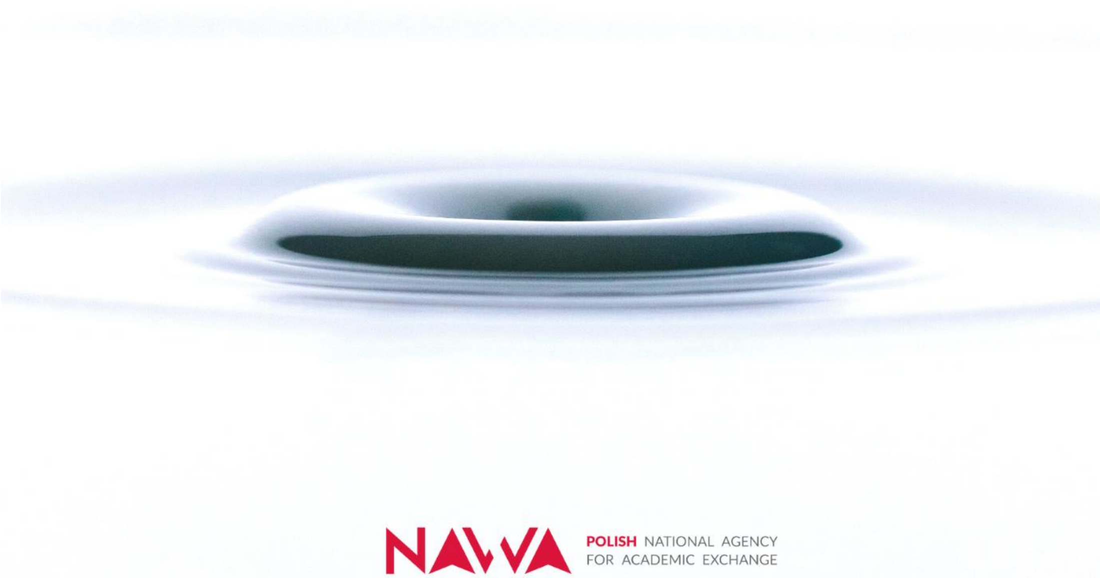
Mineral and Energy Economy Research Institute
Polish Academy of Sciences

MonGaS
International Conference 2022

Water and Sewage in the Circular Economy Model

MONOGRAPH



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CRACOW 2022

MonGOS
International Conference 2022

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PREFACE

Dear Reader,

It is my great pleasure to share a set of works on the implementation of circular economy (CE) in the water and sewage sector, which were widely discussed during the MonGOS International Conference: Water and Sewage in the Circular Economy Model, that took place in Cracow (Poland) on 30 June and 1 July 2022. This conference was dedicated to presentation of a summary of the project "MonGOS – Monitoring of water and sewage management in the context of the implementation of the circular economy assumptions", that was financed by the Polish National Agency of Academic Exchange. During 3-years project partners from Poland, Belgium, Lithuania, Latvia, Finland and Estonia were working on a framework for monitoring the transformation towards CE in the water and sewage sector.

This Monograph "Water and Sewage in Circular Economy model" contains selected papers that have been included in the conference programme. The papers present a wide range of CE implementation possibilities, in accordance with the proposed CE monitoring framework, which takes into account the prevention of wastewater generation (treated as waste that must be disposed of in accordance with the CE idea), wastewater and water purification, reuse & recycling of water, energy and raw materials (including nutrients).

I would like to thank for all Authors for sharing good practices on CE transition in the water and sewage sector. Special thanks to the Reviewers who took their time to review the papers.

I would also like to thank all project Partners for this 3-year journey of discovering different aspects for CE in the water and sewage sector.

Prof. Marzena Smol
MonGOS IC2022 Chair

IMPLEMENTING A CIRCULAR ECONOMY IN THE WATER AND SEWAGE SECTOR – SUMMARY OF THE MONGOS PROJECT

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Paper presents results of the MonGOS project – Monitoring of water and wastewater management in the context of implementing the assumptions of the circular economy, that was conducted by consortium of partners from Poland, Belgium, Finland, Latvia, Lithuania and Estonia, in 2020–2022. Project aimed to develop comprehensive CE monitoring framework and indicators that could clearly define the level of transformation towards CE in the water and sewage sector. Project also included involvement of the sector's stakeholders and environmental education for CE, aimed at popularising sustainable management of water, energy and raw materials. Important element of the MonGOS project was to exchange of good practices and dissemination of project results to various audiences, including children, students, doctoral students, specialists (including scientists) as well as entrepreneurs and authorities. Paper presents summary of the MonGOS project, that includes inventory of results in relation to the assumed goals.

Keywords: circular economy, CE, water, wastewater, monitoring framework

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1. INTRODUCTION

Circular economy (CE) is one of the key areas for achieving the goals of the European Green Deal, i.e. the new economic growth strategy of the European Union (EU), aimed at achieving climate neutrality by 2050 [2]. Circular economy is based on closing the resource cycle through rational management of primary raw materials and more sustainable methods of waste management [3]. Continuing the implementation of the initiatives included in the first circular economy action plan for the EU from 2015 [4], in 2020 the European Commission (EC) presented the second circular economy action plan, which clearly emphasized the role of the water and sewage sector in the process transformation towards CE [5]. This applies in particular to activities related to the reuse of water in a closed cycle [9], as well as the recovery of raw materials [8] and energy [16] from waste generated in water and sewage companies.

The EC indicates that circularity and sustainability have to be incorporated in all stages of a value chain to reach a fully circular economy. It takes into account stages from design to production as well as engagement of all consumers. The EC action plan sets down seven strategic areas essential to achieving the circular economy: i) plastics, ii) textiles, iii) e-waste, iv) food, water and nutrients, v) packaging, vi) batteries and vehicles, and vii) buildings and construction [5]. Achieving a climate-neutral circular economy requires full mobilisation of companies operating in the indicated sectors [1], including water and sewage sector. The water and sewage companies are important elements in building circular economy, because on the one hand, they use primary resources - water, and on the other hand, they have a great potential for the circular management of waste, such as sewage and sewage sludge, which are a valuable source of nutrients – in CE model, there can be turned into resources [10].

The implementation of the CE assumptions in different sector requires the monitoring framework that can be used for evaluations of transformation progress. To measure progress towards CE at the European level, in 2018, the EC proposed a set of ten CE indicators [6]. However, none of proposed CE indicators directly referred to the water and sewage sector. This was a large gap in determining the directions of transformation towards CE for this sector. Therefore, the MonGOS project – Monitoring of water and wastewater management in the context of implementing the assumptions of the circular economy to develop comprehensive CE monitoring framework and indicators that will clearly define the level of transformation towards CE in the water and sewage sector. An important element of implementing CE is the involvement of the sector's stakeholders and environmental education for CE, aimed at popularising the closing of water, energy and raw materials management cycles, characteristic for the water and sewage sector (including nutrients as phosphorus and nitrogen). Therefore, one of the strategic MonGOS project goals was to exchange of good practices and dissemination of project results to various audiences, including children, students, doctoral students, specialists (including scientists) as well as entrepreneurs and authorities. Paper presents summary of the MonGOS project, that includes inventory of results in relation to the assumed goals.

2. MATERIALS AND METHODS

The MonGOS project was conducted by following partners: Mineral and Energy Economy Research Institute, Polish Academy of Sciences (Poland), University of Latvia (Latvia); Kaunas University of Technology (Lithuania), Tallinn University of Technology (Estonia), Katholieke Universiteit Leuven (Belgium), Lappeenranta-Lahti University of Technology (Finland), Gdansk Water Foundation (Poland) and ERBEKA Foundation (Poland). The MonGOS project was implemented in 2020–2022 by a consortium of partners from Poland, Finland, Belgium, Lithuania, Latvia and Estonia, thanks to the support of the National Agency for Academic Exchange (NAWA) as part of the Academic International Partnerships program. The methodology adopted during the MonGOS project consisted of four main strategic goals, as shown in Figure 1.

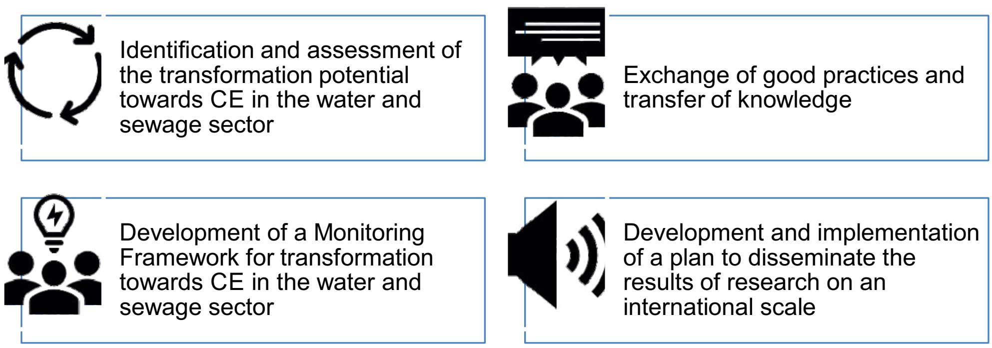

Fig. 1. Flowchart of the methodology used in the MonGOS project and in this study

The strategic goals of the project and methods used to their achievement included:

— Identification and assessment of the transformation potential towards CE in the water and sewage sector. It included a comprehensive identification and assessment of the transformation potential towards CE in this sector, and an inventory of indicators that would allow to effectively measure of the effectiveness of CE implementation in the sector. The main result was the first MonGOS project report “Transformation potential towards a circular economy in the water and sewage sector”. The selection of primary literature for the purpose of this report was based on full-text databases (Elsevier Scopus, Elsevier ScienceDirect, Web of Knowledge, Wiley Online, Google Scholar, EUR-lex, Eurostat) and available publications. The choice of literature was associated with the use of a few keywords: ‘waste management’, ‘water’, ‘wastewater’, ‘sewage’, ‘circular economy’, ‘CE’, ‘reuse’, ‘recycling’, ‘removal’, ‘eutrophication’, ‘nutrients’, ‘nitrogen’, ‘phosphorus’, ‘reclamation’, ’recovery’. The EU official documents (communications, directives, regulations) and international reports were also used. The other source of data were the Waste Framework Directive, EU statistics, CE reports on water management.

— Exchange of good practices and transfer of knowledge, by preparation good practices descriptor with the list of examples of good practice in the water and sewage sector, compliant with CE assumptions, and organising three study visits (Finland, Poland, Lithuania), two summer schools for Master and PhD students on the CE implementation in the sector (Belgium, Latvia). The main result was the second MonGOS project report "Best practices descriptor: Circular economy in the water and sewage sector". In this document, examples of sustainable and circular management practices in the water and sewage sector have been studied based on the input provided by the MonGOS Project Partners from: Poland, Finland, Lithuania, Latvia, Belgium, Estonia and other countries outside the project consortium such as Sweden, Denmark, Germany, France, Netherlands and Spain.
— Development of a Monitoring Framework for transformation towards CE in the water and sewage sector. A set of CE indicators were proposed, on the basis of which it is possible to assess the progress of a given organisation in implementing CE in the water and sewage sector. The main result here was third MonGOS project report "Monitoring framework of the circular economy in the water and sewage sector". The monitoring framework was proposed, based on 6Rs principle, and it includes six specific areas: reduction, reclamation (removal), reuse, recycling, recovery and rethink [13]. The specific indicators for each of mentioned areas were determined by advanced desk research using the methodology for scientific reviews. It included detailed review of available open access references published in scientific journals in accessible databases (ScienceDirect, Web of Science, Wiley Online, Google Scholar, Multidisciplinary Digital Publishing Institute, SpringerLink) and published reports of governmental bodies (national, regional and European) and non-governmental organisations, professional journals for water and sewage professionals. The core content of the report was based on the internal discussion of project partners. The initial results of the study were discussed with a panel of experts representing various sectors including among others, academia, research organisations, water utilities, public administration.
— Development and implementation of a plan to disseminate the results of research on an international scale, including the organisation of an international conference summarising the project. This stage included participation and organisation of various events (conferences, seminars, workshops) and preparation of scientific and non-scientific papers (ten international and ten national).

Due to the fact that at the beginning of the project's realisation, the COVID pandemic occurred, and lasted practically throughout the entire period of the project's implementation, these goals had to be verified, and some of the events had to be organized remotely. The study visits were cancelled because the internal regulations of the units participating in the project did not allow to host of foreign guests. In turn, the summer school planned to be organised in Belgium was moved to Poland, and an additional event was organised - a summer school for children. The results of the project MonGOS were systematically published on project webpage mon-gos.eu.

3. RESULTS

This section presents the results of the MonGOS project, divided into four sub-sections, dedicated to strategic objectives, indicated in section 2.

3.1. POTENTIAL TOWARDS CIRCULAR ECONOMY IN THE WATER AND SEWAGE SECTOR

The potential of the water and sewage sector in the implementation of CE concerns three main areas of resources management: i) water management in a closed cycle, ii) recovery of biogenic raw materials from waste generated in enterprises in the water and sewage sector, and iii) energy management and recovery. In the MOnGOS project, the CE potential was identified for this three areas, as presented in Figure 2.

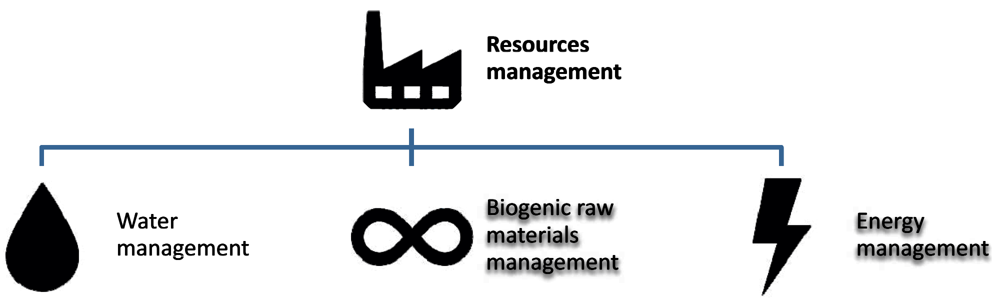

Fig. 2. Specific potential areas of CE implementation

3.1.1. WATER MANAGEMENT

Advancing climate change is contributing to increasing pressure on water resources in the EU, which is why the EC calls on the Member States to take action to protect Europe's water resources. A new regulation on water reuse requirements "Regulation EU 2020/741, Minimum requirements for water reuse" [15] was presented in 2020, which lays down minimum water quality and monitoring requirements and rules on risk management for the safe use of reclaimed water for irrigation in agriculture. Water reuse systems, which are a model example of circular economy, take into account the infrastructure and all technical elements necessary for the production, delivery and use of reclaimed water. Such a system is an integral whole – from the inlet to the sewage treatment plant to the point where the treated municipal sewage is used for irrigation in agriculture. The use of reclaimed water for irrigation was determined for plants to be consumed raw, plants to be consumed after processing and non-food plants. In addition, the reclaimed water can be reused in industry, municipal services and environmental protection. In this system, it is obligatory to carry out routine checks of compliance with the minimum requirements regarding the quality of reclaimed water, which are specified in the scope of monitoring. Risk management plans will also be necessary, which should include appropriate ways of identifying and managing the risks to ensure that the reclaimed water is used and managed safely and does not pose a risk to the environment or to human or animal health. The aforementioned regulation had a positive impact on the intensification of research and implementation works related to the reuse of water and its economic management, among others. in industrial processes. One of the interesting examples of the practical implementation of water recovery technology is the use of membrane filtration and UV disinfection for the treatment of sewage treated after the sewage treatment plant of the Kasina Ski Ski Station for the purpose of artificial snowing in winter and irrigation of green areas in summer. This installation was designed and implemented by Schwander Polska.

In addition to municipal wastewater, attention should also be paid to the possibility of using grey water and rainwater in a closed circuit, which can be used, among others for flushing toilets, watering green areas, washing facilities and selected devices, washing, as well as in car washes. Currently, more and more technologies for the recovery of grey water and rainwater are available on the market, including patented solutions offered by Green Water Solutions, which use integrated treatment methods combining biological processes with membrane filtration. Such solutions are more and more often implemented in tourist and sports facilities as well as single and multi-family buildings.

3.1.2. BIOGENIC RAW MATERIALS RECOVERY

Nutrient recovery can be widely used in the water and sewage sector. Particularly noteworthy here are municipal wastewater treatment plants, where phosphorus and nitrogen can be recovered at every stage of wastewater treatment and processing of sewage sludge, and ash from their combustion. Waste generated in sewage treatment plants can be successfully used for the production of fertilisers or agents improving soil properties (so-called soil improvers). Particular attention is now paid to the possibilities of recovering phosphorus, which is a critical raw material for the European economy [7] as well as a key resource for the national economy in Poland. Phosphorus recovery in a treatment plant can take place at several stages of waste water treatment or sludge treatment, including raw sewage, sewage sludge leachate, dewatered sewage sludge and thermal treatment ash. In Poland, an example of the implementation of such a circular solution is the installation for phosphorus recovery from the leachate stream from mechanical thickening of excess sludge and initial and final sludge dewatering at the sewage treatment plant in Cielcza, which is to be put into operation in 2022. The final product of the process will be fertiliser generated in the reactor fluid bed with a moving bed, which will be intended for fertilisation and maintenance of green areas in the Jarocin commune. Work on the recovery of phosphorus is also carried out as part of the InTOPhos project, carried out by Krakow Water Utility. The project aims to develop a universal solution for phosphorus recovery in mechanical-biological wastewater treatment plants, which will be based on the controlled precipitation of magnesium ammonium phosphate (stuvite), which is currently causing many operational problems (creating hard mineral deposits in the technological systems of treatment plants, including pumps, pipelines or drainage machines). It is worth mentioning here that the ashes generated during the thermal treatment of sewage sludge have the greatest phosphorus recovery potential (up to 95%). As part of the CEPhosPOL project, carried out at the f Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, thermochemical methods of phosphorus recovery in the presence of sodium donors (based on the assumptions of AshDec technology) from ashes generated in Polish mono-incineration plants were tested [11]. The obtained fertiliser preparations (stable, with a high content of phosphorus and a low content of heavy metals) met the standards for marketing authorization as mineral fertilizers. An interesting solution for the management of sewage sludge in accordance with the concept of circular economy is also the production of soil improvers intended to increase the content of organic substances in soils, e.g. in grasslands, crops of agricultural plants and ornamental plants. Such a solution, based on the processing of dried sewage sludge into an agent supporting the cultivation of plants, is used, among others, by in the Municipal Water and Sewage Company in Rzeszów.

3.1.3. ENERGY RECOVERY

One of the most controversial areas of circular economy implementation is waste incineration (including sewage sludge), during which the possibility of recovering selected raw materials is irretrievably lost. In the case of sewage sludge, the greatest added value of incineration is a significant reduction in the amount of waste requiring further management, reaching 80–90% of sewage volume reduction. Thermal transformation of sewage sludge may be recommended direction of circular economy only when energy is recovered at the same time, which can be used to supply the plant. Ashes generated after the incineration of sewage sludge should be directed to phosphorus recovery (applies to mono-incineration plants), and in the case of using chemical recovery methods – the residue is used in the construction sector. This allows the sewage sludge value chain to be completely closed. Processes such as methane fermentation, pyrolysis and gasification have the greatest potential for energy recovery from sewage sludge in most municipal wastewater treatment plants. Biogas produced in the process of anaerobic stabilization of sludge can be used to produce both heat and electricity. The potential of electricity production from biogas in sewage treatment plants was estimated at the level of approx. 700–850 GWh per year. This is a recommended direction, especially in the context of achievable environmental (sewage sludge management), energy (energy self-sufficiency in sewage treatment plants) and economic benefits (electricity supply at a cost lower than supply from the network) [16]. However, further support for investments in biogas energy in national wastewater treatment plants is required through appropriate regulatory support, educating investors and local communities about the technology, its benefits and limitations, and appropriate financial support.

3.2. EXCHANGE OF GOOD PRACTICES AND EDUCATION FOR CIRCULAR ECONOMY

One of the main reasons for undertaking research, conduced as a part of the MonGOS project, was the need to intensify international cooperation between the European units in the field of water and sewage management. The main approach was to intensify the exchanged of good practices dedicated to CE implementation in the sector, as well as and transfer of knowledge from developed countries to developing countries. Therefore, the joint report "Best practices descriptor: Circular economy in the water and sewage sector" was developed by the project consortium. It contains several examples of sustainable and circular management practices in the water and sewage sector. It was also important to involve young scientists who have no experience in cooperating with entities from abroad and do not publish their research results on the international area. Therefore, the project contained also education for circular economy, dedicated mainly to Master and PhD students, who underlined that participation in international grants and short-term trips abroad are the most effective tools supporting the development of their careers. During the MonGOS project, the following international education events were organized by project partners: winters school, summers schools, and mini-summer school. They are shortly described below.

Winter School for Master and PhD students "Circular Sewage Treatment Plant of the Future" (November 22–26, 2021, Krakow, Poland) – the aim was to broaden the knowledge of participants (master and doctoral students from 14 countries) in the field of implementing CE in municipal wastewater treatment plants, including the recovery of raw materials, energy and water. The event was supported by study visit to Krakow-Płaszów Wastewater Treatment Plant, operated by Krakow Water Utility. During the study visit, they had the opportunity to familiarise themselves with the entire technological line of the sewage treatment plant, sludge management carried out in the plant, and devices for biogas production and thermal processing of sewage sludge. This enabled them to learn about the practical aspects and problems during the operation of the sewage treatment plant, as well as to address emerging questions directly to the representatives of the Krakow Water Utility. Students created 5 groups, and their common goal was to work on the "case study", entitled "Circular Sewage Treatment Plant of the Future", on the example of the Kraków-Płaszów treatment plant. During group work, participants had to face three challenges (so-called "challenges"): i) materials and energy challenge, ii) economic challenge, and iii) social challenge.

Summer school for Master and PhD students "Water in Circular Economy" (May 30––June 3, 2022, Riga, Latvia) – it aimed to broaden the knowledge of participants (master and PhD students from 10 countries) in the field of sustainable water management, recovery of raw materials and energy in the water and sewage sector. The participants took part in three study visits (to the laboratories of the University of Latvia, to the municipal sewage treatment plant "Daugavgrīva" and to the Getliņi EKO municipal waste landfill in Riga, for which the participants then created new solutions and proposals for the implementation of circular economy in these facilities), lectures, workshops, discussions conducted and moderated by an

Fig. 3. Study visit to Cracow Water Utility during winter school in 2021, Poland

Fig. 4. Study visit to municipal wastewater treatment plant "Daugavgriva" during summer school in 2022, Latvia

international group of experts. The summer school was held on the Ratnieki campus (57 km from Riga, in the Gauja National Park) belonging to the University of Latvia. On the last day, the participants were asked to give a speech during the Pitch session.

Summer School for children "Water in Circular Economy" (June 6–10, 2022, Kraków––Zator, Poland) – it aimed to broaden the knowledge of primary school students in the field of water management through active workshops, games and educational games, including a visit to the Droplets Academy of the Krakow Water Utility.

Fig. 5. Study visit to Droplets Academy of the Krakow Water Utility during summer school in 2022, Poland

Mini-Summer School for children "Water in Circular Economy" (September 26, 2022, Lisow–Korzonek, Poland) – it aimed to broaden the knowledge of primary school students in the field of water management through active workshop, and educational games, including a visit to the Park Korzonek, where water related experiments were conducted. There were two parts – the first lecture, during which children were introduced to the topic of sustainable water and sewage management (in primary school in Lisow), and the second, practical, in which children took part in interactive workshops, during which they developed their examples of CE, proposed methods of saving water and protecting biogenic raw materials (in Educational Park Korzonek).

Fig. 6. Study visit to Educational Park Korzonek during mini-summer school in 2022, Poland

The organisation of presented education events, as part of the MonGOS project, aimed to broaden the participants' knowledge about the implementation of CE in the water and sewage sector, based on the following:

- analysis of barriers and factors driving the implementation of circular economy in the water and sewage management sector,
- analysis of legal, technological, organisational and environmental factors of implementing circular economy in water and sewage facilities,
- development of a set of indicators to monitor the transformation of the sector towards circular economy;
- review of existing examples of good practice.

The organisation of schools also aimed to present its participants the assumptions of the European Green Deal, the latest European Union strategy for ecological and sustainable development, for which CE is one of the main pillars.

3.3. MONITORING OF CIRCULAR ECONOMY IN THE WATER AND SEWAGE MANAGEMENT SECTOR

In 2018, the EC presented the framework for monitoring circular economy and indicated ten CE indicators (available on Eurostat) covering each stage of the product life cycle and aspects of competitiveness. The list of indicators is systematically updated, however, currently this list does not include indicators for the water and sewage management sector. Therefore, in the MonGOS project, comprehensive CE indicators were developed. They can be used to assess the level of transformation towards CE in the water and sewage sector in the EU. The developed indicators are of great importance for the strategic planning of the development of organisations using water resources in their activities, not only in the field of circular economy, but also in the area of supporting innovation, education, employment, and the development of industry and services.

The MonGOS project has developed a framework for CE monitoring in the water and sewage sector, based on 'xR' models in waste management as well as the EU waste hierarchy. The assumptions of the CE monitoring framework in water and sewage management have been classified into groups of activities that fit into the assumptions of CE, i.e. reduction, reclamation (removal), reuse, recycling, recovery and rethink [13]. They refer to:

- Reduce – prevention of wastewater generation in the first place by reduction of water usage and pollution reduction at the source,
- Reclamation (removal) – application of efficient technologies for the prevention of inclusion of hazardous pollutants into wastewater and removal of pollutants from water and wastewater,
- Reuse – reuse of wastewater as an alternative source of water supply (non-potable usage),
- Recycling – recovery or reclamation of water from wastewater for potable usage,
- Recovery – recovery of resources as nutrients and every from water-based waste,
- Rethink – rethinking how to manage resources to create a sustainable and circular economy, which is free of waste and emissions.

As in the case of the EU waste hierarchy, in the proposed model of measures for the CE implementation, they were grouped in order from the most desirable to the least desirable. The exception is the element of “rethinking”, that is, verification of the approach, which should be carried out in parallel with all other activities (Fig. 7).

The characterisation of the proposed model has been presented in works [12, 13]. For each of the indicated areas, economic, environmental (dedicated to resources efficiency) and social indicators for the implementation of CE in the sector were proposed. The economic indicators were proposed in work [14]. The environmental – dedicated to resources efficiency – were published in [8], while social indicators were indicated in joint report “Monitoring framework of the circular economy in the water and sewage sector”, available on the MonGOS project web-page (mon-gos.eu).

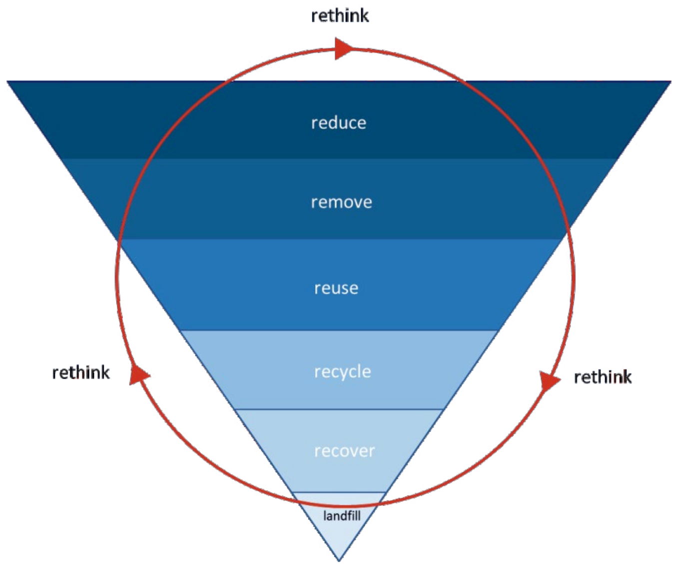

Fig. 7. Scheme of framework for monitoring circular economy in the water and sewage sector [13]

3.4. POPULARISATION OF CIRCULAR ECONOMY IN THE WATER AND SEWAGE SECTOR

Circular economy is a concept that requires stakeholders involvement in the water and sewage sector to change both in their thinking and actions. A key role is played by the popularisation of the idea of CE, which are aimed at encouraging all groups of stakeholders – including decision-makers, entrepreneurs, representatives of science and education, as well as citizens themselves – to verify and rethink their role in closing circuits water and raw materials. Therefore, an important element of the MonGOS project was the popularisation of its results, including through the activity of partners at conferences related to CE and water and sewage sector as well as participation and organisation of meetings and discussions with specialists. The most important events organised during project duration:

Online workshop “European Green Deal: Water and Wastewater in a Circular Economy” (May, 21 2021, online) – devoted to discussing possible actions aimed at using the full potential of the water and wastewater sector and accelerating its transformation in accordance with the CE model, but also in the context of challenges resulting from the implementation of the European Green Deal. The participants were representatives of the most important stakeholders representing the public administration sector (central and local government), universities and research institutions, enterprises and non-governmental organisations.

Online workshop “Water in Circular Economy” during the 2nd International Conference Strategies toward Green Deal Implementation Water, Raw Materials & Energy (December 8, 2021, online) – the aim was to exchange knowledge and present innovative solutions in the field of water and phosphorus recovery and management of waste generated in the sector in accordance with the CE. Workshop materials are available free of charge online in the Abstract book on the conference website (greendeal2021.pl) and on the MonGOS project website (mon-gos.eu).

Online workshop – Coffee with MonGOS "Phosphorus recovery in wastewater treatment plants – current trends and forecasts for the future" (March 29, 2022, online) – it focused on discussion of experta about technical, legal and economic challenges and opportunities with the participation of representatives of the water and wastewater treatment companies from all over Poland.

International Conference "MonGOS – Water and Sewage in a Circular Economy" (June 30–July 1, 2022, Krakow, Poland) – the idea of circular economy was widely discussed by experts during nine sessions related to the implementation of CE in the sector, in two key areas: sustainable management of primary resources (water, raw materials, energy) and circular management of secondary resources (waste generated in the sector, including sewage, sewage sludge and other waste). The material in the form of an Abstract book from the entire event is available on the conference website (www.mongos-conference.eu) and on the MonGOS project website (mon-gos.eu). The conference was hosted by the Mineral and Energy Economy

Fig. 8. Project partners during International Conference "MonGOS – Water and Sewage in a Circular Economy" in 2022, Poland

Research Institute of Mineral of the Polish Academy of Sciences in cooperation with Krakow Water Utility. The aim of the conference was to present the results of the MonGOS project, as well as to create a space for the exchange of knowledge and experience between key experts in the sectors of water and sewage management, reclamation and agriculture in Poland and around the world.

To increase the effective dissemination of the MonGOS project results, in 2020, it joined one of the biggest dissemination platform for water and sewage sector in the world – the European Sustainable Phosphorus Platform – ESPP (phosphorusplatform.eu/platform/espp-members-2/1979-mongos). The Members of ESPP cover a wide range of actors across the whole value chain of phosphorus stewardship: phosphorus mining and processing, water and waste treatment, food, feed and agriculture, phosphorus reuse and recycling, innovation and technology providers, knowledge institutions, NGOs and governmental organizations. ESPP actively published information about the results of the MonGOS project (articles, educational events, workshops and conferences), and also published reportage films from the winter school and the MonGOS international conference in Poland.

CONCLUSIONS

The water and wastewater sector is facing a great challenge, because in addition to fulfilling its basic activity, which is water supply and pollution removal, in order to preserve the value of water resources, the circular economy package indicates much more ambitious goals. Further works to implement practical solutions to recycle water, energy and raw materials is the basis of a sustainable and circular economy that aims to use natural resources more efficiently while ensuring their availability for future generations. During the MonGOS project, practitioners and theoreticians actively worked to promote the CE implementation in this sector, in two key areas: sustainable management of primary resources (water, raw materials, energy), and circular management of secondary resources (waste generated in the sector, including sewage, sewage sludge, and other waste). The consortium has achieved all the assumed goals of the MonGOS project by developing technical and scientific reports, organising many educational events (including summer schools and workshops), organising a conference summarising the project, as well as developing scientific and popular science articles. Further work to popularise CE in the water and wastewater sector will be carried out.

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TREATMENT OF SALINE WASTEWATER USING PRESSURE-DRIVEN MEMBRANE TECHNIQUES

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The present research studied the fractionation of saline wastewater along with the use of a multi-stage membrane system consisting of the following processes: microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF). During the experimental work, a polymer MF membrane manufactured from polyethersulfone (PES) with a pore size of 0.1 µm, a polymer UF membrane with PES with a cut of 5000 Da, and a polymer NF membrane with polyamide-TFC with a cut of 300 Da were used. MF and UF membranes are characterized by pore size or cut -off, while NF and RO membranes are characterized by cut-off, and MgSO4 and NaCl retention. The integrated membrane system achieved a high removal efficiency of organic compounds (TOC) that reached about 95.48% and also a 77.79% removal efficiency of Inorganic compounds (IC). Finally, there were three obtained waste streams with significantly different properties and thus being an easier medium for management. The last stream contained the highest salinity of 3846 mg NaCl/L.

Keywords: saline wastewater, separation, fractionation, MF, UF, NF

1. INTRODUCTION

Water scarcity affects hundreds of millions of people worldwide, making it a major global issue [1]. The increase in demand for renewable freshwater is being driven by population growth, intensive economic activity, and climate change [2, 3].

The term saline wastewater is applied not only to mine waters but also to industrial wastewater containing high concentrations of organic and mineral compounds like the one pro-

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duced by the food and the oil and gas industries. The fractionation of brackish wastewater and the appropriate treatment of each individual waste stream constitute proper industrial wastewater treatment and are fully compatible with circular economy assumptions.

One of the significant problems in Poland is mine water, which is collected in reservoirs of liquid substances (hydrotechnical facilities) and then discharged into natural water resources like rivers. One of the examples of such facilities is the “Olza” retention and dosing system, which consists of two retention reservoirs “Rybnik” and “Łąka” with a capacity of 1 million m^3 and pipelines with a total length of 73 km [4]. After pre-treatment from suspension in sedimentation tanks, brackish waters collected in retention reservoirs are dosed in the Odra rivers through a collector. Discharge of brackish water takes place only when the flow of natural waters is sufficiently high and is under constant monitoring of the natural environment. A system of nozzles at the bottom of the river allows the brackish water to mix well with the surface water. However, it is introducing large loads of chlorides and sulfates into the environment.

Another example – the largest in Europe is the “Żelazny Most” flotation tailings storage reservoir with a capacity of 7 million m^3 at the KGHM Polska Miedź copper mine [5]. Flotation wastes are wastes from the flotation enrichment of copper ores, consisting of crushed rock devoid of metal ores and underground water. The problem here is also the salinity of the water [6].

The discharge of such brackish waters into the environment is only a controlled transfer of pollutants and not a disposal of the mine water. Yet these waters can be a valuable source of industrial and drinking water. The mine waters of the “Rydułtowy” Mine are treated in the processes of coagulation, classical filtration, and a two-stage RO [7]. After the process of remineralization and water disinfection, among others, as drinking water. RO capacity is 960 m^3/d with water recovery from brackish water at 72.7%

Another example is the desalination of natural waters in order to use them for human consumption or agricultural and industrial purposes. Groundwater is the primary source of renewable freshwater used for water supply, agricultural, industrial, and domestic activities all over the world, particularly in arid and semi-arid zones of southern Europe, the Middle East, and North Africa [8]. Egypt's primary source of water is surface water from the Nile. Egypt's Nile water share is set at 55.5 billion m^3/yr. The remainder is made up of groundwater and, to a lesser extent, desalination and wastewater reuse [9, 10]. Egypt's water resources are deficient due to increased urbanization plans outside the Nile valley and insufficient Nile water resources [11–13]. Egypt's available water resources are expected to reach 70.8 billion m3/yr by 2025 as a result of new projects and irrigation system improvements, according to the Water Resources and Irrigation Ministry (MWRI). Egypt's 2017 Integrated Water Resources Plan (IWRP) aims to increase water supply quantity and quality [14].

Water could be delivered to remote Egyptian communities via pipelines and other modes of transportation such as trucks. Such methods, however, appear to be prohibitively expensive, particularly over long distances (larger than 150 km). The presence of brackish water of moderate salinity (2000–6000 mg/L) in some of these areas can provide an economical and reliable fresh water supply if an appropriate desalination scheme is used [15, 16]. Several techniques have been proposed to solve the problem, either partially or completely, but the majority of them are inefficient and expensive. Egypt is encouraging both the public and private sectors to use modern desalination technologies, which have historically included distillation, electrodialysis, and, most recently, RO [17].

Egypt's future vision for desalination is unconventional. It is based on a significant advancement in the use of renewable energy, specifically solar energy to be harnessed for operating high compression pumps required for reverse osmosis modular systems. The reasons are self -evident: Egypt has a large potential for brackish water wells, massive amounts of solar radiation in remote areas, and future integrated development projects are located far from the Nile. Egypt is focusing on this trend as a potential future for widespread desalination applications [14]. The general public believes that desalting costs are never competitive, which stifles not only the implementation of this alternative water supply but also research and development in this field, particularly in developing countries. As a result, this attitude has shifted in response to Egypt's rapidly declining conventional water resources and remarkable advances in desalination technology [18].

Policies aim for increased irrigation efficiency, infrastructure cost recovery, the use of water-efficient crops (e.g., less rice and sugar cane), groundwater use, the reuse of agricultural drainage water and sewage water, brackish water desalination, and the harvesting of rainfall and flash floods [14].

Many researchers have investigated the desalination process of Egyptian groundwater, for example, Zeolite/geopolymer membrane was used in the desalination of Siwa groundwater by Mostafa R. Abukhadra et al. [16]. It achieved 7.82 $kg/m^2 \cdot h$ water flux and 99.6% salt rejection at 90°C. The membrane was reused for five runs with significant desalination performance. The desalinated water matches the limitations of drinking and irrigation water. Also, water desalination using solar cells was thought to be an ideal solution to water scarcity because Egypt is located in an arid climate zone with a high rate of sun-shining hours almost all year. According to S.A. Mohamed's study, it can be concluded that the use of solar energy in the construction of solar water desalination projects is a strategic option to cope with future estimates of water shortage in Egypt [19].

The biggest problem is industrial saline wastewaters, which differ significantly in their properties from those discussed above. The characteristics of industrial wastewater in comparison with mine waters are given in Table 1 [20–22]. Waste streams from industries such as textile or leather are characterized by both a high content of organic compounds (COD), as well as a mineral one, and a high or low pH. The colour of the wastewater is also a problem. Therefore, different methods of cleaning them should be used, e.g. the cheapest like combination of anaerobic bioreactor and aerobic membrane bioreactor [23], combination of advanced oxidation processes with membrane bioreactor [24]. Recovery of dyes and water is possible with the combination of classical filtration, coagulation, ultrafiltration, nanofiltration and reverse osmosis [25].

The second group of saline wastewater are waste streams from the extraction and processing of crude oil. These wastewaters contain oil pollutants and heavy metals, they are colour and turbid. Fractionation of oily saline wastewater can be achieved with the use of UF membranes modified with nanomaterials. This allows for the separation of oils and dyes from monovalent and divalent salts [26].

Another group of saline wastewater that seems to be the least burdensome is wastewater from slaughterhouses and meat processing. They are characterized by the presence of fats and salt, and high COD. Blood content is also a big problem during treatment. A combination of coagulation, biodegradation and separation using RO can be used for their treatment [27].

On the other hand, fractionation of pollutants into organic and mineral from these wastewater may allow the recovery of components of a satisfactory purity for reuse. In the study, three-stage membrane filtration was used to fractionate pollution, which could then allow the recovery of some of the components and a better selection of the method of further treatment.

Table 1. Examples of industrial saline wastewater, the chloride content of which influences their treatment

Pollution	Textile industry [20]	Leather industry [21]	Mine water [22]
COD [mg/L]	150–30,000	3,980	–
BOD_5 [mg/L]	80–6,000	920	–
Cl^- [mg/L]	200–6,000	5,000	42,500
SO_4^{2-} [mg/L]	–	4,000	1,500
TSS [mg/L]	15–8,000	6,880	–
Colour [mg/L] (Pt-Co)	50–2,500	brownish	–
pH	5.5–11.8	–	–

2. MATERIALS AND METHODS

2.1. CHARACTERISTICS OF SALINE INDUSTRY WASTEWATER

Industrial wastewater used was collected from an enterprise located in the Silesian Voivodeship from a storage reservoir that only collects this one type of wastewater The composition of the wastewater was very variable in the time in terms of the content of organic and mineral pollutants. Therefore, the collected wastewater was mixed before the three-stage membrane filtration. The wastewater was characterized by the following parameters: 865 mg/L (TOC), 1,193 mg/L (IC), 2,340 mg/L (COD), 330 mg/L (BOD5), 7.89 g NaCl/L (salinity) and 2,100 mg Pt-Co/L (colour).

This wastewater is characterized by a high COD and at the same tine low BOD_5 and toxicity towards vascular plants probably because they can contain decomposition products of plastics, chemical substances, and mixtures. Hence, in further research, this wastewater will also be subject to qualitative and quantitative analysis with the use of a chromatograph in order to select organic compounds hazardous to the environment and human health.

2.2. TREATMENT METHODS

A three-stage membrane filtration consisting of successive MF, UF, and NF processes was used to treat wastewater characterized by a high content of organic compounds, high salinity, and toxicity (Fig. 1).

MF was used as a pre-treatment process for wastewater, although the wastewater contained a small number of suspended solids (MF is mainly used to remove suspended matter, and bacteria). The microfiltration and ultrafiltration processes were carried out on a plate membrane module SEPA CF-NP by GE Osmonics (USA) equipped with flat-sheet microfiltration or ultrafiltration membranes. The active filtration surface of the membrane placed in the membrane cell was 0.0155 m^2. The membrane operated in a cross-flow mode with recirculation of the concentrate to the feeding tank. The transmembrane pressure was set at 0.5 MPa and the cross-flow velocity was kept at the level of 1.0 m/s. The process was carried out to collect 33% of the initial volume of the feed. The nanofiltration process was conducted in a steel filter module with a capacity of 400 cm^3. The active membrane filtration surface area was 0.0038 m^2. The process was conducted in a dead-end filtration mode at a transmembrane pressure of 2.0 MPa. The process was carried out to collect 50% of the initial volume of the feed.

As a result of waste fractionation, 4 waste streams were obtained: 1) concentrate MF, 2) concentrate UF, 3) concentrate NF, and 4) filtrate NF.

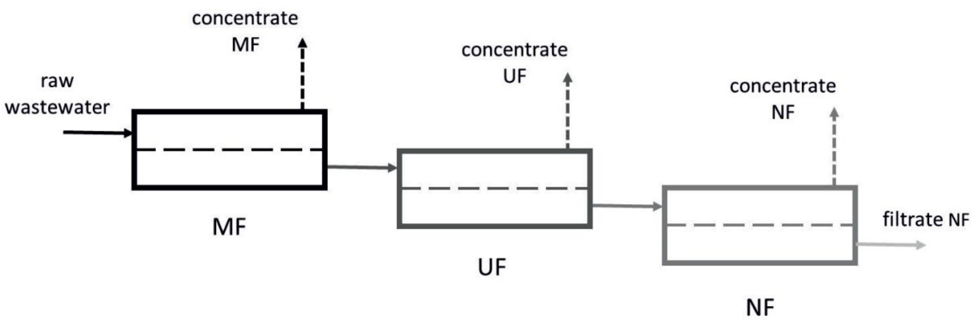

Fig. 1. Processes flow diagram of saline wastewater treatment

2.3. ANALYTICAL METHODS

The effectiveness of wastewater treatment was assessed on the basis of organic pollutant indicators, i.e. TOC, COD, BOD_5, and inorganic pollutant indicators i.e. IC, salinity. The analysis was complemented by the determination of the physical parameter, i.e. colour and toxicological tests. The TOC and IC concentrations were measured by the use of the TOC-L analyzer by Shimadzu Corporation (Kioto, Japan). The TOC value was calculated as the difference between the total carbon concentration TC and the IC. COD and colour (Pt-Co) were analyzed using the UV-VIS Spectrophotometer Pharo 300 Spectroquant® by Merck KGaA (Darmstadt, Germany). The BOD5 was determined by the OxiTop method (WTW, Poland). The multifunction meter CPC-511 (Elmetron, Poland) was used to measure salinity (conductivity measurement or conversion to NaCl). The toxicity of this wastewater stream was established by the use of the Lemna minor growth inhibition test.

3. RESULTS

Based on the results obtained in previous studies on wastewater treatment in single processes, it was decided to fractionate this wastewater using pressure-driven membrane techniques. The problems with biological treatment resulted from the toxicity of this wastewater and the amount of salinity. Problems with membrane filtration resulted from the phenomenon of fouling, and problems with AOP processes were caused by colour and also salinity. Wastewater fractionation using MF/UF/NF made it possible to obtain 4 waste streams (3 concentrates and 1 filtrate) differing significantly in physical and chemical properties. Which, in turn, made it possible to better choose the appropriate method of their further treatment or use as a raw material [28–30]. The second aim of the technology selected in this way was to protect the membranes used in the subsequent stages of treatment [31]. Hence UF was preceded by MF.

Figures 2–4 show the values of the tested pollutants in raw wastewater and in individual processes: single MF process, two-stage MF/UF membrane filtration, and three-stage membrane filtration (MF/UF/NF). TOC value decreased from 865 mg/L to 598 mg/L, 330.9 mg/L and 39 mg/L, respectively. COD value decreased from 2,340 mg/L to 1,570 mg/L, 888 mg/L and 198 mg/L, respectively. The initial BOD5 value in raw wastewater was low and amounted to 330 mg/L, therefore this index was removed to very low values of 210 mg/L, 75 mg/L, and 4 mg/L, respectively.

The best way to evaluate the wastewater treatment was visually. Colour impurities were removed from values of 2,100 mg/L to 912 mg/L, 341 mg/L and 10 mg/L respectively.

Inorganic contamination was best removed in the last process, ie NF. IC value decreased from 1.193 g/L to 1.044 g/L, 0.815 g/L and 0.265 g/L, respectively. Salinity (measurement converted to NaCl) value decreased from 7.890 g/L to 7.480 g/L, 6.750 g/L and 3.846 g/L, respectively.

4. DISCUSSION

Membrane techniques can be successfully used for the treatment of industrial wastewater containing large amounts of salt in addition to organic compounds. Membrane filtration produces concentrates that are waste streams. These concentrates have different properties among themselves. Figure 5 shows the removal of organic compounds on the basis of TOC, inorganic compounds – IC, and salinity. In the first stage of wastewater treatment (MF), only 31% of

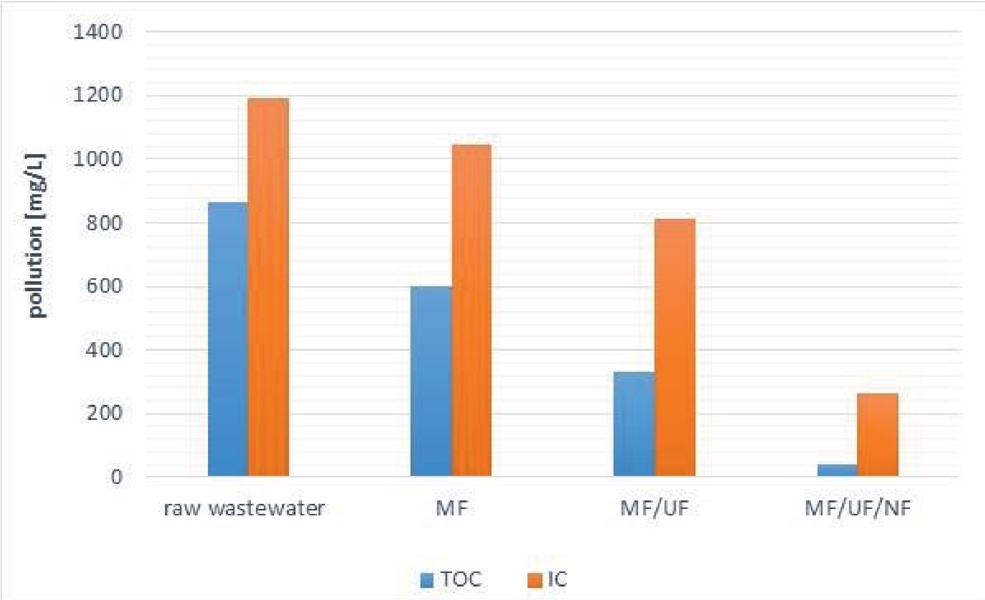

Fig. 2. The value of the TOC and IC index in raw wastewater and after individual processes

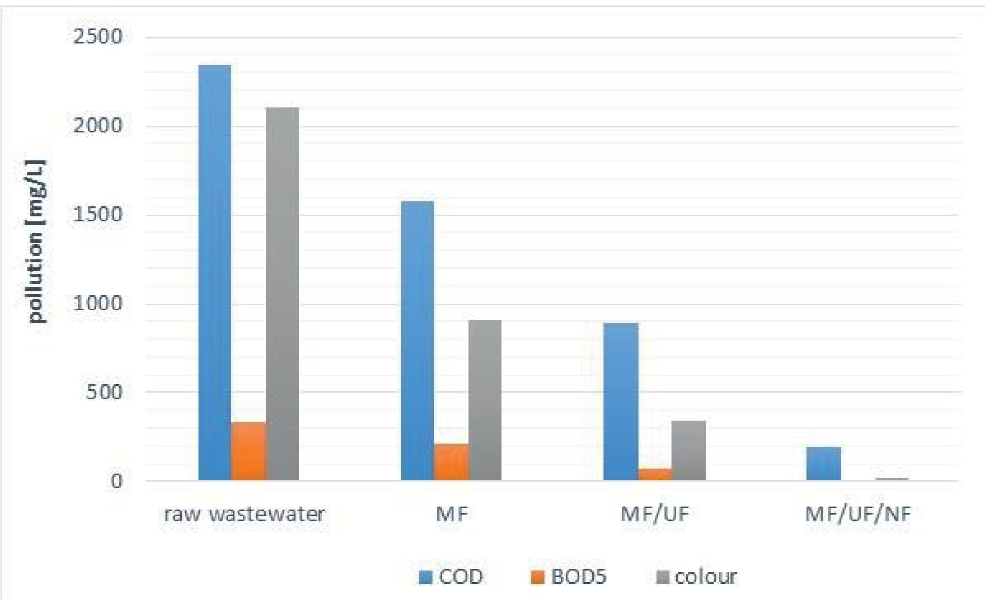

Fig. 3. The value of the COD, BOD_5 index and colour in raw wastewater and after individual processes

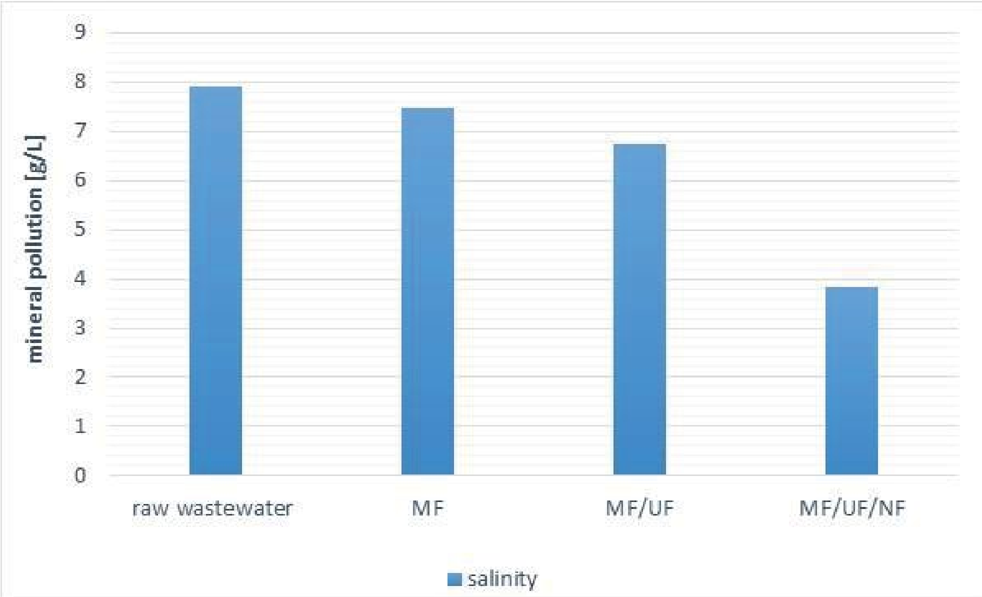

Fig. 4. Concentration of salinity in raw wastewater and after individual processes

organic compounds and 5.2% of salinity were removed, as MF is mainly used as a pre-treatment process to remove suspended solids, turbidity, bacteria, and viruses. The second role of this process was to protect the membranes used in the next stages of treatment. Typical polymer membranes (PES) for MF and UF were used in the tests [32]. During this filtration, the problem was the fouling phenomenon, which can also be observed in the UF process (in single filtration) [33]. In addition to the MF process, other pre-wastewater methods were also tested, as this step was crucial for the entire treatment. This wastewater turned out "to be quite resistant" to various pre-treatment methods.

The task of the second stage of purification (UF) was to remove organic compounds. The combination of MF/UF processes made it possible to increase the removal of organic compounds to 61.8% and salinity to 14.5% (removal of this contamination was not the aim of the process).

Advanced oxidation processes (AOP) can be used to further treat the concentrates formed in MF and UF processes [34, 35]. In our case, knowing the characteristics of these two waste streams (concentrates), it will be possible to choose the treatment method better. These concentrates contain more organic compounds. Therefore, the purpose of AOPs may be the total degradation of organic pollutants or partial degradation of organic compounds prior to biological treatment. At the same time, these concentrates are characterized by a lower content of mineral compounds, i.e. chlorides and sulphates, which negatively affect the efficiency of oxidation of organic compounds [29, 36]. The reagents used in AOP are not selective, as all the contaminants are oxidized in these processes. It is also a disadvantage of using AOP in the initial phase of wastewater treatment because then a higher dose of reagents should be used.

The addition of the next membrane process (NF) allowed for a further increase in the purification efficiency, i.e. the final efficiency was 95.5% (TOC), 77.8% (IC), and 51.3% (salinity). The NF membrane is characterized by high removal of divalent ions, therefore monovalent ions, mainly chlorides, dominated in the purified stream. In turn, this concentrate will contain little organic compounds and a lot of mineral compounds, the filtrate will mainly contain mineral compounds. Raw materials can be attempted from these two waste streams.

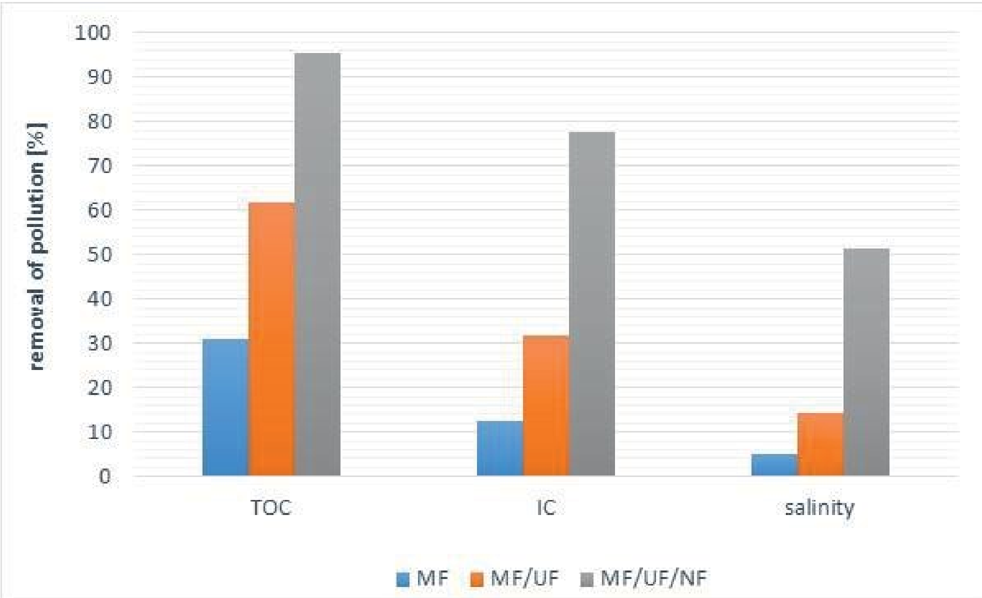

Fig. 5. Removal of TOC, IC and salinity during membrane filtration: MF (single process), MF/NF (two-stage filtration), and MF/UF/NF (three-stage filtration)

Table 2 presents the characteristics of the purified stream in the integrated processes: MF/UF/NF. The total content of organic compounds was 39 mg/L (TOC), 198 mg/L (COD) and 4 mg/L (BOD_5). The low BOD_5 value and the high COD value indicate that the purified stream still had refractive impurities with a low molar mass. Toxicity tests carried out on duckweed confirmed the assumption about the nature of this stream.

Only pressure-driven membrane processes were used in these studies, but a combination of membrane filtration with other techniques could also be used, e.g. membrane distillation, electrodialysis, and electrodeionization.

Currently, it is necessary not only to recover water from industrial wastewater but also to properly manage waste materials from this wastewater. Membrane techniques fit very well in the circular economy, allowing for optimal use of waste and optimal selection of a method for treating streams that cannot be reused.

Table 2. Characteristic of treated wastewater and removal of tested pollution

Pollution	Treated wastewater	Removal of pollution
TOC [mg/L]	39	95.48%
IC [mg/L]	265	77.79%
COD [mg/L]	198	91.54%
BOD_5 [mg/L]	4	98.79%
Salinity [mg/L]	3,846	51.25%
Colour [mg/L] (Pt-Co)	10	99.52%

CONCLUSIONS

In order to fractionate saline wastewater containing significant amounts of organic compounds, a three-stage membrane filtration was used: MF/UF/NF. This allowed for the following effects:

- remove TOC from the value of 865 mg/L to the value of 598 mg/L (MF), 330.9 mg/L (MF/UF) and 39 mg/L (MF/UF/NF), and achieve the efficiency of the entire wastewater treatment at the level of 95.48%;
- remove color from 2,100 mg/L (Pt-Co) to 912 mg/L (MF), 341 mg/L (MF/UF) and 10 mg/L (MF/UF/NF), and achieve the best efficiency at the level of 99.52%;
- complete removal of COD was 91.54% and BOD_5 was 98.78%.

During wastewater treatment, 4 waste streams were obtained: 1) concentrate MF, 2) concentrate UF, 3) concentrate NF, and 4) filtrate NF, which differed significantly in properties. Such fractionation will make it possible to select an appropriate method of further treatment of these waste streams or to be appropriately managed in order to obtain clean water and raw materials.

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DISINFECTION OF TREATED WASTEWATER

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One of the key tasks that the modern world has to face is to ensure that all residents have an effective and uninterrupted distribution of water. The dangers of microbial contamination of waters do not apply only to drinking water, directly distributed to humans. The reuse of water, e.g. for irrigation of crops in agriculture, also requires that a certain criteria of microbiological quality are ensured. That is why, in order to protect human health, it is very important to diagnose possible risks as early as possible and then carry out the necessary processes, and apply the best techniques to guarantee the proper quality of the water used. Sewage disinfection processes seem to be an inseparable element of their proper treatment. The following paper focuses on presenting the risks and prospects for the future of reusing reclaimed water from wastewater. Attention was drawn to the change in the law being in force in the EU and the consequences of this were discussed. The techniques used so far for the disinfection of sewage were indicated, with a clear emphasis on new, constantly developing technologies. The current methodologies for assessing the microbiological quality of wastewater were presented and techniques that offer a real opportunity to improve and shorten the time of implementation of this assessment in the future, were briefly discussed.

Keywords: disinfection of sewage, assessment and microbiological quality of sewage, reuse of water

1. INTRODUCTION

Progressive climate changes, extreme phenomena, including longer and more severe droughts and therefore, threats of water scarcity, create a major problem that the whole world, including the European Union, has been trying to fight over the last few decades [1]. Poland is classified as a country with low water resources [2], as evidenced by the volume of surface water per capita, which in the years 1999–2018 was 1566 m^3/inhabitant [3]. According to the Water Stress Index – total water consumption in relation to the annual available flow at

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the catchment level (for the year 2000) – Poland ranked 9th among other European countries, which proves that the changes in the hydrological cycle caused by global warming pose a significant risk to our country. [4]. In addition, according to the EU indicator – total freshwater abstraction for public water supply (as of by the year 2018) Poland has less than 60 m^3 of fresh water per capita (for comparison, the indicator for Greece is about 160 m^3/capita) [5]. Water shortages are related both to their insufficient reserves in terms of quantity and to the inability to manage currently available resources due to the constantly deteriorating water quality [4].

The fight against climate change, in the context of the global problem of water scarcity, results in a number of actions to minimize the negative impact on the proper functioning of people. The reuse of water, understood as the treatment of sewage, and then its utilization, e.g. in agriculture, in irrigation of crops is an example of such corrective actions. However, in order for the wastewater to be reused and discharged to the receivers without any risk, it must also be treated to a very high degree from microbiological contaminants. In addition, it should also be remembered that the phenomenon of meteorological drought and water shortage may cause reduced flow in rivers and streams (receivers of i.a. treated sewage), which may increase the concentration of pollutants and various harmful substances [6, 3].

2. THREATS AND PROSPECTS

Previous legal recommendations regarding the quality of wastewater discharged from sewage treatment plants, while maintaining appropriate microbiological standards, are not mandatory worldwide. In the context of the quality of treated wastewater, we are talking primarily about physico-chemical parameters, including: the content of nutrients (nitrogen and phosphorus), the amount of slurry contained in wastewater, the amount of indicators characterizing BOD_5 or COD. Anywhere in the world there are recommendations on the quality of wastewater treated in a microbiological context, they are determined on the basis of national and/or international regulations, which are usually based on the enumeration of E. coli bacteria (more precisely: total coliforms, fecal coliforms or Escherichia coli), with variable threshold values depending on the purpose of the wastewater (discharge of treated wastewater to receivers - the environment or their reuse, e.g. in agriculture).

Coliform bacteria are considered to be typical inhabitants of the intestines in vertebrates, particularly in humans. Therefore, they cannot reproduce directly and independently in the environment (reservoir). It means that their presence in the water is due to pollution and is not the result of a temporary anomaly – spontaneous growth in a given environment [7]. In addition to coliform bacteria, the microbiological quality of the discharged wastewater is also evidenced by the presence of i.a. viruses, enterococci, *Clostridia reducing sulfates*, *Salmonella spp.*, *Cryptosporidium spp.*, *Giardia spp.*, etc. In recent years a high risk of human noroviruses has also been pointed out. It is one of the types of highly contagious intestinal viruses that can be the main cause of the epidemic, through viral gastroenteritis. Studies have shown that noroviruses are characterized by high resistance and high survivability – despite the methods used to disinfect wastewater (primarily chlorination), noroviruses were still detectable in treated wastewater [8].

On the 25th of May 2020, Regulation (EU) 2020/741 of the European Parliament and of the Council on minimum requirements for water reuse was drawn up (entry into force: the 26th of June 2023). The regulation sets clear requirements for the quality of reclaimed water for irrigation in agriculture, where microbiological parameters, including the number of *E. coli and Legionella spp.*, depend on i.a. the quality class of reclaimed water. It should be noted that in the recommendations of the European Union, the disinfection process is the recommended technology for all quality classes of recycled water [9]. The aim of the EU regulation is to draw attention to the issue of more efficient use of water from treated waste water, in particular for agricultural purposes. As the web portal named wodociągowiec.pl notes: "In the EU about 1 billion m^3 of wastewater is recovered annually. According to the forecasts of EU authorities, the entry into force of the regulation may increase the recovery of water from wastewater up to 6.6 billion m^3 in 2025. Such solutions will translate directly into saving water from natural sources – the abstraction of water from natural sources for irrigation, according to the assumptions, is to be reduced by more than 5% by 2025" [10].

Over the years, it has been proven that municipal wastewater poses serious threat to the aquatic environment and man himself, because it is a source of numerous pathogenic, opportunistic, as well as antibiotic-resistant microorganisms (including multidrug-resistant, mainly of intestinal origin). Based on the research of i.a. Stampi [11], Koivunen [12] and Olańczuk-Nayman [13–16], it is known that the average percentage of reduction in the number of bacteria in the wastewater obtained in the wastewater treatment process is very high and reaches up to 99%. However, despite such a high degree of reduction, wastewater runoff from wastewater treatment plants can still contain about 100 indicator fecal coliforms per 100 ml of treated wastewater. In light of the results of the study and the EARSS report from 2007 [17], wastewater treatment processes are also ineffective in reducing the incidence of antibiotic-resistant strains of *E. coli bacteria*.

The danger associated with insufficient treatment of sewage, results from already mentioned pathogenic viruses, bacterial strains, protists, fungi or invasive parasitic worms occurring in various forms in wastewater [18]. Discharged into surface waters, they accumulate in crops (through irrigation), transferring the features of resistance to consumer intestinal bacteria. As Quant B. and others [19] note, with reference to the results of studies i.a. Reinthaler and others [20], Kay and others [21], and Shannon and others [22], "urban wastewater treatment plants can be classified as serious emitters of microbiological pollutants, including viruses, bacteria and protozoa pathogenic to humans. They pose a potential threat to human health and contribute to the progressive degradation of the waters of wastewater receivers."

The protection of surface waters against pollutants associated with the discharge of treated wastewater into them consists primarily in the dilution of wastewater and its disinfection. Disinfection processes allow the elimination of harmful pathogens that have not been completely removed during the wastewater treatment process (I and II degree). Wastewater disinfection, i.e. the so-called III stage of treatment, is used to reduce microorganisms (e.g. *E. coli*, a representative type of bacteria in wastewater) to a level consistent with applicable standards [23].

3. METHODS OF DISINFECTION OF SEWAGE

Commonly used methods of sewage disinfection can be divided into three basic groups. The first one – chemical processes, include primarily chlorination, i.e. the proper dosage of oxidizing compounds from the group of halogens, m.in: chlorine, sodium hypochlorite, chlorinated lime, calcium hypochlorite, chlorine dioxide, calcium hydroxide or calcium oxide [18]. Chlorine disinfection is currently the most commonly used method in sewage treatment plants. However, it should be noted that sewage is rich in organic matter, which contributes to the formation of by-products of sewage disinfection. Studies have shown that chlorination of wastewater caused the formation of many by-products of this process, including m.in trihalomethanes (THM), haloacetic acids (HAA), haloketones (HK), halonitromethanes (HNM), haloacetonitrile (HAN), nitrosamine (NA), etc. [24]. Another chemical way to disinfect wastewater is ozonation. Ozone is a strong oxidizer with a very effective bactericidal effect, however, it is unstable and, compared to chlorination, relatively expensive. When analysing chemical methods of disinfection of sewage, attention should be paid to i.a.: disinfection of sewage using peracetic or hypermetic acid, as well as the possibility of using alternative disinfection methods: e.g. PEROXONE method [18], disinfectant called CAC-717 (consisting of mesoscopic calcium crystals of carbonate hydrogen) or the use of ferrate (VI) (FeVIO42, Fe(VI)), which is an oxidising and disinfectant used to treat a wide range of contaminants in wastewater, including microbial contaminants [25].

The second group of methods used to disinfect sewage are physical processes, i.e. membrane techniques, ULTRAVIOLET UV radiation, pasteurization or thermal drying processes, as well as ionizing radiation, i.e. radiation disinfection and ultrasound. Compared to chemical wastewater disinfection technologies, the main advantage of physical processes is the fact that no chemicals that may enter the environment are added. Moreover, no disinfection by-products are formed. However, physical processes have their drawbacks. For example, in disinfecting sewage using the UV radiation method, it should be noted that the reactivation is possible, and that its effectiveness depends, to a large extent, on the sensitivity and the body to radiation – the greatest sensitivity is shown by vegetative bacterial cells, the smallest by viruses or spore bacteria.

In the context of the effectiveness of physico-chemical processes of wastewater disinfection, Olańczuk-Neyman and others [26], claim that "inactivation of microorganisms depend on: the type of microorganism and its resistance to the chemical agent, the physicochemical characteristics of the environment, the type of disinfectant and the way it works. The most sensitive to the chemicals used for disinfection are bacteria in vegetative form, where intestinal viruses and spore-forming bacteria are more resistant, and the greatest resistance is shown by oocysts (e.g. *Cryptosporidium parvum*), cysts (*Giardia lamblia*), spores (*Clostridium perfringens*), acid-resistant bacteria (e.g. *Mycobacterium Spp.*) and in addition helminths' eggs (*Ascaris lumbricoides*). The effectiveness of chemical disinfection can reduce elevated concentrations of various physical and chemical contaminants of wastewater, such as suspension, dissolved organic matter and inorganic ions.

The last group is the "green" disinfection of sewage. We are talking primarily about the use of green chemistry and nanotechnology, including photocatalytic properties of nano-TiO2 (used as an effective disinfectant) as well as the synthesis of AgNPs silver nanoparticles using Vitis labrusca extract, which is a fully natural weapon against Gram-positive and Gram-negative bacteria. As Raota and Others [27] point out, these materials have led to a 47% reduction in the number of Escherichia coli bacteria during the disinfection of wastewater, suggesting that they may be an effective aid in the process of "green" disinfection of wastewater. In turn, fotocatalysis is one of the newer methods of disinfection, showing high effectiveness in neutralizing i.a. viruses, fungi, bacteria and even cancer cells contained in sewage. The photocatalytic properties of nano-TiO_2 are also used to neutralize undesirable odours. As Kosmala and others [28] notes, "titanium (IV) oxide can act as an extremely effective disinfectant".

4. METHODOLOGIES FOR THE ASSESSMENT OF MICROBIOLOGICAL QUALITY OF WASTEWATER

The most important issue in dealing with pathogens in wastewater and the fact that they can have a significant impact on the quality of the receiver's waters is their fast, effective and accurate recognition. The radical methods of their diagnosis, which are in force today, have many disadvantages, i.e.: many hours of work, their breeding, which is limited by the appropriate composition of the medium, can cause many difficulties (e.g. by the need to provide appropriate conditions for growth). In view of the above, attempts are being made to gradually replace them with new techniques [29]. Among the most promising are i.a.: molecular methods, including e.g. PCR quantification, electron transmission microscopy (TEM), staining of nucleic acids with fluorescent dyes, immunofluorescencee tests (IFA), enzyme immunoassays tests (ELISA), gel electrophoresis in a pulsed field (PFGE) or single-cell techniques, such as flow cytometry (FCM) [30].

Molecular methods aroused interest a few years ago because they allow for the rapid and effective identification of many microbial species, such as bacteria, viruses or fungi. They are used in the detection and identification of microbiological threats, especially in the case of microorganisms that cause difficulties in cultivation or requiring a long term growth on microbiological substrates [31]. In the case of molecular methods, mainly PCR, various types of inhibitors contained in the tested samples may prove to be a problem in the analysis of environmental waters, including sewage. These substances can isolate together with nucleic acids, inhibiting the PCR reaction [29]. In addition, the number of identified threats, e.g. viruses, may be too large for the proper use of the PCR method. Using this method, it is impossible to clearly determine whether the detected virus is infectious or not, even if the result is positive. It should also be noted that the PCR response only makes it possible to detect one type of virus at a time, and there are many more in the environmental trials studied [32].

There are also various types of so-called “fast” tests increasingly used in the analysis of environmental samples, including e.g.: ELISA tests, consisting of the determination of immunochemical, based on the reaction of selective antibodies, giving quantitative or semi -quantitative results [33]. However, the use of antibodies with high affinity can sometimes be ineffective, e.g. if the recognized epitopes are hidden in the protein structure or if it is not possible to recognize them. The main advantage of the ELISA test, compared to other methods, is its cost-effectiveness and the fact that it is relatively simple to perform [32].

Microscopic techniques are also helpful in the analysis of environmental samples. For example, electron transmission microscopy (TEM), may be helpful in visualizing whether cell membranes have been damaged as a result of cell exposure to chloramine or free chlorine, during chemical disinfection processes [34].

Noteworthy is also the possibility of using flow cytometry in the microbiological analysis of environmental waters, including sewage. FCM is one of the rapid fluorescence-based determination techniques that focuses on direct measurement from native bacteria or their enzymatic activity [35]. The main advantages of FCM are high accuracy and high quantification rate. Flow cytometry can be used for both purified and raw wastewater analysis as well as activated sludge. Compared to other techniques (e.g. EFM or TEM), flow cytometry is characterized by a much higher sensitivity and rate of determination [36,37]. The results of the FCM analysis, in addition to indicating the total number of cells in the study sample, can help in the relative determination of cell size or the complexity and content of nucleic acids. Thanks to the phenomenon of fluorescence, flow cytometry will help in determining the integrity of the cell membrane or enzymatic activity. Most importantly, FCM can help to accurately identify specific cells of interest to us, which will translate into accurate diagnosis and detection of microbial populations, e.g. pathogenic, which is the focus of interest [38].

5. WATER QUALITY

According to the EEA report Water in Europe – Assessment of Status and Pressure from the year 2018, water quality in both Europe and Poland is not satisfactory: “the vast majority of lakes, rivers, estuaries and coastal waters in Europe have problems achieving the EU's minimum “good” ecological status target set out in the EU Water Framework Directive” [39].

The research and assessment of the quality of surface water in Poland is carried out as part of the State Environmental Monitoring and results directly from the 349(2) Article of the Water Law Act of 20th of July 2017 (Journal of Laws of 2021, item 2233, as amended). The purpose of this assessment is to provide the knowledge of the status of the waters, necessary to take measures to improve the condition and protect waters against pollution. According to paragraph 3 of the indicated article, surface water quality tests are carried out primarily in the field of physicochemical, chemical and biological elements [40]. According to the Report on the classification and assessment of the status of uniform bodies of surface water in Poland, made by the Chief Inspectorate for Environmental Protection, based on data from years 2014-2019, it was found that as much as 91.6% of rivers' body of groundwater and 88.0% of lakes' body of groundwater are characterized by poor water status [41]. The study covered biological elements: phytoplankton, chlorophyll a, phytobunthex, flora, macrophytes, macroalgae and angiosperms, benthic macroinvertebrates and ichthyofauna; hydro-morphological elements; physical state of waters: water temperature, smell, colour, transparency, general suspension; and aerobic conditions; salinity; acidification; nutrients; particularly harmful substances – specific synthetic and non-synthetic impurities; priority substances and other contaminants [42]. According to Chief Inspectorate of Environmental Protection: "in full monitoring, about a hundred parameters are classified, about half of them for ecological and chemical status (...). In 2022, the list of indicators of physicochemical elements have shortened so that one element is determined by 1-3 indicators, while the list of indicators of chemical status tends to lengthen" [43].

There are a number of microorganisms in the waters, including, i.a.: viruses, bacteria, fungi, algae, protozoa and products of their metabolism. A large part of the microorganisms living in water are pathogenic organisms. Contact with water contaminated with pathogenic microorganisms – through its consumption, bathing or use for the production of i.e. food – can pose a serious epidemiological risk. The U.S. Environmental Protection Agency (EPA) has identified more than 500 pathogens that could pose a potential pathogenic problem to humans in drinking water. Therefore, monitoring the presence of microorganisms in water, including fecal, is crucial [44]. The most important source of microbial water pollution is still fecal matter. Despite the high degree of operation of wastewater treatment plants, treated water treaty remains an important source of microbiological contamination. As Kacprzak M. notes [45] in numerous studies, i.a. Fijałkowski and others [46] the presence of Escherichia coli at the outflow from the treatment plant (intreated sewage) has been demonstrated. However, in the research of Osińska and others [47] focusing on determining the total number of bacteria resistant to β-lactam and tetracycline as well as the number of antibiotic-resistant Escherichia coli bacteria, it has been shown that, despite of a reduction of 99.9%, the number of antibiotic-resistant bacteria, including antibiotic-resistant E. coli, in treated wastewater samples, was still high and was "up to 1.25 x 105 CFU/ml in winter and 1.25 x 103 CFU/ml in summer" [45]. In conclusion, as has already been noted in the work, the average percentage of reduction in the number of bacteria in the wastewater, obtained in the process of wastewater treatment, can reach up to 99%. However, it should be kept in mind that despite such a high degree of reduction, wastewater effluents from sewage treatment plants can still contain about 100 indicator of fecal coliforms per 100 ml of treated wastewater. That is why it is important to disinfect wastewater – to eliminate dangerous pathogens and/or interrupt their migration into the environment.

Despite the above-mentioned threats and the fact that the State Sanitary Inspectorate is responsible for monitoring the microbiological status of waters, both in the aforementioned bathing areas, as well as rivers or groundwater, operating on the basis of a number of regulations of both the Minister of the Environment and the Minister of Health, lakes, ponds or municipal reservoirs are not covered by systematic microbiological monitoring [45]. As of today, when assessing the quality of water in Poland, microbiological parameters are not taken into account, and in accordance with the EU regulation, reuse of recovered water, i.a.: for irrigation in agriculture, will be possible only after a positive evaluation, taking into account the indicators microorganisms.

Ensuring safe and effective water distribution of water appropriate for reuse, requires i.a. accurate, effective and reliable methods of monitoring microbial conditions. The methods commonly used can be limited for many reasons. It is important both to search for new methods of combating pathogens and microbiological threats, as well as techniques for their quick and effective diagnostics.

CONCLUSIONS

Poland is one of the countries at risk of water deficit. The problem faced by more and more EU countries is exacerbated by the progressive climate changes, including a reduction in the amount of precipitation and a poor as well as not significantly improved, qualitative condition of the available resources. In order to adapt to the upcoming changes, it seems appropriate to reuse treated wastewater from municipal wastewater treatment plants. However, despite the high degree of removal of pollutants, including microbiological hazards (almost 99% effectiveness), sewage containing significant amounts of pathogens is still discharged into the waters, including mainly coli and *E.coli bacteria*, thus reusing them e.g. in agriculture is impossible. Currently, various methods of disinfecting treated wastewater are known and used, including chemical, physical and so-called “green”. However, most of the disinfection methods presented in the paper, despite numerous advantages, have a number of disadvantages, such as formation of disinfection by-products or high costs of their use. Therefore, further research in this direction seems to be justified. In addition, a quick and reliable assessment of its microbiological quality plays a key role in the practical use of hygienized wastewater. Compared to the time-consuming and labor-intensive traditional breeding methods, modern methodologies for the assessment of microbiological quality of wastewater seem promising, such as e.g. molecular methods, including PCR quantification, electron transmission microscopy (TEM), staining of nucleic acids with fluorescent dyes, immunofluorescence tests (IFA), enzyme immunoassays (ELISA), pulsed field gel electrophoresis (PFGE) or single-cell techniques such as flow cytometry (FCM).

To summarize, it should be stated that wastewater recovery and its reuse in agriculture will not be possible without effective disinfection and constant microbiological monitoring.

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QUALITATIVE ANALYSIS OF A GREYWATER RECOVERY SYSTEM IN A PUBLIC PURPOSE BUILDING

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In recent years, in Poland, solutions that allow the reuse of grey and rainwater as an alternative source of water in a building are more and more often used. The subject of the work is the analysis of the existing greywater treatment system in a public utility building. The aim of the research was to determine the quality of greywater and rainwater, as well as the quality of recovered water used in the facility to flush toilets. The collected samples were subject to the determination of basic physical-chemical properties and microbiological indices. The research showed high qualitative variability of greywater, related to the way and frequency of water use in the building. The quality of the treated greywater meets the requirements of the toilet flush water guidelines. Based on the conducted research, it was found that recovered water posed the possibility of re-using for flushing the toilet. Due to the need to provide sanitary safety, however, as well as operation requirements for devices, it is necessary to treat the wastewater before its reuse. The basic indicator parameters of recovered greywater should be also controlled.

Keywords: greywater quality, reuse, water recycling, rainwater

1. INTRODUCTION

Public purpose buildings such as office buildings or hotels have a great potential in terms of quantity of greywater and rainwater. Such quantity encourages considering the possibility of its reuse, e.g. for flushing toilets, watering greenery (green roofs), washing vehicles, or cleaning outdoor areas [15]. Numerous studies are currently being conducted on systems that allow them to be reused for various purposes, including toilet flushing [9]. Its management is encouraged by economic factors, but increasingly frequently also by the factor of sustainable development and choice of solutions optimal for the environment and water resources. It should be emphasised that in reference to new construction trends in the market of building

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materials, an acceleration has been observed in the area of innovative technologies allowing for greywater recycling [30]. It is related to the possibility of subsiding this construction sector through programmes supporting protection of water resources, as well as the environmental assessment of buildings through certification systems. This includes BREEAM (Building Research Establishment Environmental Assessment Method) or LEED (Leadership in Energy and Environmental Design) certificates applied in Poland. In Poland, the traditional installation market where water installations are supplied with water with very high qualitative properties is a limitation in the application of solutions for installations using greywater or rainwater [6, 20, 28].

1.1. QUALITATIVE CHARACTERISTIC OF GREYWATER

In the literature, the quality of greywater is characterized by parameters such as: suspended solids, turbidity, COD, total nitrogen and phosphorus content. The microbiological parameters include the total number of microorganisms, total number of Escherichia coli, and total number of enterococci. [14]. Literature data indicate a high variability of these parameters in the studied greywater. Table 1 presents the results of research on the quality of greywater in European countries, i.e. England, Germany and the Netherlands, similar in terms of water consumption and the level of sanitary installations to Poland. The results of research from Jordan were also presented, where the subject of recycling is intensively studied. Greywater flows from various types of sanitary facilities, as well as mixed sewage was tested.

Table 1. Qualitative characteristic of greywater [2, 6, 10, 13, 18]

Index	England [13]	Germany [18]	Netherlands [10]	Jordan [2]	Europe [6]
	shower, bath, sink	shower, bath, sink and washing machine	mixed greywater	shower, bath, sink and washing machine	mixed greywater
Turbidity [NTU]	164 (171)	nt*	nt*	nt*	nt*
Total suspended solids [mg/l]	100 (145)	nt*	nt*	1,291	6,4–240
BOD_5 [mg/l]	146 (54,3)	150–250	215 (102)	314	50–350
COD [mg/l]	451 (289)	250–430	425 (107)	870	100–681
TN [mg/l]	10,4 (4,8)	nt*	17,2 (4,7)	2	3,72–53,6
TP [mg/l]	0,35 (0,23)	nt*	5,7 (2,6)	3	0,7–22,8
Total Coli in 100 ml	7,387 (9,759)	104–106/ml	nt*	nt*	56–8,03x106

*nt – not tested.

The concentration of pollutants in greywater fluctuates significantly. Especially in the case of recycling of used water from single sources, no it is possible to clearly indicate the ranges of values of individual parameters that they are the basis for designing treatment technologies.

Knowledge of the range of values of basic properties of raw greywater is necessary for the selection of the technological process before its reuse [12].

However, currently only in a few European countries there are regulations that specify detailed rules for designing recycling systems and quality guidelines for greywater. In Poland, the document used the most frequently is a series of British norms [3, 4, 5], Document is including guidelines regarding the rules of design, assembly, and operation of the installation and its marking, depending on the purpose of treated wastewater and it's directly referring to qualitative and bacteriological requirements. Table 2 presents proposed by British norm recommended values of properties of non-drinking water obtained from greywater for different purposes: flushing toilets, supply of automatic washing machines, or watering gardens.

Table 2. Recommended estimated values of physical-chemical and bacteriological properties for biological and general monitoring [4]

Parameter	WC flushing	Garden watering	Laundry i.e., washing machine, use
Escherichia coli [number/100 ml]	250	250	not detected
Intestinal enterococci [number/100 ml]	100	100	not detected
Total coliforms [number/100 ml]	1,000	1,000	10
Turbidity [NTU]	<10	N/A	<10
pH [pH units]	5–9.5	5–9.5	5–9.5
Residual chlorine [mg/l]	< 2	< 0,5	< 2
Residual bromine [mg/l]	< 5	0	< 5
Suspended solids	free from floating debris		
Colour	visually clear, not objectionable in colour		

The solutions proposed in the paper [3], however, may not be adjusted to the specific Polish conditions due to the individual requirements towards installation materials, or due to the habits of users of water supply installations, i.e. the applied chemical agents, and variable quantity, quality, and temperature of wastewater.

The paper presents results of a study conducted in an existing public purpose building (office building). The basic objective of the study was the determination of the quality of greywater generated in the building, recovered greywater and the quality of rainwater collected from the roof. The research was carried out over a period of 6 months.

2. MATERIALS AND METHODS

2.1. SUBJECT OF STUDY

The analysed object was an existing office building with a greywater recovery system for flushing toilets. The building was designed and built based on the latest available technologies and pursuant to the rules of sustainable construction. The object was recognised with the LEED (Leadership in Energy and Environmental Design) standard, awarded as a certification to objects distinguished in terms of care for the environment during the construction process and after its completion. Modern technical solutions were applied in the building, including greywater reuse technology.

2.2. SYSTEM DESCRIPTION

Sewage system of type IV was designed for the building, approved by norm PN-EN 12056 as of 20022 (a system of separate sewage installations) to enable the separation of black and greywater [7, 8]. Greywater is discharged to the building's basement, where the treatment system is located. The system is composed of two containers made of polypropylene with a volume of 10 m^3, diameter of 2,500 mm and height of 2,200 mm each, and a membrane reactor (Fig. 1). The first container collects raw greywater from 70 sinks and 13 showers. The time of filling the buffer container depends on the intensity of use of intake points, and reaches a maximum of 24 h. The container for greywater is equipped with a blower with a capacity of 12 m^3/h for aeration and stirring, to avoid sedimentation of larger contaminants that would lead to the worsening of the wastewater quality. At the inlet to the tank there is a coarse filter (sieve), which is designed to separate larger contaminants. The coarse filter is regularly rinsed, and the rinse water flows to the sewage system through the dirt filter. After filling the tank, greywater is pumped to the membrane reactor. The reactor is stimulated by an aeration system through a blower with a capacity of 12 m^3/h. Through aeration and microorganisms present in the wastewater, biodegradable wastewater components are decomposed in aerobic conditions. The reactor contains 2 submerged membrane filtration modules with an area of 7 m^2 each, equipped with pores of 0.04 μm. The total capacity of the filters is 10 m^3/day. To protect the filters, the membranes are cleaned with an aerator at adjustable intervals. The recovered water flows into the process water container. The container is equipped with a water level sensor and overflow protection. The container is also supplied by rainwater, transported from the roof with a surface area of approximately 700 m^2 when the minimum filling level is reached. In case of insufficient amount of rainwater, the process water tank is filled with tap water. The process water tank supplies the toilet flushing system through a double-pump hydrophore unit. In order to protect the process water, it is pumped through sterilization using a UV lamp with an intensity of 2 m^3/h. In addition, a biocyte is dosed into the pressure line for disinfection. The tanks and the reactor are connected by an overflow at the highest point. When process water is not collected, greywater is discharged directly to the sewage system. If the tank is overfilled, the filling units are switched off.

According to the information obtained from the building's managers, the greywater recovery system used allows for full coverage of the water demand for flushing toilets. At the same time, equipping the building in modern faucets allows for reduction of tap water in the building by approximately 60% annually.

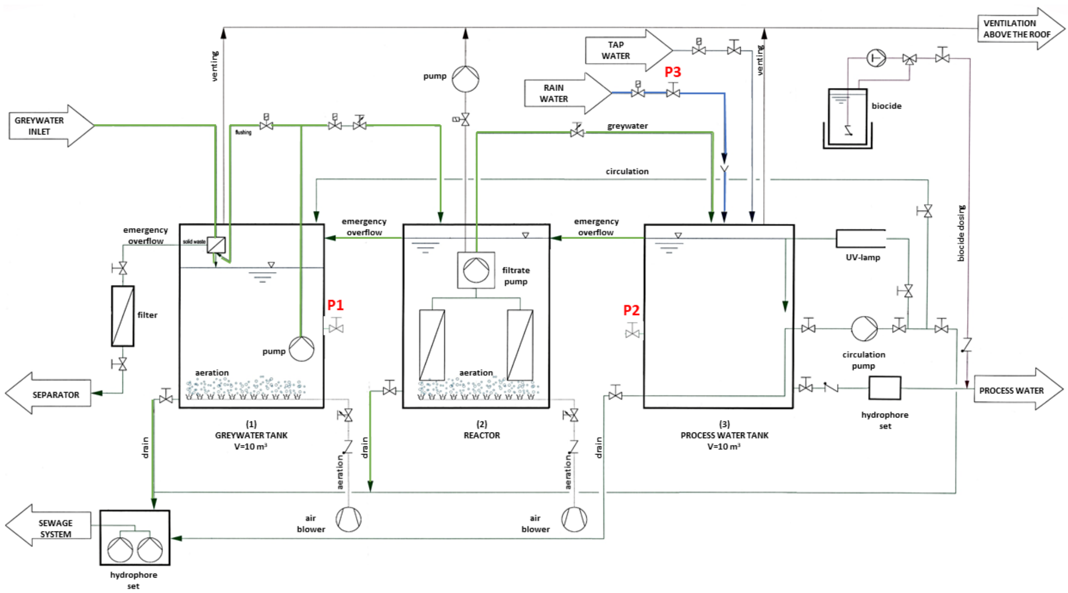

Fig. 1. Greywater treatment system applied in a public purpose building

2.3. STUDY SCOPE

The paper presents a qualitative analysis of greywater, treated water and rainwater samples from an existing public building (office building). The scope of the study covered the determination of microbiological, organoleptic, and physical-chemical indices. Sampling points are marked as P1, P2 and P3 in the Figure 1.

Greywater and rainwater samples were collected to closed containers and transported to the laboratory of the Faculty of Building Services, Hydro and Environmental Engineering, where they were immediately subject to analyses. The determinations were based on the methodology provided in the literature, and norms [1, 21, 22]. In the paper, the assessment of the quality was based on values of physical-chemical indices such as: temperature, pH, turbidity, oxidisability, conductivity, total suspended solids, COD, and total phosphorus, as well as microbiological values of indicator parameters, including: total number of microorganisms at 36°C and at 22°C, number of coli and Escherichia coli bacteria, and total number of enterococci.

3. RESULTS

The qualitative characteristics of the analysed samples expressed in physical-chemical properties and microbiological indicator parameters are presented in Tables 3–7.

Table 3. Results of physical-chemical determinations in greywater samples collected from the container no. 1 (sample point – P1)

Index [unit]	P1.I	P1.II	P1.III	P1.IV	P1.V	P1.VI
Temperature [°C]	29.4	23.8	23.5	24.6	24.8	23.9
pH	8.19	7.4	7.8	7.02	6.9	7.5
Turbidity [NTU]	33.2	362	89.9	10	34	78
Total suspended solids [mg/l]	14	13	88	51.3	110	95
COD [mgO_2/l]	48.2	329	11.2	32.9	77.8	112
TN [mg N/l]	10.6	10.1	nt*	nt*	nt*	10.4
TP [mg P/l]	<0.5	<0.5	<0.5	0.738	0.814	0.628
Oxidisability with $KMnO_4$ [mgO_2/l]	nt*	nt*	nt*	5.12	10.4	8.6
Electrolytic conductivity [µS/cm]	nt*	nt*	947.67	1,130.9	1,138.3	1,015.8

*nt – not tested.

Table 4. Results of microbiological determinations in greywater samples collected from the container no.1 (sample point - P1)

Microbiological index [unit]	P1.I	P1.II	P1.III	P1.IV	P1.V	P1.VI
Total number of microorganisms at 36°C [CFU/1ml] sample dilution 1:10	120	82	131	76	116	>300
Total number of microorganisms at 22°C [CFU/1ml] sample dilution 1:10	107	109	145	>300	>300	>300
Coli and Escherichia coli [CFU/1ml]	3	4	1	1	5	32
Enterococci [CFU/1ml]	32	0	0	2	0	24

The diagrams 1–4 below show changes in the values of selected physicochemical and microbiological parameters before (P1) and after greywater treatment (P2) in the reactor.

Table 5. Results of physical-chemical determinations in greywater samples after treatment from the container no.3 (sample point – P2)

Index [unit]	P2.I	P2.II	P2.III	P2.IV	P2.V	P2.VI
Temperature [°C]	26.4	22.5	22.5	23.2	23.7	19.1
pH	7.7	7.7	7.6	6.8	6.6	7.1
Turbidity [NTU]	8.8	5.3	1.85	1.0	2.0	1.6
COD [mgO_2/l]	68.6	18.2	nt*	1.82	15.2	23.5
TN [mg N/l]	2.27	2.27	nt*	nt*	nt*	2.5
TP [mg P/l]	nt*	nt*	nt*	<0.5	0.565	0.35
Oxidisability with $KMnO_4$ [mgO_2/l]	nt*	nt*	4.16	2.4	1.6	2.1
Electrolytic conductivity [µS/cm]	nt*	nt*	241.8	783.06	425.01	734.6

*nt – not tested.

Table 6. Results of microbiological determinations in greywater samples after treatment from the container 1 no.3 (sample point – P2)

Microbiological index [unit]	P2.I	P2.II	P2.III	P2.IV	P2.V	P2.VI
Total number of microorganisms at 36°C [CFU/1ml]	83	118	51	96	99	59
Total number of microorganisms at 22°C [CFU/1ml]	160	93	64	146	227	146
Coli and Escherichia coli [CFU/1ml]	0	0	0	0	0	0
Enterococci [CFU/1ml]	9	0	0	0	0	12

Table 7. Results of physical-chemical determinations in rainwater samples (sample point – P3)

Index [unit]	P3.I	P3.II	P3.III	P3.IV	P3.V	P3.VI
Temperature [°C]	22.9	21.3	22.7	23.6	23.9	22.6
pH	7.4	6.6	7.0	6.6	7.0	7.1
Turbidity [NTU]	11.3	22.1	4.22	5.23	3.0	4.61
COD [mgO_2/l]	129	9.6	nt*	1.05	12.3	10.1
TN [mg N/l]	4.36	4.3	nt*	nt*	nt*	nt*
TP [mg P/l]	nt*	nt*	nt*	<0.5	<0.5	<0.5
Oxidisability with $KMnO_4$ [mgO_2/l]	nt*	nt*	4.24	3.2	2.08	3.62
Electrolytic conductivity [µS/cm]	nt*	nt*	188.79	180.42	365.49	195.6

*nt – not tested.

Table 8. Results of microbiological determinations in rainwater samples (sample point – P3)

Microbiological index [unit]	P3.I	P3.II	P3.III	P3.IV	P3.V	P3.VI
Total number of microorganisms at 36°C [CFU/1ml]	92	15	8	94	84	53
Total number of microorganisms at 22°C [CFU/1ml]	187	17	19	121	183	68
Coli and Escherichia coli [CFU/1ml]	0	0	0	0	0	0
Enterococci [CFU/1ml]	5	0	0	0	0	1

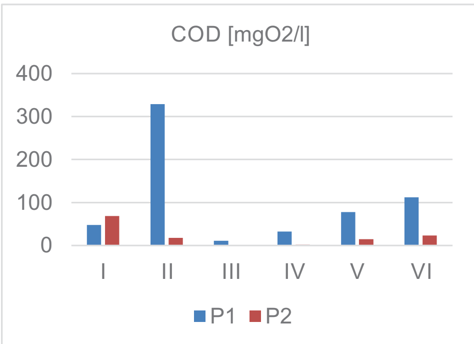

Diagram 1. COD values in greywater samples before and after treatment

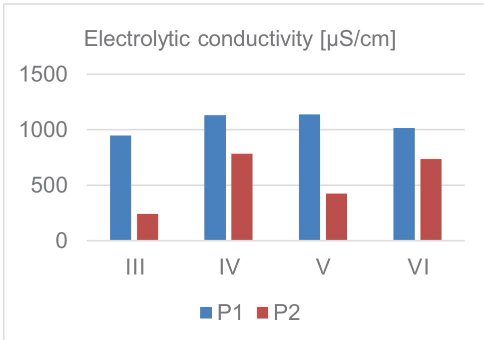

Diagram 2. Electrolytic conductivity values in greywater samples before and after

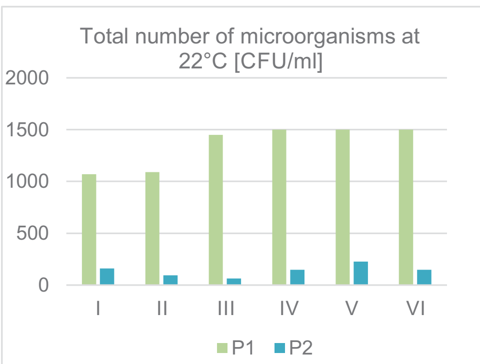

Diagram 3. Total number of microorganisms at 22°C in greywater samples before and after treatment

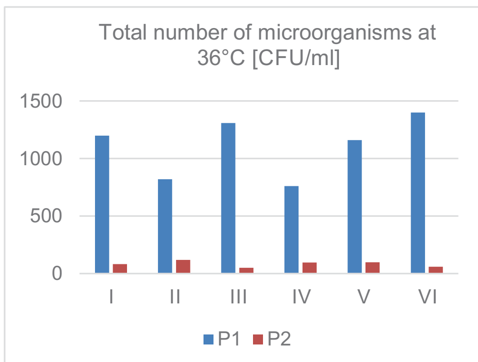

Diagram 4. Total number of microorganisms at 36°C in greywater samples before and after treatment

4. DISCUSSION

The obtained values are close to the data available in the literature [6, 10, 13, 18]. The wide range of values that can be taken by the indicators proves a significant diversification of water consumption in buildings. Greywater may show various degrees of contamination due to the application of surfactants also.

The qualitative analysis of greywater (P1-samples) showed approximate temperature in all samples, reaching around 25°C. The samples showed high turbidity and suspended solids content. The values are probably caused by the presence of cleaning agents in the used water. The samples showed variable values of oxidisability in a range of 5–10.5 mg O_2/l. They also showed low phosphorus concentration below 0.9 mg P/l.

The results of the microbiological analysis of greywater samples revealed the presence in all samples of total number of microorganisms exceeding 1000 units/ml incubated at 36°C and 22°C. The study also showed the presence of bacteria dangerous for human health such as Escherichia coli and Enterococcus. In the treatment process, it is necessary to disinfect treated wastewater to eliminate the possibility of contamination of users of sanitary facilities.

The analysis of P2 – water samples showed that the treatment system used (membrane reactor) allows for the reduction of physicochemical indicators, i.e. turbidity, COD, TN or Electrolytic conductivity (Diag. 1, 2). Obtained values meet the requirements of the toilet flush water guidelines. When it comes to microbiological parameters, the total number of microorganisms has also been reduced (Diag. 3, 4). Coliforms and Escherichia coli were no longer detected in the P2 samples. However, enterococci were detected, indicating the need to disinfect the water before reusing it in the toilet flushing system.

The analysis of rainwater samples revealed turbidity in a range of 3–22 NTU. It may be related to contaminants carried by rain water, as well as its stagnation in the retention container for rainwater. None of the samples showed values of oxidisability exceeding the norm specified for water for human consumption [27]. Results of microbiological determinations in the analysed samples showed no total number of microorganisms exceeding the norm of 200 units/ml incubated at 36°C in reference to the norm for drinking water. The analysis showed no presence of Escherichia coli in any rainwater samples, although the presence of Enterococcus was detected in two samples.

CONCLUSIONS

In buildings where the traditional approach to designing water supply and sewage disposal systems is applied, the use of toilets wastes high quality drinking water.

Research on the quality of greywater suggests that appropriate treatment of greywater generated during the use of showers and washbasins makes it possible to reuse it, and thus reduce the demand for tap water.

Qualitative characteristics of greywater is very varied and dependent on many factors that it is difficult to speak of a single method and degree of treatment of the water [7].

Poorly treated greywater can cause a number of operational problems, such as blocking distribution pipes, pumps or making it difficult to keep toilet bowls clean. It can also negatively affect the health of users due to the presence of pathogenic microorganisms that may appear in aerosols when flushing the toilet.

Lack of specified provisions and legal norms in Poland that would consider the application of alternative water sources in buildings through greywater recovery systems makes it difficult to design and implement modern technological solutions and sell related products. It is necessary to normalize activities regarding management of treated greywater in the scope of its quality and sanitary safety of its users.

The market offers finished devices for treatment of greywater that use basic physical, biological, and chemical processes [4]. Systems of partial grey wastewater treatment could usually apply mechanical partial treatment, aeration, and biological treatment in the process of filtration on membranes. The final stage would be disinfection of the treated wastewater by means of a UV lamp.

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ANAEROBIC CO-DIGESTION OF WASTE ACTIVATED SLUDGE AND DISTILLERY RESIDUE FROM SUGAR BEET MOLASSES – AN EXAMPLE OF INDUSTRIAL SYMBIOSIS

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The objective of this study was to analyse the methane potential of sewage sludge and distillery reside mixture in reference to the methane potential of sewage sludge while taking into account the possibility of increasing the value of this parameter via applying hydrodynamic disintegration. The paper also determines the effect of the introduction of distillery residue as a co -substrate on the quality of sludge liquid, with consideration of total nutrient concentration. The application of distillery residue as a co-substrate allowed for a 78.2% increase in the amount of generated methane per gram of volatile solids as compared to mono-fermentation of sewage sludge and might be an example of industrial symbiosis. The introduction of the hydrodynamic disintegration process would require consideration of separating the streams of co-substrates and carrying out disintegration only for one of them, because the disintegration of the mixture of these substrates may result in a reduced amount of generated methane. Disintegration of sewage sludge at an energy density of 35 kJ/L resulted in a 5.5% increase in methane production compared to the sample not subjected to pretreatment.

Keywords: anaerobic digestion, co-digestion, distillery residue, hydrodynamic disintegration, specific methane production, waste-activated sludge

1. INTRODUCTION

High amounts of distillery residue, i.e. DR (also known as vinasse or stillage), are obtained as a by-product of the alcohol production process. Management of DR is a serious challenge. Depending on the raw material from which the alcohol is obtained (e.g. cereals,

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molasses, corn, potatoes, fruit) and the production technology, from 9 to 20 litres of distillery residue are obtained per litre of produced alcohol [1–2]. The way that the alcohol is produced also affects the composition and properties of the resulting residue, which is always a coloured liquid (usually dark brown) with a low pH (pH: 3–5.5) and a total solids (TS) content that remains in a relatively broad range of 4.1–12.4%, including 66–91% of organic substances (Table 1). Distillery residue is characterised by a high content of organic matter expressed as chemical oxygen demand (COD) and high concentrations of nutrients. It also has a high temperature immediately after production, i.e. 70–80°C [1–5].

Table 2. Characteristics of distillery residue depending on its origin

Distillery residue origin	Total solids concentration TS [%]	Volatile solids concentration VS [% TS]	Value of pH [–]	Value of chemical oxygen demand COD [g/L]	Total nitrogen concentration TN [g/L]	Total phosphorus concentration TP [g/L]	Reference
From sugar beet molasses	6–6.75	69–83.5	4.3–5.5	45–147	0.05–7.3	0.09–0.22	[2, 4, 5]
From sugarcane molasses	4.1–5.3	66–78.6	3.3–5.1	50–176	0.6–4.2	0.03–3.03	[1, 4, 5]
From corn	7.1–12.4	87–90.6	3.3–4.6	60–129	0.55–2.0	0.23–4.1	[4, 5, 6]

Knowing the composition and properties of the distillery residue allows to select the most suitable solution for the management and/or disposal of this waste. One of the possibilities is agricultural use of the residue which involves its application on land as a soil fertiliser or to improve the quality of the soil, thus allowing for a reduction in the amount of applied artificial fertilisers [7–9]. It should be emphasised that soil fertilisation is profitable when transporting the obtained residue over large distances is not required [10]. Moreover, some reports based on long-term observations point to negative effects, such as accumulation of potassium in the crops, odour nuisance, or even environmental pollution [11]. Distillery residue can also constitute valuable fodder for farm animals [10, 12], although due to its high water content it must be previously dewatered and/or dried, which affects this solution's economic aspect. Distillery residue is also used for the cultivation of yeast (as a substrate or component) [5, 12], algae [2], and as a component in the production of composts together with solid waste that is poor in mineral elements [12].

Another approach is the management of the obtained distillery residue as wastewater and subjecting it to treatment processes such as membrane systems, adsorption processes, catalytic and oxidative treatments, enzymatic transformation, biological transformation, and phytoremediation, before it is discharged into the environment [5, 12]. One of the biological methods of treating distillery residue is the process of anaerobic digestion. Besides reducing the content of organic compounds, it allows to obtain energy in the form of biogas [4]. Distillery residue is characterised by a high temperature and a high content of organic compounds, and a high C/N ratio constitutes a suitable substrate for the process, as was confirmed in a paper on the biogas productivity of distillery residue in the range of 207–340 mL CH4/g CODremoved [13, 14].

Distillery residue's high methane yield is thus an incentive in applying this waste in the co-digestion process at agricultural and industrial biogas plants. The distillery residue can be co-digested with another substrate, e.g. manure [15, 16] or poultry litter [17], or more co-substates – as in Moraes et al. [16], where sugar beet vinasse was co-digested with cow manure and straw, or Kaparaju and Rintala [18], where potato stillage was subject to anaerobic digestion with potato peels and tuber and pig manure. In industrial installations, distillery residue constituting a by-product in the production of a given product is very often co-digested with other wastes from the same process, e.g. distillery residue resulting from the production of sugar from sugarcane molasses with sugarcane press mud [1], sugarcane straw with sugarcane vinasse [19], or sugar beet pulp silage and sugar beet vinasse [20].

Irrespective of the type of distillery residue that is analysed, simulations and research studies aimed at verifying how profitable the solutions are [21] or at determining the parameters of anaerobic digestion that will provide higher than average generation of biogas [13]. The degree of mixing of co-digested substrates is also analysed [1, 15, 20]. Pretreatment of substrates and/or co-substrates before their digestion is also an important issue [19, 22–24].

One of the pretreatment methods in which the supplied energy causes a change in the physicalphysicochemical properties of the substrate is the disintegration process. The application of the method before anaerobic digestion may contribute to an increase in the bioavailability of substrates for bacteria performing acetogenesis and methanogenesis, and may consequently allow for an increase in the amount of produced biogas or/and its better composition (higher content of methane in biogas) [25, 26].

Poland is one of the largest producers of sugar from sugar beet in the EU (sugar production in 2020 was 1,992,000 tons – Statistic Poland, 2021 [27]). Moreover, due to the growing prices of cereals, sugar beet molasses (a waste product in the process of sugar production from sugar beet) is increasingly frequently used to produce ethyl alcohol. Due to the above, high volumes of distillery residue are annually obtained in Poland as a result of the production of alcohol from sugar beet molasses with limited applicability in agriculture. Discharge of distillery residue on to agricultural fields (R10 recovery) is only legal during specific seasons of the year (in Poland usually except for the period from December to February) when the ground is neither frozen nor covered with snow [28], and according to information obtained by the authors of this paper from the distillery industry, there is no demand for distillery residue from molasses for fodder production in the Polish market. High amounts of the residue are subjected to digestion and co-digestion processes in agricultural biogas plants (in 2021 in Poland, production of agricultural biogas used 932,499 tonnes of distillery residue, according to data from the National Support Centre for Agriculture [29]). There are no reports, however, on co-digestion of this waste with sewage sludge. The effect of the application of the disintegration process preceding the co-digestion of sewage sludge with distillery residue has also not been determined to date. To fill this gap, research was conducted with the following two objectives: i) analysis of the methane potential of sewage sludge and distillery residue mixture in reference to the methane potential of sewage sludge, and consequently the assessment of how the introduction of distillery residue as a co-substrate in municipal wastewater treatment plants can contribute to obtaining energy independence by the objects; ii) analysis of the effect of pretreatment by means of hydrodynamic disintegration on the methane potential of substrates subjected to the anaerobic digestion process. Moreover, the effect of introduction of distillery residue as a co-substrate on the quality of sludge liquid was determined, with particular consideration of total nitrogen concentration.

2. MATERIALS AND METHODS

2.1. KEY ASSUMPTIONS OF THE EXPERIMENT

The experiment was divided into two stages:

Stage I. Variant with no pretreatment in which different mixing ratios of waste activated sludge (WAS) and distillery residue from sugar beet molasses (DR_SBM) were tested.

Stage II. Variant with pretreatment with two subvariants: Series 1 – the disintegration of the mixture of WAS and DR_SMR and Series 2 – the disintegration of only WAS.

The research covered the following analytical tasks:

- Determination of specific methane production (SMP) of mixtures of WAS and DR_SMB waste activated sludge (WAS) and distillery residue from sugar beet molasses (DR_SBM) – stage I and stage II.
- Determination of the characteristics of the liquid phase in the samples after the BMP tests i.e. in the digestate: soluble chemical oxygen demand (SCOD), soluble total nitrogen (STN), soluble total phosphorus (STP) – stage I and stage II;
- Determination of SCOD in the samples before and after disintegration and the sludge disintegration degree (DD) according to Nickel and Neis [30] – Stage II.

In Stage I, the SMP of substrate mixture was determined for mixing ratios of 1:1 and 3:1 (samples marked WAS+DR_SBM 1:1 and WAS+DR_SBM 3:1, respectively). Additionally, SMP for WAS and DR_SBM was specified.

In stage II, SMP was determined for mixtures of WAS and DR_SBM subjected and not subjected to pretreatment via the hydrodynamic disintegration method with two subvariants: disintegration of the mixture (series 1) disintegration of only WAS (series 2).

It was assumed that the mixing ratio of WAS and DR_SBM would be selected based on the results of stage I and that the disintegration process in both series would be conducted at three levels of energy density (EL), i.e. at 35, 70, and 140 kJ/L. Energy density, i.e. the amount of energy corresponding to 1 L of disintegrated medium, was selected as the parameter expressing the amount of energy used in the disintegration process, as it was necessary to maintain the amount of energy used in the disintegration process at a constant level in both series of the experiment. Stage II involved the following manner of designating the samples: (WAS + DR_SBM) raw, which was a mixture of WAS and DR_SBM not subjected to the hydrodynamic disintegration process (i.e. without pretreatment); (WAS+DR_SBM) 35 kJ/L, which was a mixture of WAS and DR_SBM subjected to the hydrodynamic disintegration process at an energy density of 35 kJ/L; WAS 35 kJ/L + DR_SBM, which was a mixture of WAS and DR_SBM where only WAS was subjected to the hydrodynamic disintegration process at an energy density of 35 kJ/L, etc.

2.2. MATERIALS

Thickened waste activated sludge (WAS) and digested sludge (DS) (used as an inoculum for the BMP tests) originated from a local WWTP with PE = 2,100,000 in Warsaw, Poland. WAS was collected directly from the output of the centrifuge, while DS was sampled from the recirculation loop of the anaerobic digester. DR_SBM was obtained from a distillery in central Poland that primarily uses sugar beet molasses for the production of alcohol. In the distillery, annual spirit production at a level of 2,640 m^3 is accompanied by the production of as many as 26,400 m^3/year of residue. The characteristics of WAS, DS, and DR_SBM are presented in Table 2.

Table 2. Characteristics of WAS, DS, and DR_SBM as used in this study

Indicators	DS (Inoculum)	WAS	DR_SBM
TS [%]	3.47 ± 0.42	5.65 ± 0.44	7.20 ± 1.61
VS [%]	2.17 ± 0.32	4.22 ± 0.37	5.49 ± 1.22
pH [–]	7.50 ÷ 7.61	6.44 ÷ 6.80	4.37

2.3. DISINTEGRATION SETUP

A newly designed hydrodynamic disintegrator was used in this study [patent application WP-84/JW 13766118, 27 Dec. 27.12.2018]. The device consists of a rotor (revolutions n = 3000/min), driven by an electric motor (power P = 5.5 kW), that is placed in a cylindrical tank with a total volume of ca. 13 litres. A detailed description of the device is presented in a previously published paper [31].

2.4. BMP TEST

Biochemical methane potential (BMP) tests were conducted in an Automatic Methane Potential Test System (AMPTS II; Bioprocess Control Sweden). The tests were conducted for the substrates mentioned in 2.1. above. Each assay was performed in three repetitions with the assumption that the initial organic loading rate was 5 gVSof introduced substrate/L. Before incubation, the entire system was rinsed with pure gas nitrogen in order to establish anaerobic conditions. The generated biogas passed the unit absorbing CO2 (composed of 3 M of sodium hydroxide solution with 0.4% thymolphthalein as a pH indicator), and its volume was automatically converted into standard temperature and pressure (0°C and 1 bar). A constant temperature of 37°C was maintained in the test reactors, and their content was stirred for 30 seconds every 10 min. All tests were carried out until daily gas production during three consecutive days reached <1% of the total gas production [32]. Observations of endogenous methane production were simultaneously conducted in samples with only the inoculum.

2.5. ANALYTICS

All chemical analyses were performed in duplicates in accordance with APHA Standard Methods, 1998 [33]. The liquid phase in the samples before and after disintegration, as well as in the digestate samples, was obtained by 30 min centrifugation (15 000 rpm), then by filtration with 0.45 μm filters.

3. RESULTS AND DISCUSSION

3.1. SPECIFIC METHANE PRODUCTION FOR THE MIXTURE OF DISTILLERY RESIDUE AND WASTE ACTIVATED SLUDGE WITHOUT AND WITH PRETREATMENT VIA THE HYDRODYNAMIC DISINTEGRATION METHOD

In accordance with data presented in Table 3, SMP for WAS and DR_SBM mixed in a ratio of 3:1 was 45.6% higher than for WAS, and an increase in the contribution of DR_SBM in the mixture (WAS+DR_SBM in a ratio of 1:1) allowed for an even higher increase in SMP (by 78.7% in comparison to WAS). Such a high increase in the SMP value for mixtures of WAS and DR_SBM resulted from the higher methane potential characterising DR_SBM than WAS. It also suggested that in the case of the analysed mixing ratios of WAS and DR_SBM, DR_SBM showed no inhibiting effect on methane production. The SMP of DR_SBM in this study was slightly higher than in the results obtained by Ziemiński et al. [20], namely 289.7 mL CH4/g VS, and Moraes et al. [16], namely 267.4 mL CH4/g VS d, also for DR_SBM, and comparable with SMP of DR from sugarcane molasses studied by Wang et al. [34], where it was 311 NL CH4/ kgVS. The analysis of the curves of cumulative specific methane production (Fig. 1) shows that the curve obtained for DR_SBM differs from the curve for WAS in that there was a very intensive increase in the amount of produced methane over the first 4 days of the culture. The phenomenon can be explained by the considerably higher content of dissolved organic compounds in DR_SBM, thus allowing to obtain high activity of methanogenic bacteria. To sum up, the results of stage I of the research show that distillery residue is characterised by high potential as a co-substrate in the process of anaerobic digestion of waste activated sludge, and its application may constitute an important step in gaining energy self-sufficiency in wastewater treatment plants.

Table 3. Specific methane production determined for substrates analysed at stage I of the research

Indicators	Unit	WAS	DR_SBM	WAS+DR_SBM 1:1	WAS+DR_SBM 3:1
SMP	NmLCH4/g VS	136	312	243	198

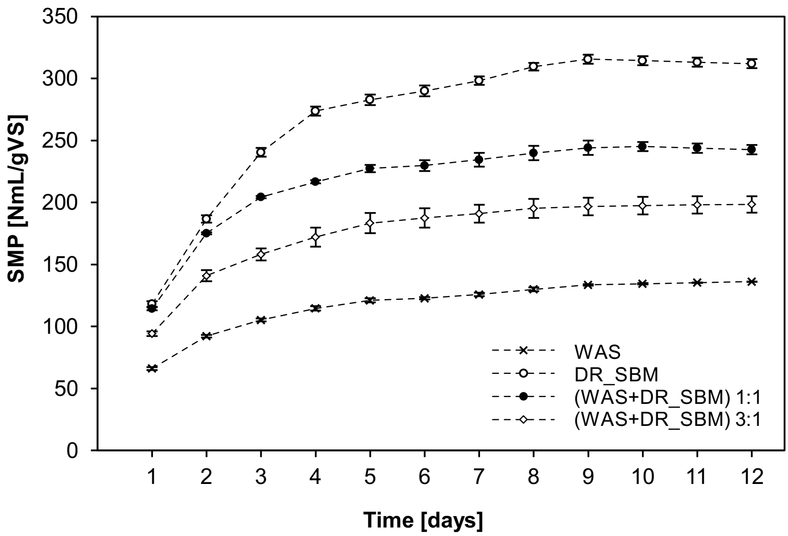

Fig. 1. Cumulative specific methane production for co-digestion of waste activated sludge (WAS) and distillery residue (DR_SMB) in comparison to mono-digestion of waste activated sludge

The known amount of DR_SBM produced annually in the distillery studied here equal to 26,400 tons was estimated to allow for the production of 452,200 m^3 of methane. Assuming that the calorific value of methane is at a level of 35.73 MJ/m3 and that the efficiency of the electricity-heat block is 40%, in reference to both the production of heat and electricity, it was calculated that an amount of heat of 6,463 GJ and electricity of 1,795 MWh would be possible to be produced from such an amount of methane. It seems interesting to verify how electricity resulting from increased methane production could contribute to an improvement in the energy efficiency of a wastewater treatment plant that would decide to use DR_SBM as a co-substrate in the digestion process. According to data published in the IWAMA – Interactive Water Management project [35], in the case of 50% of analysed wastewater treatment plants in the Baltic Sea Region, specific energy consumption was a minimum of 37 kWh/PE·year. Assuming that the entire DR_SBM produced in the distillery in one year as a by-product (26,400 m^3/year) would be subjected to the co-digestion process, the resulting excess energy would cover the complete requirement for electricity for a wastewater treatment plant with PE = 48,520, or allow to obtain a wastewater treatment plant's electricity self-sufficiency characterised by PE = 88,218, with a 45% degree of electricity self-sufficiency before the introduction of co-digestion (according to Rettig et al. [35], half of the considered WWTP achieved 45% of self-supply in terms of electrical energy).

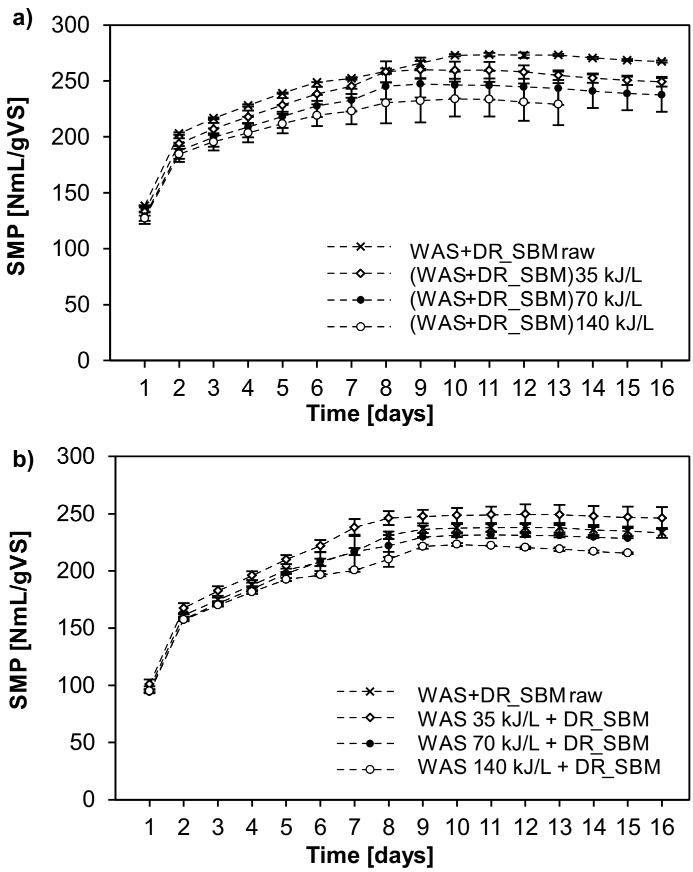

Fig. 2. Cumulative specific methane production for co-digestion of waste activated sludge (WAS) and distillery residue (DR_SMB) without and with pretreatment via hydrodynamic disintegration:
a) disintegration of the mixture of WAS and DR_SMB, b) disintegration of only WAS

The objective of the second stage of the research was to answer the question whether applying hydrodynamic disintegration as a pretreatment method in the process of co-digestion of WAS and DR_SBM would allow for an increase in the methane potential of feedstock introduced to the digesters, and therefore whether it would offer a chance to increase methane production. Hydrodynamic disintegration has successfully been applied to treat WAS in order to intensify its anaerobic digestion [36,37]. In the cited papers, a 12.7% [36] and 33.9% [37] increase in biogas production was obtained. According to the best of our knowledge, we are the first to apply hydrodynamic disintegration as a pretreatment method in the process of co-digestion of WAS and DR_SBM. BMP tests. At this stage of research were conducted for a constant value of the mixing ratio of WAS and DR_SBM at 1:1 (the value was selected based on results obtained at stage I of the research). The results of series 1 showed that hydrodynamic disintegration of the mixture of WAS and DR_SBM resulted in a reduction in SMP, and the application of an increasingly higher energy density in the disintegration process caused an increasingly higher decrease in the SMP value (Fig. 2a, Fig. 3a). Specific methane production for the mixture of WAS and DR_SBM not subjected to disintegration was 267 NmL-CH4/g VS, whereas SMP for the mixture subjected to disintegration at EL 35, 70 and 140 kJ/L decreased by 6.8%, 11.2%, and 14.3%, respectively (Fig. 4). It is worth emphasising that throughout the culture period, the amount of methane generated in all of the samples subjected to the disintegration process was lower than that observed for the sample not subjected to pretreatment (Fig. 2a). In the case of the disintegration process of only WAS (series 2), the following was observed: i) a ca. 5.5% increase in specific methane production of the mixture of WAS and DR_SBM when disintegration of WAS was conducted at EL = 35 kJ/L, and ii) a ca. 2.1% and 7.6% decrease in SMP for EL = 70 kJ/L and EL = 140 kJ/L, respectively (Fig. 3b, Fig. 4). In order to explain the phenomena recorded in series 1 and 2, changes in the characteristics of the analysed samples' liquid phase that resulted from the disintegration process were analysed (Fig. 3a,b). For the mixture of WAS and DR_SBM, it was observed that the disintegration process led to a reduction in the value of dissolved COD (Fig. 3a). Because the disintegration of the separated substrates resulted in an increase in the SCOD value for WAS and a decrease in this indicator's value for DR_SBM (Fig. 5), it was concluded that the decrease in SCOD recorded for the mixture of WAS and DR_SBM had resulted from a loss of organic compounds from DR_SBM. This loss of organic compounds was probably the primary cause of a reduction in SMP for the mixture of WAS and DR_SBM subjected to the disintegration process, especially since DR_SBM was characterised by considerably higher SMP than WAS. The disintegration process most probably caused a loss of a part of the organic compounds whose presence had allowed for such a considerable increase in the produced methane during the first four days of culture in the sample from DR_SBM that was recorded at the first stage of research (Fig. 1). This hypothesis is also justified by the following observations: i) when the disintegration process was conducted only for the stream of WAS, an increase in SMP of the mixture of WAS and DR_SBM was obtained (the increase was obtained for EL = 35 kJ/L – Fig. 3b), ii) a percentage reduction of SMP of the mixture of WAS and DR_SBM recorded for an energy density of 70 and 140 kJ/L was considerably lower for disintegration of only WAS (series II) as compared to disintegration of both substrates (series I) – Fig. 4. If the loss of organic compounds from DR_SBM was the only cause of a decrease in SMP, disintegration of only the stream of WAS should be expected to result in no negative effect of the disintegration process on the methane potential of the mixture of WAS and DR_SBM. Because such an effect did occur (for EL of 70 and 140 kJ/L), it was assumed to have resulted from changes occurring in the disintegrated stream of WAS. Considering that other research papers had suggested the possibility of a reduction in the methane potential of WAS subjected to a prior disintegration process [38,39], it was assumed that re-flocculation could have occurred in the WAS samples disintegrated at an energy density of 70 and 140 kJ/L, thus resulting in a decrease in the biological accessibility of organic matter and contributing to a reduction in SMP for the samples. It is worth mentioning that re-flocculation is the consequence of the release of intercellular substances functioning as biopolymeric flocculants.

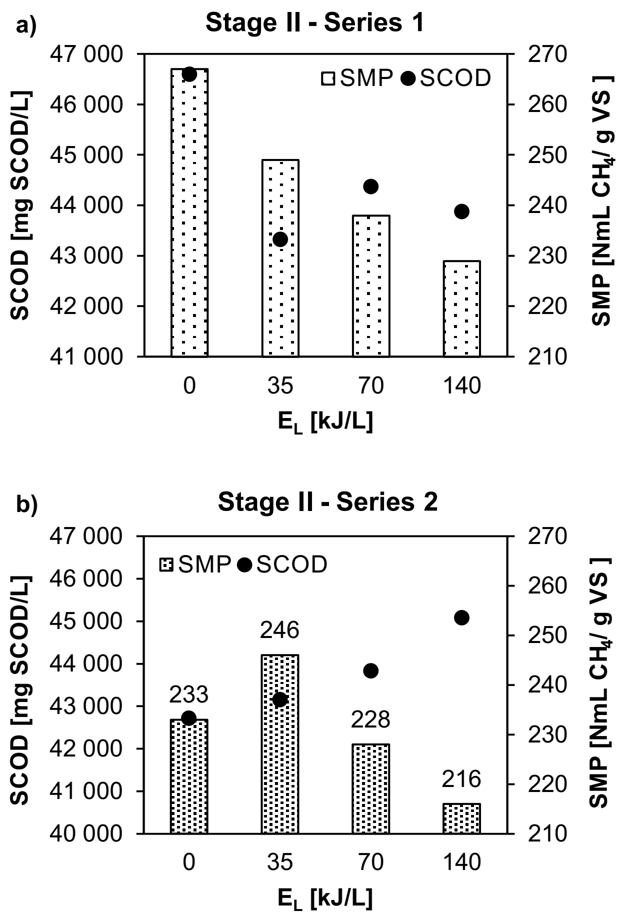

Fig. 3. Specific methane production determined for substrates analysed at stage II of the research and initial SCOD values in samples subjected to anaerobic digestion: a) stage II series 1, b) stage II series 2

An increase in SMP in the sample in which WAS was subjected to the disintegration process at the lowest of the analysed energy densities (EL = 35 kJ/L), recorded in series II of this study, can be explained by sludge floc deagglomeration which resulted in an increase in the biological accessibility of organic matter. Sludge floc deagglomeration was recognised as one of the mechanisms responsible for an increase in methane potential by, among others, Cella et al. [40] and Lippert et al. [39].

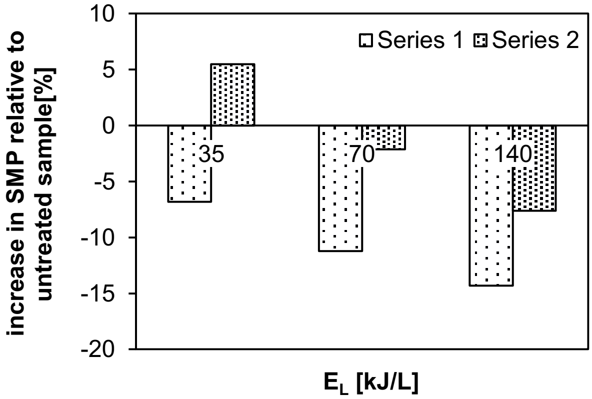

Fig. 4. Effect of hydrodynamic disintegration at different energy densities on SMP of the mixture of WAS and DR_SBM, taking into account two variants: the disintegration of the mixture of WAS and DR_SBM (series 1), and disintegration of only WAS (series 2)

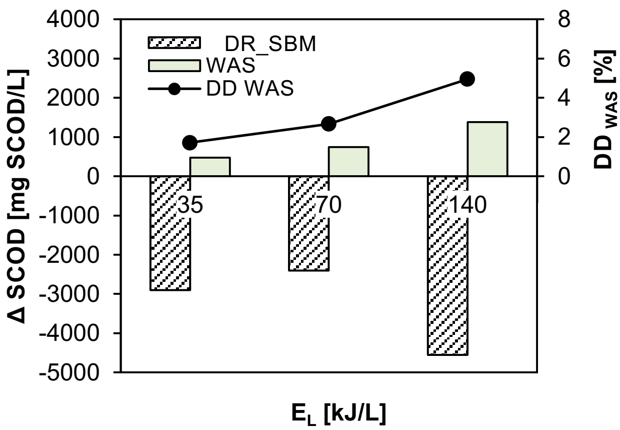

Fig. 5. Changes in SCOD as a result of the process of DR_SBM and WAS disintegration, and values of the degree of disintegration (DD) of sludge depending on energy density applied in the disintegration process

To sum up, an additional increase in the efficiency of anaerobic digestion can be obtained in a technological configuration where only WAS is subjected to hydrodynamic disintegration. For the sample subjected to the disintegration process at energy density of 35 kJ/L (WAS 35 kJ/L + DR_SBM) an energy balance was made (Table 4). Taking into account the energy expenditure on pre-treatment, and the amount of energy obtained from the additionally produced methane no positive net energy gain was recorded. The possibility of obtaining a positive energy balance will be the subject of further research. Moreover, it should be emphasised that obtaining a relatively low, namely a 5% increase in SMP as a result of WAS disintegration in own research does not mean that a comparable result will be obtained by disintegrating waste activated sludge from other wastewater treatment plants. This is evidenced by the study results of Lippert et al. [39] who ran the disintegration process with the same process parameters and obtained considerably different methane potential values for sludge from three separate wastewater treatment plants.

Table 4. Energy balance

Parameters	Unit	WAS+DR_SBM raw	WAS 35kJ/L+DR_SBM
Methane energy content[1)]	[Wh]	2.33	2.47
Electricity[2)]	[Wh]	0.93	0.99
Extra electricity[3)]	[Wh]	–	0.06
Energy applied for HD	[Wh]	–	0.11
Net energy production	[Wh]	–	–0.05

[1] Methane energy content calculated by assuming methane calorific value equal to 36 MJ/m^3.
[2] Electricity calculated by assuming electrical efficiency of engine equal to 40%.
[3] Extra electricity = electricity dez. – electricity untreated, (Wh):
electricity dez., amount of electricity produced in a disintegrated sample at a predefined energy density level (Wh);
electricity untreated, amount of electricity produced in an untreated sample (Wh).

3.2. NUTRIENTS IN DIGESTATE

In the case of a wastewater treatment plant that is considering the introduction of the co-digestion process and/or the disintegration process to increase biogas production, it should be taken into account that the process will affect the characteristics of the leachate that results from the process of dewatering digested sludge. It is widely known that the leachate introduced to the main treatment stream causes: i) a 10–20% increase in a load of nitrogen compounds supplied to the treatment plant which results in, among others, a higher demand for oxygen for the nitrification process, and ii) a disturbance of the proportions between COD and TN in wastewater subjected to treatment, to the disadvantage of the denitrification process, which possibly results in a reduction of the efficiency of nitrogen removal. The introduction of DR_SBM as a co-substrate in the anaerobic digestion process may magnify the problems mentioned earlier, especially since the waste is characterised by a high concentration of total

Table 5. Characteristics of the liquid phase of the digested samples

Indicators	Unit	Stage I				
		Inoculum (I)	WAS	DR_SBM	WAS+DR_SBM 1:1	WAS+DR_SBM 3:1
SCOD	mg/l	542	546	705	611	556
STN	mg/l	1,175	1,220	1,290	1,258	1,260
STP	mg/l	13.8	16.5	12.9	14.1	15.2
SCOD:STN	–	0.46	0.46	0.46	0.46	0.46
%STNWAS+DR_SBM	%				84.4	88.9
Indicators	**Unit**	**Stage II – Series 1**				
		Inoculum (I)	WAS+DR_SBM raw	(WAS+DR_SBM) 35 kJ/L	(WAS+DR_SBM) 70 kJ/L	(WAS+DR_SBM) 140 kJ/L
SCOD	mg/l	522	671	669	657	651
STN	mg/l	1,176	1260	1,232	1,268	1,242
STP	mg/l	79.2	77.9	78.4	68.5	68.8
SCOD:STN	–	0.44	0.53	0.54	0.52	0.52
%STNWAS+DR_SBM	%				9.52	
Indicators	**Unit**	**Stage II – Series 2**				
		Inoculum (I)	WAS +DR_SBM raw	WAS 35 kJ/L + DR_SBM	WAS 70 kJ/L + DR_SBM	WAS 140 kJ/L + DR_SBM
SCOD	mg/l	676	1,042	1,117	856	1,049
STN	mg/l	1,218	1,338	1,354	1,368	1,362
STP	mg/l	69.2	78.8	86.6	90.1	78.5
SCOD:STN	–	0.56	0.78	0.82	0.63	0.77
%STNWAS+DR_SBM	%			13.3	25.0	20.0

nitrogen (Table 1). The introduction of disintegration of feedstock supplied to the digesters can also lead to an increase in the concentration of nutrients in the liquid phase of the digested sludge. The process causes a release of nutrients from the sludge flocs, and by additionally contributing to an increase in the efficiency of anaerobic digestion it leads to higher "production" of ammonium nitrogen as a result of anaerobic bioconversion of organic matter.

Table 5 shows the characteristics of the liquid phase of the digested samples for stages I and II of the research, respectively. Data collected in Table 5 suggest that the application of DR_SBM as a co-substrate had an inconsiderable effect on the concentration of dissolved nitrogen in the samples after the anaerobic digestion process. The values of the indicator in the case of mixtures of WAS and DR_SBM increased only by ca. 3% in comparison to the sample in which only WAS was used as a substrate. It should be noted, however, that a considerable part of STN occurring in the digested samples originated from the inoculum (I). Taking this observation into account, the percentage increase in the concentration of STN in the digested samples was calculated in accordance with the formula:

$$\%STN_{WAS+DR\_SBM} = [(STN_{WAS+DR\_SBM} – STN_I) - (STN_{WAS} – STN_I)]/ (STN_{WAS} – STN_I) *100 [\%] \quad (1)$$

The obtained results showed that the effect of introducing DR_SBM as a co-substrate was an over 80% increase in the STN value as compared to the sample with WAS. It could be expected that the application of a higher share of DR_SBM would result in a higher increase in the concentration of STN. No such dependence was observed in the research conducted here. It should be taken into account, however, that the final concentration of STN depends on many factors that are related to the efficiency of the anaerobic bioconversion of organic matter [41] and to potentially occurring simultaneous processes of struvite precipitation, which is favoured by the simultaneous presence of ammonium, phosphate, and magnesium ions [42, 43]. An analysis of the data obtained in series 1 of stage II shows that the disintegration of the mixture of WAS and DR_SBM did not contribute to an increase in the concentration of dissolved biogenic compounds in the digestate (Table 5). For the disintegration process of only the stream of WAS (series 2 of stage II), the concentration of STN in the digestate increased by 13.3, 25, and 20%, respectively, for samples WAS 35 kJ/L + DR_SBM, WAS 70 kJ/L + DR_SBM, and WAS 140 kJ/L + DR_SBM, as compared to the sample that was not subjected to pretreatment. A considerable increase in the concentration of STP was also observed by 81.3% for WAS 35 kJ/L + DR_SBM and by 118% for WAS 70 kJ/L + DR_SBM (the increase in the concentration of STN and STP was determined by taking into account the STN and STP concentrations in the inoculum).

To sum up the introduction of distillery residue as a co-substrate to the digester and the application of hydrodynamic disintegration should be accompanied by a holistic approach, and particular attention should be paid to changes in the characteristics of the supernatant resulting from the process of digestate dewatering.

CONCLUSIONS

Distillery residue obtained after the production of alcohol from sugar beet molasses as a co-substrate in the process of anaerobic digestion of sewage sludge is a productive way of increasing the amount of generated biogas, thus offering a chance for municipal wastewater treatment plants to attain energy self-sufficiency. In this study, the application of DR_SBM as a co-substrate (the mixing ratio of DR_SBM and WAS was 1:1) allowed for a 78.7% increase in the amount of generated methane per gram of volatile solids as compared to mono-fermentation of WAS. Introducing the hydrodynamic disintegration process to the system should take into account separation of the streams of WAS and DR_SBM, as the disintegration of the mixture of WAS and DR_SBM may result in a reduction of the amount of generated methane.

It is worth emphasising that the anaerobic digestion process which results in obtaining biogas from distillery residue from molasses, which in turn is waste from alcohol distillation that constitutes a by-product in sugar refineries, corresponds with the latest trends of a circular economy, as the electricity and heat generated from the resulting biogas constitute an added value to the used residue.

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REVIEW ON THE SONOCHEMICAL DEGRADATION OF SELECTED ORGANIC MICROPOLLUTANTS FROM WATER

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Recently, the ultrasonication process was found to be an interesting alternative for the removal of many harmful substances which enter the aquatic environment daily. It was proved by many authors that due to urbanization and population increase more and more organic micropollutants are identifying in water. These groups of substances attract the attention of many researchers because they could be harmful to humans even in low doses. The organic micropollutants include among others pharmaceutical and personal care products (PPCPs), polycyclic aromatic hydrocarbons (PAHs), pesticides, hormones, flame retardants, detergents, and medicines. Thereby, this work presents a review of the literature on the degradation of selected microorganic pollutants including bisphenol A, carbamazepine, triclosan, ethinyloestradiol, and pyrene by ultrasonication process from various water matrices. Literature data showed that the degradation rate of micropollutants in most cases was proportional to the power density, temperature, and sparging gas presence. Furthermore, the removal rate of micropollutants was also affected by the pH value of the treated solution, usage of pulsed ultrasonication mode, volume of the treated sample, dosage of the oxidant, and time of the treatment. It was also proved that usage of sonocatalysts and sonosensitizers (e.g. presence of glass bead, H_2O_2, Fe^0 addition, TiO_2 and NaCl) can increase ultrasound treatment efficiency. Moreover, researchers suggested that ultrasonication can be effective both in high and low frequency of ultrasound. Although ultrasound technology is known for many years, its mechanism of micropollutants removal from water and the impact of the operational parameters on the process efficiency was not completely explained and tested, thus its influence is included in this review.

Keywords: ultrasound, ultrasonication, organic micropollutants, PPCPs, PAHs, wastewater, sonochemistry

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1. INTRODUCTION

Organic micropollutants (OMPs) are a group of widely spread substances in the environment, which maximum concentration is in most cases not regulated by existing law and guidelines. Although OMPs occurs in the environment in very low concentration (from ng L-1 to μg L-1) they can affect human health and their occurrence in water are a potential threat to environmental ecosystems [4]. OMPs include many groups of substances such as pharmaceuticals and personal care products (PPCPs), endocrine-disrupting compounds (EDCs) e.g. steroids and hormones, disinfection by-products (DBPs), detergents, flame retardants, preservatives, plasticizers, gasoline, and pesticides [50,70]. Wastewater treatment plant facilities are considered major sources of OMPs in the aquatic environment, and conventional wastewater treatment methods are low effective in OMPs removal leading to the indirect discharge of pollutants into the aquatic environment [19,62]. Moreover, it is expected that the use of some OMPs will be higher as a result of the increase in human life standards coupled with population growth [60]. Thus to prevent the discharge of harmful micropollutants into the environment, modern and effective techniques should be developed e.g. advanced oxidation processes (AOPs). This group of methods can be efficient in many different micropollutants removal, particularly hardly biodegradable or non-biodegradable compounds. During AOPs methods highly reactive species are formed, namely ozone (O_3), hydrogen peroxide (H_2O_2), and hydroxyl radicals (HO•) which react with the pollutants leading to their decomposition [35]. AOPs may be classified into four main groups: photocatalytic processes (e.g. H_2O_2/UV, UV/O_3, UV/TiO_2), Fenton reaction-based processes (e.g. Fe^{2+}, H_2O_2, Electro-Fenton), and ozone-based processes (e.g. O_3/UV, O_3/activated carbon, O_3/H_2O_2) [55]. However, recently also ultrasonication process (US) was found to be an interesting alternative AOP, which could be effective in many different substances removal including bacteria, fungi, dyes, viruses, algae, polycyclic aromatic hydrocarbons (PAHs), pesticides, industrial chemicals, PPCPs and other OMPs [20, 44, 69].

Thus, the degradation of selected organic micropollutants (bisphenol A, carbamazepine, triclosan, ethinyloestradiol, and pyrene) characterized by various chemical and physical properties by using the ultrasonication process is described in this review. Moreover, in the study effect of ultrasound combined with other advanced oxidation, processes were analyzed. There is lack of knowledge about the effect of catalysts in mentioned micropollutants removal thus, in this work, the use of diverse sonocatalysts and sonosensitizers in micropollutants elimination was also summarized. The properties of the mentioned compounds are listed in Table 1.

Moreover, in this literature review effect of ultrasonication parameters on removal efficiency was shown and the effect of ultrasound combined with other AOPs were analyzed.

Table 1. Properties of tested compounds [34]

Compound name	CAS no.	Molecular formula	Molecular weight, g mol^{-1}	Solubility in water, mg L^{-1}	Octanol-water partition coefficient Log K_{ow}
Bisphenol A	80-05-7	$C_{15}H_{16}O_2$	228.29	300^a	3.32
Pyrene	129-00-0	C_6H_{10}	202.25	0.135^a	5.18
17α-ethinylestradiol	57-63-6	$C_{20}H_{24}O_2$	296.4	11.3^b	4.14
Carbamazepine	298-46-4	$C_{15}H_{12}N_2O$	236.27	18^a	2.45
Triclosan	3380-34-5	$C_{12}H_7C_{13}O_2$	289.5	10^c	4.76

^{a}at 25°C, ^{b} at 27°C, ^{c} at 20°C.

2. ULTRASOUND PROCESSING

Recently, the use of ultrasound become popular in many different areas such as medicine, surface cleaning, soil remediation, and sewage sludge disintegration. Moreover, in the last decades ultrasound technology attracts attention due to its effectiveness in water disinfection and wastewater treatment [7, 80]. Theoretically, ultrasound is a sound wave with a frequency above 20 kHz. There are three frequency ranges of ultrasonic waves: low (20–100 kHz), medium (300–1000 kHz), and high (2–10 MHz). In sonochemistry and environmental engineering generally, low and medium range frequencies are used, while higher ranges are used mainly in diagnostic medicine [23]. Application of intense ultrasound to the liquids could result in acoustic cavitation phenomenon occurrence which is defined as a formation, growth, and violent implosion of the acoustic bubble. The bubble can be formed due to the periodic movement of liquid particles caused by the propagation of ultrasonic waves in the so-called rarefaction phase (at negative pressure conditions). Subsequently, the bubble is growing until it reaches the critical size and collapses in the so-called compression phase (at a positive pressure value). As shown in figure 1, bubble implosion leads to a local increase of pressure and temperature in the bubble interior up to 5,000 K, and 100 MPa, respectively [15, 76, 77]. In this region, micropollutants can be eliminated due to the result of pyrolytic reactions. In bubble also hydroxyl radicals are generated as a result of thermal dissociation of vaporized water. At the bubble-liquid interface, hydrogen peroxide could be formed characterized by high oxidative potential similarly to hydroxyl radicals. In the bubble surrounding the liquid region, free radicals migrated from the bubble interior, and bubble interface can react with micropollutants and other oxidizing species. Furthermore, microjets, shock waves, and high shear forces are generated during bubble collapse, especially when the frequency of ultrasound is low [2, 8, 47].

To generate ultrasound several piezoelectric transducers which transform electrical energy into vibration could be used. A horn-type transducer (sonotrode) is one of the most common devices. It is characterized by the low diameter of the probe immersed into the treated sample,

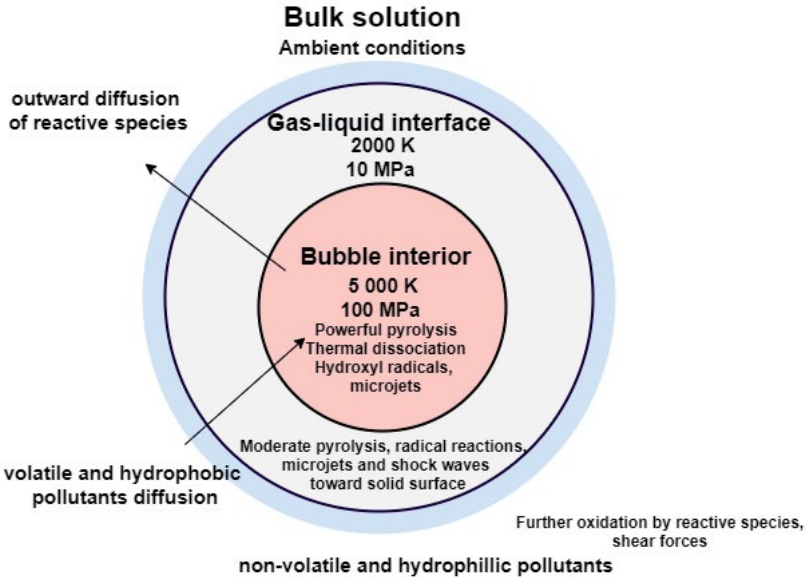

Fig. 1. Degradation zones of pollutants during acoustic cavitation [47,53]

thus the cavitation intensity is very high due to acoustic energy transmission through a small area. The horn is made of a conductive material such as titanium and it needs to have high resistance to cavitational erosion and high temperatures. The other type of frequently used type of device is the so-called ultrasonic bath. In this type of device, unlikely the ultrasonic horn, the ultrasonic waves enter the solution indirectly due to the transducer position which is placed under the container with treated solution. An ultrasonic bath can generate ultrasound with a relatively high frequency of ultrasonic waves, however, the ultrasound intensity in this type of device is low. Furthermore, some unconventional equipment can be used to generate acoustic cavitation phenomena, e.g. vibrating plates [6, 20, 32, 36, 71, 80].

3. OCCURRENCE AND SOURCES OF SELECTED MICROPOLLUTANTS

Carbamazepine (CBZ) is one of the most frequently studied pharmaceuticals which is widely spread in the environment and extensively used by people [12]. It is a substance considered persistent in the environment because of its resistance to degradation in well-known treatment methods. It is used for treating various mental disorders, epilepsy, and pain [5, 58]. CBZ is commonly found in environmental matrices. Hebrer et. al [28] found that surface water in Berlin, Germany contained 1.08 μg L^{-1} of CBZ and that removal efficiency of this compound was lower than 10% at different municipal treatment plants. Ginebreda et al. [22] et al reported that CBZ concentration in groundwater can reach the value of 0.61 μg L^{-1}, while Heberer et. al [29] found that drinking water contained 0.03 μg L^{-1} of CBZ. It was also reported that CBZ present in the environment can have a very negative impact on aquatic life (e.g. bacteria, algae, fish), and ecosystem dynamics [27, 33].

As a result of detection of many endocrine-disrupting compounds (EDCs) in the environment, Bisphenol A (BPA) gained much scientific attention [24]. It is a colorless solid substance characterized by low solubility in water and it is the most produced bisphenol all over the world [34, 40, 42]. BPA can be found in plastic bottles, books, thermal paper, toys, CDs, and electronic devices. It is also commonly used in polycarbonate, flame retardants, epoxy resins, and other polymer material production [45, 57, 77]. Literature data indicated that exposure to BPA might be related to lung, prostate, and breast cancer. Furthermore, it has a negative impact on the nervous system as well as metabolic and immune function [42, 67, 78]. It was reported that BPA is ubiquitous in many environmental matrices including wastewater treatment plant effluent, surface water, groundwater, and rain. It could be found even in tap water [10, 43]. According to Wells [73], most people have detectable levels of BPA in their urine.

Pyrene (PYR) is one of over 100 identified in the environment polycyclic aromatic hydrocarbons (PAHs) [16, 68]. This colorless solid compound contains four fused rings and it is characterized by slight blue fluorescence [34]. PYR enters the aquatic environment as a result of natural and anthropogenic processes including fires, petroleum spills, volcano eruptions, incomplete combustion of fuels, and transportation [1, 9, 25, 37]. PYR presence in water can have a negative impact on human health due to its toxicity and mutability. Furthermore, PYR is one of the persistent organic pollutants thus it is persistent to degradation by using classical treatment methods. Although it is not cancerogenic it could be transformed into some cancerogenic substances as a result of various processes [18, 81]. Moreover, PYR is ubiquitous in the environment including soil, sediments, and drinking water [39, 41].

Triclosan (TCS) as one of the PPCPs is daily used by people due to its occurrence as an active ingredient in detergents, soaps, deodorants, toothpaste, clothes, kitchenware, shave gels, skin cleaners, and other cosmetics [14, 72, 79]. It is widely spread in the environment. The concentration of TCS in surface waters, effluents from the wastewater treatment plant, and groundwater can reach the maximum value of 40,000, 5.37, and 328.8 μg L^{-1}, respectively [46, 61]. The half-life time of TCS is equal to 8 d in fresh water and 4 d in salt water. However, in the soil, half-life time of TCS could reach even 120 d [3, 26]. It was proved that TCS exposure disturbs cell functioning and leads to cytotoxicity. Moreover, it has an impact on DNA stability, the reproductive system, and it causes teratogenicity. Furthermore, TCS can degrade into even more toxic, and persistent by-products [11].

The synthetic estrogen 17α-ethinyloestradiol (EE2), one of the widely spread in the environment EDCs tends to accumulate in the organisms and it has high environmental persistence. EE2 can disrupt reproductive processes even at very low concentrations. Furthermore, it causes a reduction in fecundity and altered sex behaviors [65]. EE2 can enter the environment mainly due to a woman's excretion via urine and feces. Literature data showed that EE2 concentrations in municipal wastewater treatment plant influent and effluent can reach up to 7.89 μg L^{-1} and 0.55 μg L^{-1}, respectively. Moreover, the average concentration of EE2 in effluent from wastewater treatment plants was 0.012 μg L^{-1} which is much greater than the concentration causing undesirable effects on organisms [64].

4. REMOVAL OF MICROPOLLUTANTS USING ULTRASOUND

The application of ultrasonication or sonolysis in micropollutants removal is an area of increasing interest. Several authors reported successful application of CBZ removal in different water matrices. Rao et al. [54] examined sonolytic and sonophotolytic removal of CBZ from wastewater treatment plant effluent. They found that the ultrasonication process was more efficient at the frequency of 200 kHz than at 400 kHz. The total CBZ removal was proportional to the power of ultrasound and the initial concentration of CBZ. After 60 min of the sonication degradation rate of CBZ was around 81%, and 60% at frequencies 200 kHz and 400 kHz, respectively. The degradation rate was also slightly dependent on pH value (increased pH value was related to higher effectiveness). They reported that hydroxyl radicals occurrence are responsible for CBZ degradation at the bubble interface and in bulk solution, due to high Log K_{ow} value and low water solubility. Moreover, they found that UV irradiation enhanced the efficiency of ultrasonication by around 5% at 60 min treatment time.

Xiao et. al [75] used continuous and pulsed mode ultrasound for the degradation of a few pharmaceuticals including CBZ. They proved that pulsed ultrasound (100 ms on and 100 ms off mode) was more effective than a continuous mode of ultrasonication. They found that lower molar volumes of compounds increase the pulsed ultrasound efficiency due to its diffusion to bubble interfaces, and 30% of CBZ degradation occurs in the bulk solution. Similarly, Xiao et al. [74] found that pulsed ultrasound enhanced sonication efficiency by about 6% in comparison to continuous ultrasound mode.

Fraiese et al. [17] investigated CBZ removal by using ultrasound with ozonation assistance (US/O_3), and sonication with 0.5 mg L^{-1} TiO_2 addition (US/TiO_2). In US/O_3 process they obtained a 52% degradation rate of CBZ at 40 min sonication using 20 kHz frequency horn -type transducer. The degradation rate during US/TiO_2 reached 37% after 30 min sonication time. However, they stressed that dissolved organic carbon (DOC) was not reduced after treatment thus some by-products were generated.

Similarly to the other studies, Tran et. al [66] concluded that ultrasonication time and electric power value had a significant impact on CBZ removal efficiency. Moreover, CBZ was transformed mainly into anthranilic acid and acridine. They reached a 58.7% removal rate of CBZ at 520 kHz and 12.5 min of sonication time. Naddeo et al. [49] found also that the degradation rate of CBZ can be increased in acid conditions and when the treatment is carried out in the presence of dissolved air. Ghauch et al. [21] investigated the degradation of CBZ by combining ultrasonication treatment with improved Fenton's process and hydrogen peroxide addition obtaining high efficiency of the treatment.

Degradation of TCS from water matrices by using ultrasound was studied only by a few authors. Vega et al. [69] investigated sonochemical degradation of TCS in 215, 373, 574, 856, and 1134 kHz at 40 W L^{-1} of power density. They revealed that the highest efficiency of the process was at 574 kHz and the degradation rate was 88% after 60 min of sonication. Moreover, increasing power density to 140 W L^{-1} leaded to the complete removal of TCS after 25 min at the same frequency. They showed also that degradation of TCS takes place at the liquid/bubble interface area. However, literature data showed that TCS can be efficiently degraded also using low-frequency ultrasound. Naddeo et al. [48] obtained 95% degradation of TCS from water containing 23 pollutants using 45 kHz ultrasonication in 180 min at a power density of 100 W L^{-1}. Furthermore, Sanchez-Prado et al. utilized 80 kHz frequency ultrasound (at 135 W acoustic power) waves to degrade TCS from seawater, deionized water, urban run-off, and wastewater influent revealing that the most efficient degradation was obtained in seawater due to high presence of ions which can integrate with the organic pollutant. Moreover, solid particles could be nuclei for acoustic cavitation bubbles. Ren et al. studied sonoelectrochemical degradation of triclosan in water. They found that 15 min of the treatment at the frequency of 850 kHz, resulted in 90% TCS removal. Moreover, the highest efficiency was obtained at the lowest concentration of TCS in water (1mg L^{-1}).

The aim of research conducted by Park et al. [52] was to determine the removal degree of EDCs including EE2 by using three different frequencies. The degradation rate of EE2 followed the order: 97% at 580 kHz > 94% at 1000 kHz > 67% at 28 kHz after 30 min of the treatment. Ifelebuegu et al. [31] found that the degradation rate by using ultrasound is favored in acidic conditions. They found also, that air spangling and temperature increase had a significant impact on EE2 removal degree. EE2 could be also removed using ultrasound equipment combined with different catalysts. Her et al. [30] used among others stainless steel wire mesh and glass beads during 60 min sonication at 28 kHz which increased the process efficiency. Glass beads were also effectively applied by Park et al. [53]. They proved that 580 kHz ultrasound treatment was more effective than 28 kHz, especially while mentioned catalyst was used (degradation constant rate increased from 0.054–0.136 min^{-1}). Moreover, they indicated that an increased pH value leads to a higher decomposition rate of EE2. Similarly, Suri et al. [63] concluded positive relation between pH value and degradation rate of estrogen hormones from neutral to basic pH. Furthermore, they proved that NaCl presence in the solution could lead to an increase in ultrasonic treatment efficiency of EE2.

Meng et al. [45] showed the efficient degradation of BPA by using 200 kHz, and 400 kHz ultrasound treatment from distilled water and river water. They proved that the use of the latter frequency resulted in higher efficiency due to the stronger capability of hydroxyl radicals generation. Furthermore, acidic conditions, the presence of ions, and high temperature values increased the ultrasonication efficiency. Park et al. [52] demonstrated, that BPA degradation was lower than EE2 in the same conditions of ultrasound at 28, 580, and 1000 kHz. Furthermore, they showed that BPA, correspondingly to EE2 is degraded at liquid – bubble interface or nearly to this area. Similarly, in other work [53], BPA was found to be harder degradable by ultrasound than EE2. They obtained 97 and 61% degradation rates of BPA after 30 min sonication at 580, and 28 kHz, respectively. Moreover, Lim et al. [38] showed that BPA degradation could be efficient at 35 kHz when the ultrasonication was combined with H_2O_2 addition.

Using ultrasonication as a single process resulted in 30% BPA degradation after 60 min, while 20 mM of H_2O_2 addition led to a 17% increase in degradation ratio under the same treatment conditions. Similarly, Zhang et al. [77] investigated the effect of H_2O_2 dosage on the removal ratio of BPA during ultrasonic irradiation. They proved that the addition of this oxidant could lead to increased efficiency of the process, however high dosage of H_2O_2 led to decreased degradation rate efficiency. They also found that BPA degradation was inhibited by aeration. Oppositely, Gultekin et al. [24] proved increased efficiency in the presence of air due to the formation of acids and excess radicals. Furthermore, they revealed that the degradation rate was much higher in acidic pH than in the alkaline range.

Park et al. [51] provided further evidence that ultrasonication was more effective in acidic conditions and that increasing the acoustic power lead to enhanced degradation of PYR. Furthermore, they proved that the efficiency of the treatment can be higher when argon gas is used. Importantly, in this study, none of the toxic to humans compounds were identified after treatment. Manariotis et al. [44] presented ultrasonication at 582, 862, and 1,142 kHz and a power of 133 W to remove PAHs from water. They concluded that in all of these frequencies, PYR degradation was higher than 90% after 100 min of the treatment, however, the removal rate of PYR was the highest at 582 kHz and the lowest at 1,142 kHz. On the other hand, in the study [13], PYR degradation at 506 kHz was much higher than at 20 kHz, and according to their study at both frequencies, PAHs are mainly pyrolyzed within the bubble and less than hydroxyl radicals. The literature data on the sonochemical degradation of mentioned compounds are listed in Table 2.

Table 2. Literature review on CBZ, TCS, EE2, BPA, and PYR sonochemical degradation

Compound name	Process	Operating parameters	Efficiency	Main conclusions	Reference
1	2	3	4	5	6
CBZ	US	f = 200 kHz/400 kHz P = 100 W t = 60 min pH = not regulated V = 200 ml volume C_0 = 0.025 mM	81% (at 200 kHz) 60% (at 400 kHz)	Degradation rate proportional to acoustic power, degradation by hydroxyl radicals at the bubble interface, efficiency proportional to the pH value	[54]
CBZ	US/UV	f = 200 kHz P = 100 W t = 60 min pH = not regulated V = 200 ml C_0 = 0.025 mM	86%	UV irradiation enhanced sonication process by around 5%	[54]
CBZ	US	f = 205 kHz P = 45 W L^{-1} t = 35 min	0.52 μM min^{-1}	Pulsed ultrasound can enhance the sonochemical	[75]

1	2	3	4	5	6
		pH = 3.5 V = 300 ml C_0 = 10 μM		degradation of CBZ	
CBZ	US+O_3	f = 20 kHz P = 370 W L^{-1} t = 40 min V = 200 ml C_0 = 10 mg L^{-1} O_3 = 3.3g h-1	52%	Ozone dosage is proportional to degradation rate of CBZ, dissolved organic carbon (DOC) was not changed after treatment, and by-products were formed	[17]
CBZ	US+TiO_2	f = 20 kHz P=370 W L^{-1} t=30 min V=200 ml C0=4 mg L^{-1} TiO2=0.5 mg L^{-1}	37%	Dissolved organic carbon (DOC) was not changed after treatment, formation of by-products	[17]
CBZ	US	f = 520 kHz P=40 W t=12.5 min V=250 ml C0=12 mg L^{-1}	58.7%	Treatment time and electrical power had the most influence on ultrasonication efficiency, CBZ was transformed mainly into anthranilic acid and acridine.	[66]
CBZ	US	f = 20 kHz P = 100 W L^{-1} t = 60 min pH = 7.5 V = 200 ml C_0 = 5 mg L^{-1}	42% (in a mixture with amoxicillin and diclofenac) 8% TOC removal	Low pH and air sparging enhanced ultrasonic efficiency	[49]
CBZ	US/Fe^0/H_2O_2	f = 40 kHz t = 60 min pH = 5 V = 200 ml C_0 = 42 μM H_2O_2 = 100 μL Fe^0 = 200 mg	82%	Under 40 kHz sonication frequency hydrogen peroxide generation is insignificant, hydroxyl radicals were primary oxidative species, lower pH conditions can increase the treatment efficiency.	[21]
TCS	US	f = 574 kHz P = 40 W L^{-1} t = 60 min V = 300 ml C_0 = 1 mg L^{-1}	88%	Toxicity increases after complete removal of TCS, degradation takes place at bubble/liquid interface, pulsed ultrasound had	[69]

1	2	3	4	5	6
				a positive impact on removal efficiency	
TCS	US	f = 45 kHz P = 100 W L^{-1} t = 180 min V = 300 ml C_0 = 1 μg L^{-1} (mixture of 23 contaminants)	95%	Increased power density leads to higher efficiency of the sonication process	[48]
TCS	US	f = 80 kHz P = 135 W t = 30 min C_0 = 5 μg L^{-1} (seawater)	95%	The fastest degradation was obtained during the removal of TCS from seawater (compared to deionized water, urban run-off water, and wastewater influent) due to the presence of many ions, degradation was not accompanied by the formation of by-products	[59]
TCS	US/Electric	f = 850 kHz P = 170 W t = 15 min V = 400 ml C0 = 1 mg L^{-1} 1 mS cm^{-1}, 10 V	90%	Diamond-coated niobium electrode was highly efficient, Removal efficiency was inversely proportional to the TCS concentration	[56]
EE2	US	f = 28, 580, 1000 kHz P = 0.2 W mL^{-1} t = 30 min V = 1000 ml pH = 6.8 C0 = 1 μM L^{-1}	97% (at 580 kHz)	Degradation of pollutant probably occurs at the bubble-liquid interface, and degradation in presence of CCl4 increases. Highest degradation rate at 580 kHz	[52]
EE2	US	f = 850 kHz P = 50 W t = 30 min pH = 3 V = 200 ml C_0 = 1 mg L^{-1}	Around 95%	Increased temperature, low pH value, high temperature, and air sparging increased degradation rate, mechanism of degradation is a result of an intermediate reaction, ion-molecule	[31]

1	2	3	4	5	6
				reactions, or pyrolysis.	
EE2	US + Stainless steel wire mesh	f = 28 kHz P = 0.2 W mL^{-1} t = 60 min pH = 6.8 V=1000 ml C_0 = 1 µM	82% (with the use of catalyst) 59% (without catalyst)	Glass beds and stainless steel wire mesh catalyst were very effective in the degradation of EE2	[30]
EE2	US + glass bed	f = 28, 580 kHz P = 0.2 W mL^{-1} t = 30 min pH = 7.5 V = 200 ml C_0 = 1 µM 25 g of glass bed (0.1 mm size)	59% (at 28 kHz without glass bed) around 95% (at 580 kHz without glass bed)	The degradation rate of EE2 was higher in deionized water than in synthetic seawater. The removal rate increased at higher pH, glass beads increased the efficiency	[53]
EE2	US	f = 20 kHz P = 640 W L^{-1} t = 30 min pH = 7.0 C_0 = 10 µg L^{-1} water with estrogen hormones mixture	60% (reduction of all hormones used in the study)	NaCl presence could increase the process effectiveness, increasing pH from neutral to basic increased the degradation rate	[63]
BPA	US	f = 200, 400 kHz P = 100 W t = 45 min pH = 6.5 V = 250 ml C_0 = 0.01 mM	96% (400 kHz) 87% (200 kHz)	The degradation rate was proportional to the frequency, temperature, And inversely proportional to the BPA initial concentration, pH value, degradation is mainly caused by hydroxyl radicals oxidation	[45]
BPA	US	f = 28, 580, 1000 kHz P = 0.2 W mL^{-1} t = 30 min pH = 6.8 V = 200 ml C_0 = 1 µM L^{-1}	96% (at 580 kHz)	Degradation of pollutants probably occurs at the bubble-liquid interface, and degradation in the presence of CCl4 increases. Highest degradation rate at 580 kHz	[52]
BPA	US	f = 28, 580 kHz P = 0.2 W mL^{-1} t = 30 min	97% (580 kHz), 61% (28 kHz)	Degradation of BPA was lower than EE2, lower degradation rate in seawater	[53]

1	2	3	4	5	6
		pH = 7.5 V = 1000 ml C_0 = 1 μM L^{-1}		than in deionized water, high pH value increased the efficiency	
BPA	US + H_2O_2	f = 35 kHz P = 40 W t = 30 min V = 500 ml H_2O_2 = 20 mM	30% (US) 47% (H_2O_2 and US)	Some formed intermediates cannot be completely removed by sonochemical reaction, H_2O_2 addition increased the ultrasonication efficiency	[38]
BPA	US+H_2O_2	f = 800 kHz P = 1 W mL^{-1} t = 60 min C_0 = 1 mg L^{-1} H_2O_2 = 0.1 mM L^{-1}	99%	The too high value of H_2O_2 led to efficiency decreased, aeration inhibited BPA degradation, and degradation was proportional to frequency and power density	[77]
BPA	US	f = 300 kHz P = 0.19 W mL^{-1} t = 60 min pH = 6.0-6.3 V = 100 ml C_0 = 10 μM L^{-1}		Decomposition increased with the BPA initial concentration due to the possibility of degradation not only in bubble liquid, faster decomposition in acid and neutral pH range (in alkaline pH range BPA in ionic form is hydrophilic and less likely approach negatively charged bubbles, air injection lead to higher degradation rate	[24]
PYR	US +Ar+ H_2O_2	f = 20 kHz P = 50 W t = 120 min pH = 6.8 C_0 = 10–40 mg L^{-1} (30% of organic solvent, 70% of water solution) 5 psi Ar, 1% H_2O_2	70%	Degradation is feasible mainly due to hydroxyl radicals reactions, degradation of PAHs increased in low pH, Number of benzene rings has a significant impact on the degradation rate.	[51]

1	2		4	5	6
PYR	US	f = 582, 862, 1142 kHz P = 133 W t = 120 min V = 500 ml C_0 = 10 μg L^{-1}	96% (at 582 kHz)	Acoustic power increase leads to the higher efficiency of the treatment and more number of cavitation bubbles	[44]
PYR	US	f = 20, 506 kHz P = 6.1 W cm^{-2} (20 kHz) P = 2.4 W cm^{-2} (506 kHz) t = 30 min V = 150 ml C_0 = 118 μg L^{-1}	86% (at 506 kHz) 63% (at 20 kHz)	At both frequencies, PAHs are mainly pyrolyzed within the bubble and less than hydroxyl radicals	[13]

f – frequency, P – acoustic power/power density, t – sonication time, V – volume of the treated sample, C_0 – initial concentration of treated pollutant.

CONCLUSIONS

Nowadays, the development of novel techniques in water and wastewater treatment is needed due to the increase of harmful substances present in the environment. As can be seen from the summarized literature data, ultrasonic irradiation can be very effective in organic micropollutants removal as opposed to classical methods. Most of the reviewed articles are focused on high-frequency ultrasound treatment which was reported as very effective due to the high number of cavitational events that consequently lead to increased production of oxidants and increased degradation of undesirable substances. It was reported that selected micropollutants are degraded dominantly at the bubble/liquid interface. Nevertheless, literature data showed that in some cases lower frequency of ultrasound waves could be more effective [44, 52, 54]. Moreover, the literature review showed also that the effectiveness of the sonication process can be increased due to the use of various types of catalysts such as sparging gas (e.g. Ar, O_2, or air), presence of glass bead, H_2O_2, Fe^0 addition, TiO_2, and NaCl. Most of the researchers suggested that increased power density, temperature, and sparging gas presence led to a higher degradation rate of selected micropollutants. However, the removal ratio of micropollutants was also affected by the pH value of the treated solution, usage of pulsed ultrasonication mode, volume of the treated sample, dosage of the oxidant, and time of the treatment. Although the high degradation rate of pollutants by using ultrasound, some research proved that toxicity of the treated samples can increase after treatment due to the occurrence of degradation by-products, thus future research on this technology should contain detailed ecotoxicological of the post-treated samples. Furthermore, to improve the efficiency and to decrease the energy consumption of the treatment, sonocatalysis process should be used and developed.

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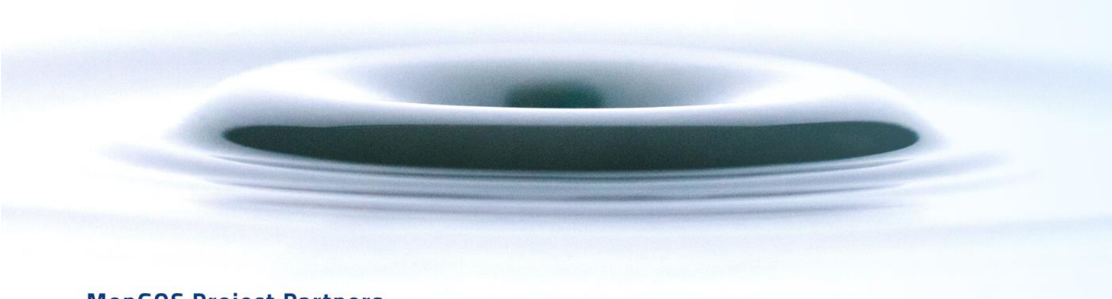

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