the first two materials).
A question remains open concerning the use of bio-drying in extreme cases of waste management. This question is twofold, as it can refer to two very different cases such as:

- low percentage of putrescible matter in the RMSW with consequences on the role of the exothermal reactions performed by the bacterial population (Case A);
- location of a bio-drying plant in an inhabited area with consequences on the incidence of the emissions, generally managed by open biofilters, that release a flow at low high, low speed (Case B).

The first case belongs to the strategies where a bio-mechanical treatment plant can be put before a waste-to-energy plant, such as a conventional combustion facility or a gasifier. This option has been recently analyzed for a specific case [5]. A final decision has not been taken yet in the cited case (in Trentino, Italy), but what emerged from there is the importance of analyzing in detail the composition of RSMW and considering the role of the overall amount of waste to be locally treated: the trend of the sector, in enhanced contexts, seems to go towards small plants for final treatment. That opens a discussion on which process/technology could be adopted for closing the loop, as conventional options could suffer from the reduced capacity scale. In the materials and methods section, we can see how twofold integrated research is in progress on these topics, having as a reference case the Trentino one, but also looking to a wider perspective.

METHODS

The following steps refer to a dynamic research activity performed by an inter-university research group (the University of Trento, University of Insubria and University of Padua) and are still in progress, which characterise Cases A and B.
For Case A, the conceptual approach is:

a) Seek regions with very high source separation efficiency in MSW management.
b) Select cases where the selective collection of food waste and green waste is very efficient.
c) Verify the consequences of food waste percentage in the RMSW.
d) Analyze the viability of bio-drying in these extreme cases.
e) In case of demonstrated criticalities that do not allow adequate efficiency of the biological process, analyze the potentiality of assisting bio-drying with additional products thought for accelerating composting.

For Case B:

a) Seek sites where bio-drying could be of local interest to RMSW management.
b) Perform a dispersion modelling of open biofilter emissions.
c) Verify the local incidence of these emissions.

d) Analyze the case of conveyed emissions through a bio-trickling filter [6].
f) Verify the compatibility of the approach in terms of pollutant concentration before bio-trickling. In case of demonstrated criticalities that do not allow adequate efficiency of bio-trickling, analyze the potentiality of assisting it with additional biotechnological products.
e) Verify the effects of the different ways of releasing treated air (higher point of emission, higher velocity of release).

RESULTS AND DISCUSSION

What emerges in Cases A and B is that biotechnology could make available a biological solution (bio-drying and bio-trickling filter) in cases that generally divert towards alternative options because biotechnology is not yet fully explored. Indeed, steps a–d in Case A demonstrated that a limited percentage of food waste in RMSW can significantly inhibit the performance of bio-drying. Presently, in case of such context the decision makers prefer to avoid biological treatments of RMSW in the considered scenarios. An example is the case of Trentino [5], where bio-mechanical processes were excluded from the future scenarios of interest. This decision makes sense today, but it can be considered also a starting point for future research.

The case of bio-trickling filter results as not specific to a local context, as all the biological processes applied to MSW fractions show a reduced viability because of the relatively low concentrations of substances in the exhausted air to be treated before releasing it into the atmosphere.

CONCLUSIONS

Biotechnology could help to make bio-mechanical treatments like RMSW bio-drying more viable, working in two directions:

- enhancing the valorisation of VS in the RMSW through an assisted bioconversion;
- enhancing the performances of bio-trickling filters in a context like the MSW sector where this process today suffers from a limited concentration of pollutants/nutrients in the exhausted air to be treated.

An interdisciplinary approach is compulsory to go beyond the present limits.

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INNOVATIVE CLAY-BASED BIOLOGICALLY ACTIVE POLYPHENOL COMPOSITES AND THEIR POTENTIAL FOR BIOECONOMY DEVELOPMENT

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INTRODUCTION

The increasing human population and growing health consciousness have led to a significant rise in the demand for fruits and processed food products. Nevertheless, the production life-cycle of fruits generates a substantial quantity of waste, imposing a significant environmental burden. Adopting the principles of bioeconomy these fruit by-products can serve as sustainable and renewable resources, ripe for incorporation into biorefinery processes for the creation of various value-added products. In order to attain the objectives of the bioeconomy, it is vitally important to invest in research and innovation that encourage the generation of new knowledge, novel products, advanced technologies, and the substitution of fossil material-based goods with those derived from biomaterials [1].

Berries represent a potential product for advancing the development of bioeconomy. In the context of Latvia's bioeconomy development, particular importance is attributed to bilberries, lingonberries, cranberries, blueberries, and other berries belonging to *Vaccinium spp*. These berries are either indigenous to Latvian forests and wetlands or are effectively cultivated by local farms. Berries are great for their nutritional benefits and therapeutic properties thanks to the high concentration of bioactive constituents like polyphenols, inulin, vitamins, and minerals. Consequently, they can be harnessed for the extraction of bioactive compounds, such as polyphenols, suitable for use in cosmetic applications [1], [2].

Polyphenols such as flavonoids, phenolic acids, lignans, and anthocyanins are biologically active compounds. Polyphenols are known for having important bioactivities, such as a preventer of UV-induced skin photodamage and premature skin ageing and also are able to controll the risk of skin cancer. However, despite the biological activity, polyphenols, have a significant limitation – they are unstable under several conditions. Clay minerals can be used to stabilize polyphenols and prevent them from degradation, thus expanding the range of applications [3], [4].

The aim of the study was to intercalate various polyphenol groups into smectite type minerals to enhance their stabilization and evaluate the physicochemical properties for application in innovative biocosmetic and nutraceutical products. For example, phyllosilicate-based biologically active composites can be used as skin protective products that are a non-toxic alternative to chemical UV filters. UV radiation stands as a significant environmental stressor for human skin, capable of inducing a range of issues, including burning, redness, itching, premature ageing, and skin cancer. Consequently, safeguarding against UV exposure has become an essential part of daily skincare, leading to a notable surge in the usage of topical sunscreen products. However, in recent years there is evidence for possible side effects, e.g., skin allergy, endocrine and nervous system disrupting effect of selected chemical UV-filters in cosmetics [5].

METHODS

In this research, industrially made clay mineral and smectite-type natural clay from Latvia and Lithuania was modified with polyphenols from black chokeberry (*Aronia melanocarpa L.*), large cranberry (*Vaccinium macrocarpon*), elderberry (*Sambucus nigra*), and grape (*Vitis vinifera*) press residue. The sorption of polyphenols into a clay mineral was studied depending on the weight of the sorbent, the concentration of sorbate, the pH of the environment, time and temperature. Properties of the obtained composite materials were characterised by Fourier transformation infrared spectroscopy (FTIS), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD) methods, UV radiation screening and toxicity tests.

RESULTS

The synthesis of montmorillonite-anthocyanin composites is influenced by anthocyanin concentration, the type of clay mineral, and the amount of clay mineral used. Of the studied anthocyanins, higher sorption is provided using anthocyanins from aronia berries. Among the clay samples, the industrially produced montmorillonite clay (Mt-K10) showed the highest sorption efficiency, and from the natural ones, the Saltiški deposit clay (Fig. 1). The highest sorption

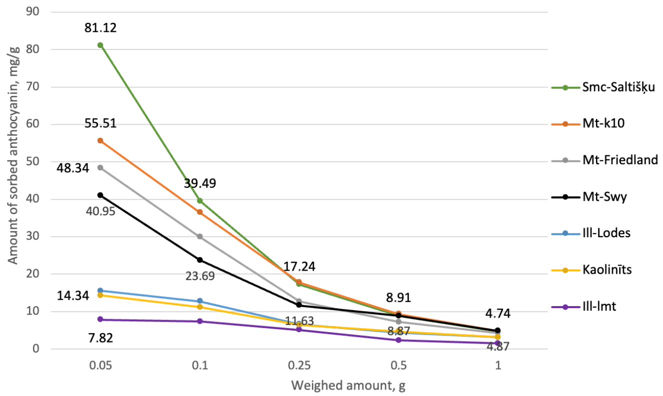

Fig. 1. Sorption of anthocyanins depending on the type and weight of the clay mineral.

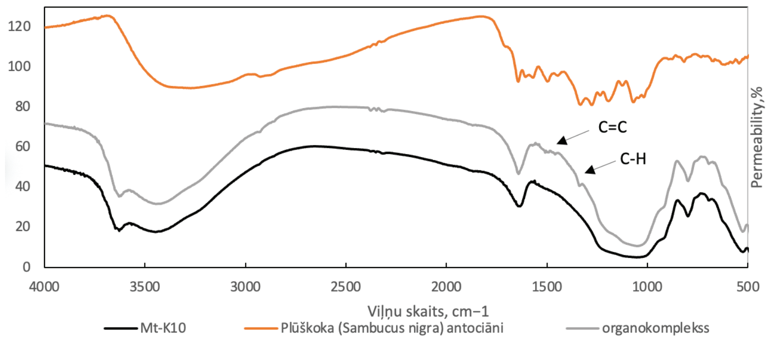

Fig. 2. FTIS spectrum of anthocyanin, clay-anthocyanin composite and untreated Mt-K10.

capacity is achieved at a pH range of 2–3, the optimal temperature is 24 °C.
XRD analysis data show that sorption of anthocyanins using Mt-K10 Mt-Swy and Mt-Friedland clay minerals takes place in the interlayer space. FTIS analysis shows changes in the functional groups of montmorillonites, anthocyanin and their composite material (Fig. 2).
Cell toxicity and UV transmittance tests showed that clay-anthocyanin composite materials can potentially be used as low-toxic UV filters in sunscreens and products with very low SPF values. The presence of iron compounds improves protection against UV radiation.

DISCUSSION & CONCLUSIONS

The study will expand the exploitation of Latvia's natural resources in the field of new technologies and will contribute to the development of a smart specialization strategy (RIS3), as evidenced by the development of innovative natural resource-based products in the economy.

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EXERGY AND CLIMATE IMPACT MODEL

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BACKGROUND

The study describes the cause of the global climate change problem or anthropocene [1]–[9]. Extreme weather events such as droughts, heat waves, heavy rain, floods and landslides are increasingly occurring in Europe as well. Below is a comparison of energy consumption between 1820 and 2018. The 1820 data shows 236.425 MTOE (1 MTOE = 1013 kcal = 41.868×10^{15} J). In the 2018 data, in addition to coal and wood, fossil fuels, oil and gas are included. And the energy consumption, produced is 12975.914 MTOE. The increase in energy consumption over the period is 54.88 times (12975.914/236.425) [10]. It should be noted that renewable and nuclear energy sources and volumes are developing, but as the US Energy Information Administration predicts, the demand for fossil fuel- generated energy will increase between 2020 and 2050 [11]. The world's largest source of CO_2 emissions comes from the combustion of fossil fuels used for energy. According to the Intergovernmental Panel on Climate Change (IPCC), the burning of fossil fuels (including minerals) accounts for 78.31 % of global CO_2 emissions and is the primary cause of global warming [12]. Scientists point out that the environmental impact of energy use and the increase in resource efficiency should be addressed, inter alia, through exergy calculations (EX). While EX is a measure of the efficiency of an energy form or substance, EX is also a measure of the change in its potential. The latter point suggests that EX can provide a basis for effectively assessing the potential of a substance or energy form to affect the environment. The costs of energy systems are typically energy-based. However, many researchers have suggested that costs are better allocated between outcomes based on EX [13]. EX destruction is a major cause of root causes of emissions [14]. In 2018, the fossil energy volume Efos = 12975.914 MTOE, and consequently, CO_2 reached an MCO_2 volume of 33.1 GigaTonnes (10^9 t) [15]. Cullen and Allwood estimated that 63 % of the world's primary energy consumption is lost (or converted to energy – EA) in combustion and heat transfer processes [16]. EX is calculated using the formula – Efos × 0.37 (12975.914 × 0.37) = 4801.088 MTOE. The corresponding EA is 8174.826. This shows that the existing energy calculation units do not represent the true useful energy. Expressing CO_2 emissions from EA – $MCO_2 \times 0.63$ = 22.177 Gt. This is the amount of CO_2 emissions from lost energy.

RESEARCH OBJECTIVES

Research hypothesis: Optimising EX reduces energy consumption and CO_2 emissions. The aim of the study is to show how the use of EX reduces overall energy consumption and CO_2 emissions.

METHODS

The research plan started with a literature review. Literature searches were conducted using search and bibliographic tools such as SCOPUS, ScienceDirect and RESEARCHRABBIT, and Google Scholar. The results of the study will be published.

CONCLUSIONS

It is necessary to clarify the life cycle EX of an energy system, as the current approach is incomplete, and EX calculations do not include a life cycle assessment of energy systems.

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EXERGETIC ANALYSIS OF WASTEWATER SYSTEMS WITH CO_2 EQUIVALENT ASSESSMENT

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BACKGROUND

The aim of the research is to reduce the emission of greenhouse gases (including the total amount of CO_2 emission) by applying Exergy (Ex) analysis for optimization of wastewater systems. Wastewater systems (Wwst) accumulate 1–3* percent of total energy consumption[1]. In 2022, total energy consumption was 14612 MTOE (million tonnes of oil equivalent) and from total energy consumption Wwst accumulate from 146.12 MTOE till 438.36 MTOE [2]. The fact is that 63 % of the total energy is lost in combustion and heat transfer processes. We have a working platform for 146.12 × 0.63 MTOE and 438.36 × 0.63 MTOE.

The following approaches are currently known: Ex calculations for energy chemicals (e.g. phosphorus and lithium ($(NH_4)2SO_4$), use of water, recycled products (e.g. gas) and sludge in wastewater treatment plants [3]. The idea of kinetic energy recovery is missing, and it equates to '0'. The challenges of the study are many, ranging from determining the accuracy and error of the data, weighing the impact of the technical state of the system on the Ex quantitative indicators, and choosing the right analytical and probabilistic methods. The follow-up direction is chosen in this study, a case study on heat recovery from wastewater, case study on the use of renewable resources in wastewater treatment plants, the impact of wastewater pumping plants on quantitative indicators and infiltration effects, etc. Rationale – to take a comprehensive, in-depth look at the subject under study.

RESEARCH OBJECTIVES

Research hypothesis: Optimizing Ex of wastewater systems reduces total CO_2 equivalent emissions. The main goal of the study is to find out the total exergy balance in the entire system and CO_2 equivalent emission assessment. Practical application of the result, for instance, to determine the wastewater treatment concept – connect to the public sewer network or solution can be local. Global wastewater production at 359.4 × 10 billions $m^3\ yr^{-1}$, and 37 percent of the total volume is not collected.

METHODS

The research plan begins with a literature review. The result of the literature review is the first publication on the topic "Exergy calculations in wastewater plants to date. Research review". For literature search, search and bibliography tools SCOPUS, ScienceDirect and RESEARCHRABBIT were used.

CONCLUSIONS

Existing studies show incomplete exergetic calculations of the entire wastewater system. They are limited to the CO_2 equivalent emission assessment of the entire system.

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FUNGAL-ASSISTED FLOCCULATION TECHNOLOGY FOR MICROALGAE HARVESTING AFTER WASTEWATER TREATMENT

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INTRODUCTION

The potential of microalgae biomass exploitation has been recognized by a wide spectrum of industries, including wastewater treatment [1], [2]. However, one of the major technological bottlenecks in wide-scale application of microalgae for wastewater treatment is related to biomass harvesting, which can contribute up to 30 % of the total production costs mainly due to the small size of the microalgae cells (2–20 µm) and their colloidal stability in suspension [3].
In recent years, bio-flocculation using other microorganisms has been offered as a method for microalgae harvesting [4], [5]. The process of microalgae bio-flocculation with filamentous fungi of the genus *Aspergillus* is the most widely described. By employing pellet-assisted harvesting, more than 90 % removal efficiency of *Chlorella vulgaris* was achieved after 24 hours due to bio-flocculation caused by *Aspergillus niger* [6]. With *Aspergillus fumigatus*, the concentration of *Scenedesmus quadricauda* was reduced by more than 95 % in 48 hours [7] and *Chlorella protothecoides* by 80 % in 24 hours [8]. Further, when the biomass flocculation is performed, it can be removed with sedimentation, non-reagent flotation or sieving. Given the non-toxicity of this technology in general, the potential cost-effectiveness and the high harvesting efficiency [4], microalgae co-cultivation with filamentous fungi can be considered as a potentially efficient and optimal method of micro-algae harvesting. Despite the well-demonstrated efficiency of the technology [6]–[8], it is still blanked out by lack of large-scale testing and limitations in reuse of the obtained biomass after wastewater treatment, and possible wastewater contamination with *Aspergillus* spp. and its leakage into the environment.
Therefore, the application of non-*Aspergillus* filamentous fungi to induce microalgae bio-flocculation in wastewater was studied. Experimental studies also allowed to come up with the most suitable cultivation and handling conditions and demonstrate the reuse of the material during the harvesting process.

METHODS

Tetradesmus obliquus (CCAP 276/10), *Desmodesmus communis* (CCAP 276/4B), and *Chlorella vulgaris* (CCAP 211/11B) were used in this study. Microalgae suspension was prepared in 1000 ml Pyrex® bottles in BG-11 growth medium at 20–27 °C. Continuous 10 Lh-1 aeration and the blue-red spectrum fluorescent light (180 µmol m^2 s^{-1} at a 16 : 8-h lighting regime) was provided.

White-rot fungi *Irpex lacteus* (Fr.) Fr., *Pleurotus dryinus* (Pers.) P. Kumm, *Pleurotus ostreatus* (DSM 1020), *Trametes versicolor* (DSM 6401), *Pycnoporus cinnabarinus* (Fr.) P. Karst, and soil fungus *Trichoderma reesei* (DSM 768) were maintained on Potato Dextrose Agar (Oxoid Ltd., Basingstoke, Hants, UK) at 2–8 °C. Each fungal species was inoculated into 250 mL Erlenmeyer flasks in a culture medium containing 0.8 g KH_2PO_4, 0.4 g K_2HPO_4, 0.5 g $MgSO_4 \cdot 7H_2O$, 2 g NH_4NO_3, 2 g yeast extract, and 10 g glucose per L and then cultivated for 3 days in an orbital shaker (New Brunswick™ Innova® 43, Eppendorf Austria GmbH, Wien, Austria) at 150 rpm and 30 °C. The pH was adjusted to 5.3–5.5.

Primary and secondary effluents were collected at a biological wastewater treatment plant, “Daugavgrīva” (Riga, Latvia, PE > 100 000), after primary and secondary settlers, respectively. Prior to use, the wastewater was filtered through a 0.45 µm cellulose-acetate filter to remove indigenous bacteria and micro-particles. To ensure the flocculation process, re-cultured fungal pellets were mixed with microalgae culture in Schott Duran 100 mL laboratory bottles, which were then placed on an orbital shaker (PSU-20i, Biosan, Riga, Latvia) at 150 rpm 20 °C (in lower temperature test experiments the shaker was inserted in a cooling incubator). During each experiment, the concentration of microalgae was measured daily in three repeats to determine the progress of microalgae harvesting. To determine the reduction in microalgae concentration during the bio-flocculation process, microalgae cell concentration was measured using a UV-visible spectrophotometer (GENESYS 150, Thermo Fisher Scientific Inc., Waltham, MA, USA) at 680 nm absorbance wavelength. Microalgae cell concentration in the samples was calculated by measuring its absorption using a UV-visible spectrophotometer in a linear interval.

RESULTS & DISCUSSION

The application of white-rot fungi has been recognized in biomass pretreatment, bio-chemical and enzyme production, biofuel production and bioremediation [9]. In this study, *I. lacteus* provided an average of 98.53 % ± 0.36 % percentage reduction of microalgae cells after 24 hours of harvesting and an average of 99.95 % ± 0.05 % after 72 hours.

Further, good harvesting results were obtained with *P. ostreatus* – an average microalgae reduction of 67 % was achieved after 24 hours, and more than 90 % after 48 hours. Similar results were obtained after 48 hours using *P. dryinus* and *T. versicolor* (85.96 % ± 5.74 % and 90.53 % ± 2.57 %, respectively). However, compared to *I. lacteus*, the efficiency of reduction for these fungal species was significantly lower ($p < 0.05$). Bio-flocculation induced by *T. reesei* provided more than 80 % microalgae removal efficiency, but after 72 hours, an increase in turbidity of the suspension was observed due to active fungal growth. The only fungal species that did not demonstrate any significant results was *P. cinnabarinus*.

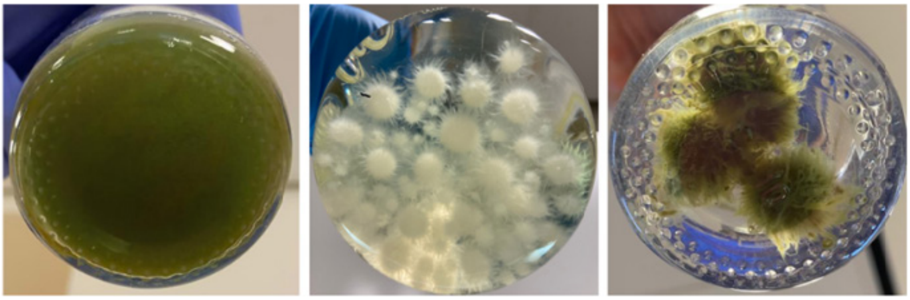

Fig. 1. (a) T. obliquus suspension before bio-flocculation; (b) I. lacteus before adding to the T. obliquus suspension; (c) algal-fungal pellets formed during bio-flocculation.

The maximum microalgae removal efficiency (38.56 % + 9.97 %) was obtained after 48 hours, following an increase in the turbidity and chromaticity of the suspension. This could be explained by the fact that *P. cinnabarinus* produces red-to-orange pigmentation due to phenoxazinone pigments [10]. The obtained results demonstrated that by using white-rot basidiomycetes, in general, more significant bio-flocculation results can be achieved than with *Aspergillus* spp. that typically provide more than 95 % after 48 hours or longer time [6]–[8].

CONCLUSIONS

This study confirmed the highly efficient bio-flocculation capacity of *Irpex lacteus*, which can provide more than 95 % reduction in *Tetradesmus obliquus* within 24 hours of bio-flocculation. Given that no chemicals were needed to induce the flocculation, the proposed microalgae harvesting method is environmentally friendly, as well as safer for human health when compared to the use of natural or genetically improved *Aspergillus* spp. The algal-fungal pellets formed during bio-flocculation are characterized by a rather large size (about 5–10 mm) and high durability. These factors potentially facilitate the removal of microalgae after flocculation, which, in turn, can also reduce the capital and operational costs of microalgae harvesting.

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INVESTIGATING THE DETECTION LIMIT OF WASTEWATER CONCENTRATION DEVICE FOR ACCURATE QUANTIFICATION OF SARS-COV-2 VIRAL PARTICLES: A CASE STUDY FROM LATVIA

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INTRODUCTION

Wastewater-based epidemiology (WBE) is one of the public monitoring tools capable of tracking the presence of infectious diseases, their spread, and outbreaks. The data obtained from wastewater monitoring can provide essential information for health institutions to take timely action to protect the population from the spread of diseases. Since the worldwide outbreak of the SARS-CoV-2 virus caused by the global pandemic, WBE has been actively used to monitor the spread of infections, including in Latvia. Viral RNA is released from infectious individuals into the sewage systems with faeces, saliva, and phlegm. Establishing evidence that the SARS-CoV-2 virus is detectable and quantifiable in wastewater samples, public health surveillance systems have integrated WBE. The main steps of WBE contain wastewater sample collection, sample concentration and analysis, sample data processing, normalization, interpretation, and reporting. Among all the challenges, the most urgent one is the concentration and detection of relatively low viral particle loadings in large volumes of wastewater. For large-volume wastewater concentration, a wastewater concentration device that utilizes microfiltration and membrane ultrafiltration methods was constructed. The main objective of this study is to test the detection limit for the wastewater concentration device to further enhance the wastewater sample processing of WBE.

METHODS

The concentration device was tested using surrogate-recombinant, replication-defective, and GFP gene-containing Semliki Forest virus (SFV) particles (constructed at the Latvian Biomedical Research and Study Centre). These particles replicate a similar structure as the SARS-CoV-2 virus. For accurate detection limit experiments, concentrations of 10^2 and 10^3 SFV were used and spiked into 4 L of wastewater. These SFV concentrations were added to wastewater samples. Large-volume samples with added SFV were concentrated with a wastewater concentration device, taking a sample of each section in the experimental concentration process.

To better understand the detection limit accuracy of the wastewater concentration device, samples were taken in experimental stages: first circulations of wastewater in the device, samples of concentrate, permeate and samples after the wastewater concentration device cleaning process. Further, these samples were analysed using the PEG-precipitation method. For SFV detection and quantification, RT-ddPCR was used, the target regions of SFV were the GFP gene. Control experiments without added SFV were carried out for each wastewater batch that was used. Wastewater concentration experiments with each SFV concentration were done in triplicate. For each experiment, the sample volume was 4 L.

RESULTS

The study demonstrated that tested SFV concentrations are not substantial enough for wastewater concentration device of further detection and quantification. The experiment with spiked 10^2 SFV concentration was successful, and a recovery rate of 45.31 % was detected in the concentrate sample (Fig. 1). For further studies in wastewater concentration device accurate detection, concentrate volume samples should be decreased to minimum volumes by improving the concentration tank and sampling process.

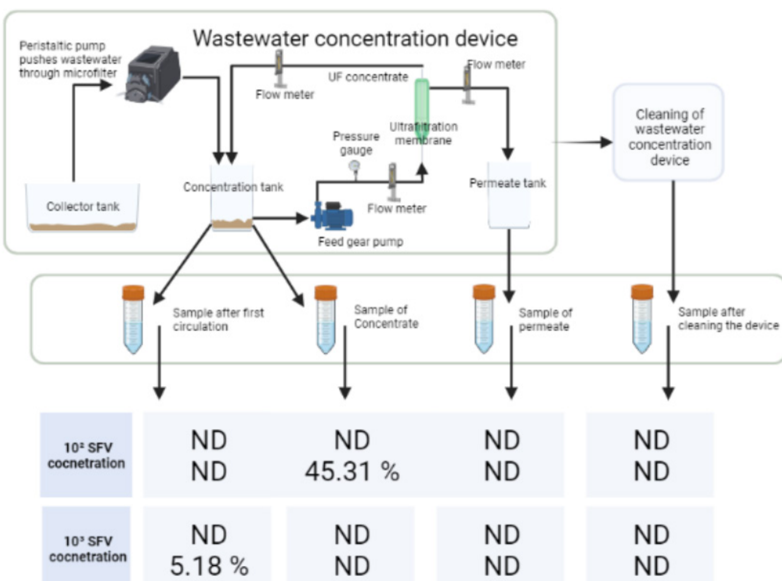

Fig. 1. Wastewater concentration device scheme and results from the collected samples. Each section samples are represented with obtained results recovered percentage of added SFV concentration. (ND – not detected)

DISCUSSION & CONCLUSIONS

The results of experiments represented that it is possible to detect viral concentrations of 10^2 SFV; nevertheless, more experiments should be performed for reliable results of wastewater concentration devices for detection limit accuracy. The main reasons for such results could be dilution and pipetting errors with SFV concentrate [1], as well as errors in further sample processing with PEG-precipitation [2] and analysis with RT-ddPCR [3]. Analyzed sample volumes are relatively small, i.e. 4 mL per sample, for such experiment execution, given the relatively large wastewater sample volume of 4 L. Previous studies demonstrated that recovery rates for ultrafiltration, surrogate enveloped virus concentration of 3×10^4 MHV (Murine Hepatitis Virus) spiked in 250 mL wastewater samples, the recovery rate of MHV was 25.1 % ± 3.6 % or 30.12 copies per mL [4]. In summary, from this study's results, wastewater concentration device needs improved experimental protocol, and for precise measurements, concentrate samples need further processing to the relatively smallest possible sample volume. Classification of relatively low viral SARS-CoV-2 concentrations in wastewater is under 90 copies per mL [5]. In further research, wastewater concentration devices should be tested with concentrations of 2.5 copies per mL (10^4 SFV), 25 copies per mL (10^5 SFV), and 250 copies per mL (10^6 SFV) if spiked in 4 L of wastewater.

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TRACKING THE SPREAD OF SARS-COV-2 STRAIN VARIANTS IN LATVIA: A DYNAMIC ANALYSIS

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INTRODUCTION

Although SARS-CoV-2 virus caused COVID-19 disease with a high number of infected people and a considerable number of deaths, it is not an issue of high concern in the world anymore. However, new variants are developing and appearing globally and locally [1]. This requires monitoring, analysis, and evaluation of the possible impacts. One of the advanced and feasible monitoring methods is wastewater-based epidemiology (WBE) [2], which is also efficiently used in Latvia.

METHODS

Based on recommendations of the EU Commission, a wastewater-based epidemiology monitoring of the SARS-CoV-2 is taking place in Latvia's towns, collecting samples from 16 Latvian municipal wastewater treatment plants (i.e. Riga, Daugavpils, Liepaja, Jelgava, Jurmala, Venstpils, Rezekne, Valmiera, Jekabpils, Salaspils, Tukums, Bauska, Saldus, Talsi, Limbazi, and Madona). The monitoring has been performed by the Institute of Food Safety, Animal Health, and Environment "BIOR", the Latvian Biomedical Research and Study Centre "BMC", and Riga Technical University since July 2021, as a national-scale wastewater-based epidemiology monitoring programme on surveillance of Covid-19 and other risk factors. Monitoring is performed by taking 24-hour composite samples twice per week at the inlets of the wastewater treatment plants.

RESULTS

Since July 2021, the wastewater-based SARS-CoV-2 monitoring programme in Latvian towns has been started and eleven of the virus variants have been detected: DeltaM, OmicronM; BA.1; BA.2; BA.4/5; BQ.1; BA.2.75, BN, XBB, XBB.1.5, with latest detection of EG.5 first detected in Salaspils in August, 2023. Prevalence of the virus variants detected in Latvia within the monitoring programme can be divided into six waves. For instance, the major prevalence in wastewater of Riga city, which serves more than 600 thousand inhabitants or one-third of the population of Latvia, has been recorded for SARS-CoV-2 variants: Delta (July 2021–January 2022); BA.2 (January 2022–June 2022); BA.4/5 (June 2022–January 2023), and finally XBB.1.5

Table 1. Spreading time of SAR-CoV-2 virus variants in Latvian wastewater

Variant	Earliest detection date	Latest detection date	Spreading time, days
BA.1	16.12.2021	04.01.2022	19
BA.2	04.01.2022	15.02.2022	42
BA.4/5	12.05.2022	16.06.2022	35
BQ.1	27.09.2022	24.11.2022	58
BA2.75	13.10.2022	08.12.2022	56
BN.1	27.10.2022	08.12.2022	42
XBB	27.10.2022	20.12.2022	54
XBB1.5	23.02.2023	14.03.2023	19
EG.5	10.08.2023	05.09.2023	26

(February 2023–current), which now is still the prevailing variant of SARS-COV-2 in Latvia. However, from November 2022 to February 2023, there was a period of concurrence among variants BQ.1, BA.2.75, BN.1, and XBB, during which there was not one dominating prevailing variant of SARS-CoV-2 recognized. It also shall be mentioned that variant BA.1 has been showing attempts to increase in prevalence but did not succeed from January 2022 to March 2022, giving over prevalence to BA.2. Very similar dynamics were also detected in other towns.

Data from the national WBE monitoring program showed the time span necessary for a SARS-CoV-2 virus variant to spread in Latvia, i.e., how much time was needed from the first earliest detection in the country in some of the wastewater monitoring sites to the moment when current variant was detected in all monitoring sites. The observed data summary is shown in Table 1. Though RNS concentration in Latvian wastewater showed a sliding increase, which is mostly related to towns such as Riga, Liepaja, Jelgava, Valmiera, Daugavpils, Bauska, Talsi, and Madona; however, there is no data available on the number of infected people since June 2023 [3].

DISCUSSION & CONCLUSIONS

New prevailing virus strains of COVID-19 have been appearing every three to six months. Lately, WHO has announced that there are three variants of the SAR-CoV2 under interest (VOIs) as of August 17, 2023: XBB.1.5; XBB.1.16 and EG.5, and seven variants under monitoring: BA.2.75, CH.1.1, XBB; XBB.1.9.1, XBB.1.9.2, XBB.2.3, and BA.2.86 [4]. Comparing the above-mentioned lists, three virus variants, XBB.1.5, EG.5, BA.2.75, and XBB, have been detected in Latvian wastewater and are now the focus of the Latvian SARS-CoV-2 WBE monitoring as well. At the moment, prevailing dominance belongs to type XBB.1.5 virus. The last detected new virus variant in Latvia is EG.5. It was first reported on February 17, 2023, and designated as a variant under monitoring on July 19, 2023 [5]. In its latest update from August 9, 2023, WHO informed that since August 7, 2023, the global database for gene sequences GISAID has received 7354 sequences in total, in which EG.5 has been detected in 51 countries.

A larger proportion of EG.5 sequences were received from China (30.6 %), the United States of America (18.4 %), the Republic of Korea (14.1 %), Japan (11.1 %), Canada (5.3 %), Australia (2.1 %), Singapore (2.1 %), the United Kingdom (2.0 %), France (1.6 %), Portugal (1.6 %), and Spain (1.5 %). WHO reports that globally, there has been a steady increase in the proportion of EG.5. During epidemiological week 29 (from July 17 to July 23, 2023), the global prevalence of EG.5 has raised from 7.6 % up to 17.4 %, comparing four weeks prior (week 25, June 2023) [5]. The WHO risk assessment states that based on the available evidence, the public health risk posed by EG.5 is evaluated as low at the global level, aligning with the risk associated with XBB.1.16 and the other currently circulating VOIs. While EG.5 has shown increased prevalence, growth advantage, and immune escape properties, there have been no reported changes in disease severity to date and no associations have been made between hospitalizations and EG.5. While Latvia has just recently detected a new EG.5 virus variant in wastewater, world is looking towards another new variant of SARS-CoV-2 designated as BA.2.86, which has been detected and showing a trend of increase in number of the world countries [4]. While the SARS-CoV-2 virus is continuing to change and amend, there is still a need for proper monitoring, including the WBE approach and assessment of the risks imposed by the virus.

ACKNOWLEDGEMENTS

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SYNERGIZING OPTICAL FIBER AND MEMBRANE TECHNOLOGIES FOR ENHANCED WATER PURIFICATION IN A PHOTOCATALYTIC REACTOR

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INTRODUCTION

Membrane separation technologies, such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis, forward osmosis, membrane electrolysis, and dialysis, have gained significant attention in large-scale treatment processes [1], [2]. These membrane-based technologies find extensive use in water purification, seawater desalination, food and textile industries, electronics, metallurgy, and energy sectors, as well as in biology and medicine [3]–[5]. Currently, membrane filtration stands out as a highly promising advanced method for diverse applications. In parallel, photocatalysis has emerged as a widely employed technology for water treatment [6]. The integration of these two approaches in an innovative manner holds the potential to unlock new and promising avenues for cost-effective water purification solutions. The inclusion of a photocatalyst on the membrane surface offers several advantages, including anti-biofouling properties, reduced concentration in the retentate effluent, cleaner permeate, and higher flux. To realize practical applications that provide affordable and accessible clean water, the development of photocatalytic membranes is indispensable. Previous research has primarily focused on surface coating of the membrane with a photocatalyst, which necessitates modification of the membrane and may compromise its filtration properties [7]–[9]. In this study, we present a novel approach utilizing universal spacers comprising side-scattering optical fibres coated with catalytic material. These spacers can be employed for both flat sheet and tubular membranes, addressing the limitations of existing methods. The objective of this work is to investigate a specific type of membrane and module design that can efficiently purify water, taking advantage of the unique features offered by the universal spacers.

METHODS

The membrane used in this study consists of polyvinylidene fluoride (PVDF) with 100 kDa MWCO as the main membrane material and polyethylene terephthalate (PET) as the support material. The length of the tubular membrane module is 350 mm and the inner diameter is about 8 mm. The chemicals used for live/dead bacterial analysis is SYBR Green I nucleic acid labelling dye stock solution,

purchased from Invitrogen, Switzerland. Titanium tetra n-butoxide (97 %), n-butanol (≥ 99.5 %), acetylacetone (≥ 99 %), 4-dodecylbenzene sulfonic acid (≥ 95 %), N, N–dimethylformamide (99 %), HPLC grade methanol, Propidium iodide (≥ 94.0 %), Dimethyl sulfoxide (≥ 99.7 %), and Tris Base, Molecular Biology Grade were acquired from Sigma Aldrich, Germany.
To check the biofouling removal efficiency of the membrane and TiO_2-coated optical fibre, two modes of filtration were tested, i.e. dead-end and cross flow. Each of the tests was done for 5 days in continuous tap water flow. The biofouling propensity and water flux of ultrafiltration membrane systems having TiO_2-coated optical fibre were separately evaluated using a dead-end and cross-flow filtration technique at a velocity of 60 RPM using 10 L of tap water (in Riga, Latvia) as feed water under 2 bar pressure for 5 d.

RESULTS

To determine the elemental composition on the sample surface, the XPS spectra of the tubular membrane were analysed, as shown in Fig. 1. Drinking water characteristics refer to the physical, chemical, and biological properties that determine the quality and suitability of water for consumption. The parameters like colour, odour, pH, total dissolved solids (TDS), microbial count, chemical oxygen demand, turbidity, conductivity, nutrient content, hardness, etc., should be analysed before the distribution of water for drinking purposes. These characteristics are typically regulated by water authorities around the world. Before the flux measurement through the tubular membrane, some of the above-mentioned water characteristics were analysed and presented in Table 1.

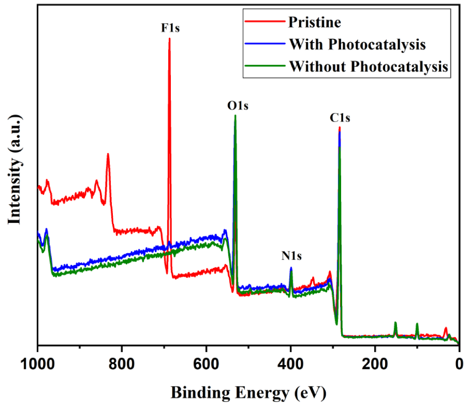

Fig. 1. XPS wide-scan spectra of the tubular membrane.

DISCUSSION & CONCLUSIONS

The XPS wide-scan spectra of the pristine tubular membrane, along with the tubular membrane used for water treatment with photocatalysis and without photocatalysis, are shown in Fig. 1. There are strong signals attributed to carbon,

Table 1. Physico-chemical parameters of tap water collected at Riga Technical University

Parameters	Values
Colour	colourless
Odour	odourless
Total Dissolved Solids (TDS)	153 ppm ± 5.0 ppm
Turbidity	0.08 ± 0.02 (NTU)
pH	7.4 ± 0.1
Conductivity	311 µS/cm ± 10 µS/cm
Chemical oxygen demand (COD)	8.0 ppm ± 3.0 ppm

nitrogen, oxygen, and fluorine. All the elements present in XPS spectra are the main chemical composition of membrane material. Compared to the pristine spectrum, a reduction in fluorine intensity (F1s) occurs together with an increase in the intensity of the oxygen peak (O1s).

All the physico-chemical parameters are within the permissible limits (Table 1) given by the EU regulation for drinking water. However, the microorganism counts are slightly high.

In summary, we have demonstrated a novel method of drinking water disinfection by using a tubular membrane coupled with a photocatalytic spacer. TiO_2 nanoparticle is highly effective for the microorganism under visible light irradiation allowing to increase fluxes by some 25 %. Thus, the principle of applying TiO_2-coated optical fibres in membranes for reducing biofouling has been proven by our experiments. The tubular membrane module, along with photocatalytic spacer, has been tested by two different filtration modes using UV-A LED light. This research not only reports a promising method that is expected to be used in drinking water treatment but also proposes ideas for industrial applications.

ACKNOWLEDGEMENTS

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ULTRAFILTRATION MEMBRANE MODIFICATION FOR IMPROVED FOULING RESISTANCE

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INTRODUCTION

Ultrafiltration (UF) membranes have emerged as pivotal tools in modern water treatment processes, addressing the pressing need for efficient separation of contaminants from water sources. Their ability to effectively remove microorganisms, suspended solids, and particles makes them indispensable for numerous applications, including seawater desalination, wastewater treatment, and potable water production [1]. Nonetheless, membrane fouling remains a critical challenge, leading to reduced water flux rates, diminished separation efficiency, and increased energy consumption [2].

Biofouling, primarily characterized by the accumulation of microorganisms, is the predominant fouling type of concern [3]. The membrane biofouling starts with the conditioning phase, followed by microorganism attachment, growth and biofilm development, and detachment. This process can take from several hours to days [4]. Traditional fouling mitigation approaches include feed pretreatment, during which most nutrients and microorganisms are removed or killed. The elimination of microorganisms can be done by simple feed water disinfection. In practice, even if 99.9 % of microorganisms are eliminated, a fraction can survive, multiply, and regrow back [3].

To combat the fouling issue and unlock the full potential of membrane technology, filtration process modification strategies are essential. In the context of non-solvent-induced phase separation (NIPS) membranes, numerous methods for membrane modification are available, including polymer blending, surface grafting, and surface coating techniques [5]. However, in practical applications, some of these methods may prove to be less feasible for large-scale manufacturing. For instance, surface coating can be quite time-consuming, particularly when it entails the application of multiple layers. Surface grafting is considered energy-intensive, resulting in higher membrane costs [6]. In contrast, polymer blending offers a faster and more straightforward approach. This is because polymer casting solutions can be prepared in advance and then easily applied using standard membrane casting equipment. Once manufactured, such a membrane is ready to use, and additional surface modification is not necessary.

The use of organic and inorganic nanoparticles for blending in casting solutions has gained traction as a successful strategy for fouling mitigation. Various materials, such as titanium dioxide (TiO_2), silver, graphene oxide, polyvinylpyrrolidone (PVP), and polyethylene glycol (PEG), have been extensively studied and have demonstrated improved antifouling properties [6]. In many cases, researchers limit their fouling assessments primarily to organic fouling tests, thereby leaving the membrane's antibacterial capabilities largely unexplored. Therefore, modified membranes were developed to assess their antibacterial properties. The aim was to investigate the capability of microorganism inactivation as a targeted strategy for mitigating biofouling.

METHODS

Flat sheet UF membranes were fabricated using a casting solution of polyethersulfone (PES) via the NIPS technique. Polymer blending was chosen as a strategy for membrane modification. Several inorganic nanoparticles were introduced into the casting solution and served as antibacterial agents.

Filtration experiments were conducted on a membrane testing device to assess the filtration and fouling characteristics. A solution containing a mixture of different molecular weight dextran proteins was employed to simulate the fouling.

The membrane structure was characterized through scanning electron microscopy (SEM), which included the analysis of membrane surface and cross-section morphology. This allowed for a detailed exploration of the distribution of added particles and their impact on membrane structure.

To evaluate antibacterial properties, a bacterial suspension of *E. coli* in a diluted nutrient solution was applied to membrane samples. Following an overnight incubation at room temperature, cultivation tests were conducted the next day.

RESULTS

SEM analysis showed classical asymmetric structures in all modified membranes, typical of UF membranes. The added particles were distributed within the modified layers of the membranes and were also detected on the surface. The distribution of particles depended on the material. Mostly an even distribution of fine nanoparticles was observed. However, in some membranes, large agglomerates were found.

The incorporation of inorganic particles resulted in an overall reduction in clean water flux, which was probably caused by additional flow resistance. However, the addition of organic additives, such as PVP, caused a significant increase in flux. This leads to possible combinations of multiple additives to achieve the desired result. During membrane fouling tests, modified membranes with added inorganic particles showed an improvement in flux recovery, meaning that such membranes could be rinsed from foulant more efficiently.

Several variants of modified membranes exhibited a consistent antibacterial effect. In a 24-hour period, membranes demonstrated more than 2 log reduction. This equates to the elimination of over 99 % of *E. coli* cells.

DISCUSSION & CONCLUSIONS

The developed membranes showed an improvement in various characteristics, including fouling resistance and antibacterial properties. The results correspond to many previous studies [6]. Despite the decrease in flux, combinations of different additives can be used to achieve an improvement of antifouling properties, while maintaining the hydraulic and antifouling properties.

The manufacturing process of the polymer blended membranes demonstrates promise for creating straightforward and ingenious antibacterial membranes, opening doors for enhanced microbiological research. The stability of added particles on the membrane surface and the persistence of antibacterial activity remain uncertain. To assess their practicality in everyday filtration, it is crucial to assess biofilm formation under filtration conditions.

ACKNOWLEDGEMENTS

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EFFICIENCY OF PHOSPHORUS REMOVAL AND RECOVERY FROM MUNICIPAL WASTEWATER USING NATURAL MINERAL MATERIALS

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INTRODUCTION

Natural phosphorus (P) sources are depleting, yet waterbody eutrophication remains a significant issue due to ineffectively treated wastewater and excessive fertilisation of agricultural soils. Effluents from wastewater treatment plants (WWTPs) are major sources of P in surface waters. Recently various methods, including adsorption, have been explored for phosphorus removal and recovery, offering sustainable solutions.

The aim of this research is to efficiently remove and reclaim P as a ready-to-use fertiliser from municipal WWTPs with a population equivalent (p.e.) of 10,000–100,000, utilising natural mineral materials like calcium/iron (CaFe) composites.

METHODS

The sorption performance of the obtained composite materials belonging to the Brownmillerite mineralogical subgroup and commercially available Polonite® (Polonite Nordic AB) was evaluated for the removal of P from the municipal WWTP "Ādažu ūdens" (23,066 p.e.) in Ādaži, Latvia. Mineral-based sorbents were characterised by the X-ray powder diffraction (PXRD) and X-ray wavelength dispersive fluorescence spectroscopy (WDXRF) techniques, specific surface area analysis by Brunauer-Emmett-Teller (BET) method and scanning electron microscope (SEM). Also, studies on kinetics and thermodynamics were started to evaluate the potential of the proposed CaFe composites as an alternative to chemical coagulants for efficient P removal from municipal wastewater. Furthermore, preliminary experiments were conducted on the utilisation of spent sorbents as potential alternative fertilisers. Experiments included analysis of heavy metal and agrochemical parameters as well as their phytotoxic effect on the early phase of plant growth.

RESULTS

The development of CaFe composites was optimised and resulted in a stable repeatable product in a scale of 5 kg of finished material for P removal and recovery. Various forms of CaFe composites were obtained in the laboratory, i.e. oxide, hydroxide and "regenerated" forms. All the transformations of the composites were monitored by PXRD (see Fig. 1).

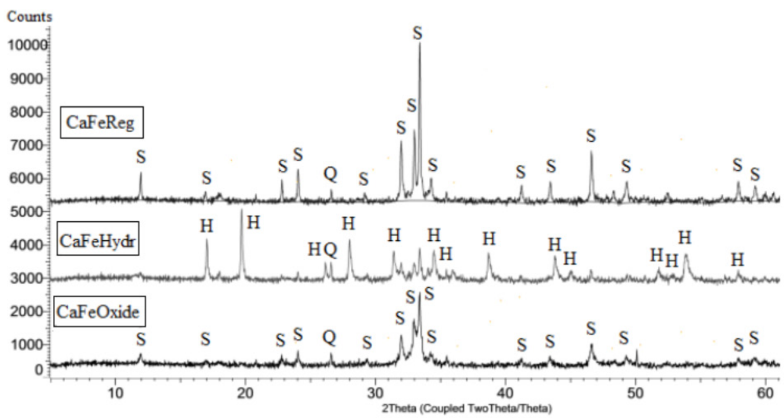

Fig. 1. PXRD patterns of CaFe composites: oxide, hydroxide and regenerated form (S – Srebrodolskite $Ca_2Fe_2O_5$; H – calcium iron hydroxide $Ca_3Fe_2(OH)_{12}$; Q – quartz SiO_2).

The specific surface area (SSA) value for the regenerated CaFe composite is 3–4 times higher than for the initial one (2.588 m^2 g^{-1} vs 10.616 m^2 g^{-1}), thus indicating higher P sorption potential.

Initial screening tests were performed to select the optimal sorbent/coagulant dosage. Concentrations of 1, 2, 3, 5, and 10 g L^{-1} of sorbent and real wastewater were used. Results indicated that at the concentration of 2 g L^{-1}, the P sorption was the highest for CaFeOxide and CaFeHydr materials: 17.75 mg g^{-1} and 8.25 mg g^{-1}, respectively. For CaFeReg, the highest sorption rate was achieved by utilising 3 mg L^{-1}, and the amount of P adsorbed was only 4.46 mg g^{-1}. The following experiments were then performed using 2 g L^{-1} of sorbent.

All three CaFe composites, as well as Polonite® material, adsorbed phosphorus

Table 1. Textural properties of CaFe composites

Composite	Specific surface area (m^2 g^{-1})	Pore volume (m^3 g^{-1})
CaFeOxide	2.588	0.006
CaFeHydr	3.804	0.014
CaFeReg	10.616	0.044

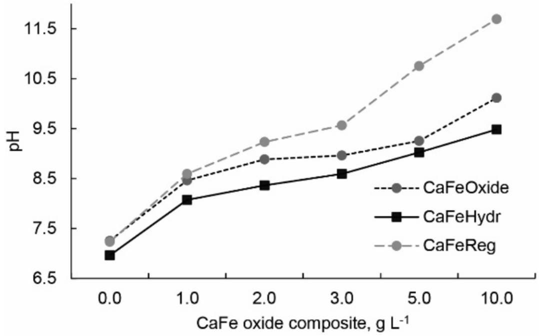

Fig. 2. Changes in wastewater pH after the sedimentation depend on the amount of calcium/iron composite added.

from "Ādažu ūdens" wastewater samples in a dosage of 2 g L^{-1}. The initial P limit for the raw wastewater sample of 19.4 mg L^{-1} was reduced by 94.5 %, 85.8 %, 88.5 %, and 61.2 % when treated with CaFeOxide, CaFeHydr, CaFeReg, and Polonite®, respectively.

Experiments showed that with the addition of individual CaFe composite to wastewater, pH increased with the increase of concentration of composite added (Fig. 2).

The evaluation of the safety regarding the utilisation of mineral sorbents after wastewater treatment in agriculture was conducted. For this, an analysis of heavy metal concentrations was performed, revealing that all three forms of synthesised CaFe composite samples are within Class I, indicating negligible heavy metal pollution and suitability for agricultural use based on Latvia's regulations (Cabinet Regulation No. 362 of 2006). To assess the phytotoxic effect of spent sorbent materials saturated with P on seedling growth, part of the common wheat (*Triticum aestivum L.*) seeds were grown in distilled water and another part in CaFe oxide composite and Polonite® with various target concentrations. Results indicated that all calculated seedling growth parameters were significantly enhanced for germinated seeds treated with spent CaFe oxide and Polonite® compared to

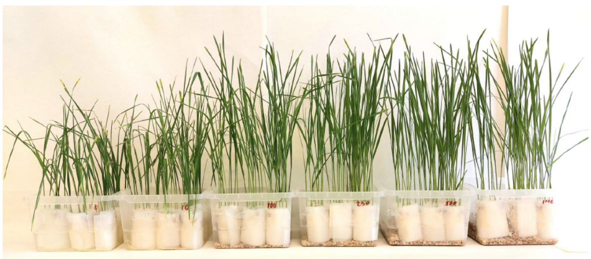

Fig. 3. Common wheat seeding growth in various Polonite® concentrations (from left to right: 0 g, 10 g, 100 g, 250 g, 500 g, 1000 g).

the control. In addition, with increasing spent sorbent material concentration, a significant increase in total seedling length, shoot weight and greater vigour was observed (Fig. 3).

Optimal concentrations for both spent sorbent materials were achieved at 250 g L^{-1} with seedling lengths of the first leaf 221.82 mm and 220.74 mm, and length of the second leaf 144.65 mm and 183.36 mm for CaFeOxide and Polonite® materials, respectively.

DISCUSSION & CONCLUSIONS

The ability to adsorb phosphorus of three obtained CaFe composites from real municipal wastewater was evaluated. It was confirmed that all three CaFe composites are able to adsorb P from difficult municipal wastewater matrix. The highest adsorption rate, 94.5 %, was achieved using CaFe oxide. Previous results (data not shown) indicated similar results (84.8 %) with real municipal wastewater from the Daugavgriva WWTP, Latvia (initial P concentration was 24.6 mg L^{-1}). The characterization of developed composites proved that CaFe oxide changed to hydroxide after the treatment of wastewater. Studies of kinetics and thermodynamics should be intensively continued to get more statistical data for the proper evaluation.

Preliminary experiments revealed that the composition of the elements in the spent CaFe oxide composite is balanced, the mineral nutrition of plants is not disturbed, and high concentrations of Ca, Fe, and Cr in the CaFe oxide material do not have a toxic effect on seedling growth. Also, heavy metal concentrations are low, indicating material safety for agricultural applications.

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