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Technical Annals

Journal of the Technical Chamber of Greece

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About

With particular joy, respect and commitment to the history of TEE (TCG), to the future of the scientific role of the Chamber and to the work of Greek Engineers as a whole, the Technical Chamber of Greece is proceeding with the publication of an international scientific journal. After several years without regular scientific publications, due to the special economic situation of the country, but having as a source of our history the TECHNICAL ANNALS, published by the TCG for decades, we undertake this role again to give another scientific podium to the Engineering community.

More specific, the Governing Committee of TCG, in accordance to Decisions No A14/Σ39/2021, A16/Σ7/2022 and A41/Σ16/2022, proceeded to publish of the Scientific Journal entitled «Technical Annals» by the Technical Chamber of Greece (TCG) concerned with Advances in Engineering, in English language. The content of the journal will be available electronically and via Open Access, through the e-Publishing service of the National Documentation Centre (EKT).

The Governing Committee of the TCG assigned the responsibility of the publication to the Editorial Board and the Scientific Board of the Journal.

We inform all Engineers IN Greece and in the World, the Academic and Research Community that we are proceeding with this publication in order to give the floor for communication, publicity and recognition, by the International Community, of the Research and Innovation that Engineers produce in practice, on construction sites,in urban space, in regional areas, in industry, in development, in environment, in energy, in the digital world, in universities, in research centers, in startups, in businesses, etc.

We aspire to attract your interest, find in you critical readers, feed your scientific work and publish the results of your research through the International Scientific Journal of TCG.

Looking forward to an important publication that we'd like to become everyone's business.

Topics

The scope of the journal will include all Fields of Engineering:

1. Civil Engineering
2. Architectural Engineering
3. Mechanical Engineering
4. Electrical & Computer Engineering
5. Rural & Surveying Engineering
6. Chemical Engineering
7. Mining & Metallurgical Engineering
8. Naval Architecture & Marine Engineering
9. Electronic Engineering
10. Engineering of Urban Planning & Regional Development
11. Environmental Engineering
12. Mineral Resources Engineering
13. Production & Management Engineering

Furthermore, it will be concerned with Interdisciplinary Thematic Areas, which are at the cutting edge of Research and Innovation, such as:

> Agricultural Engineering and Food Processing, Artificial Intelligence, Aerodynamics, Bioengineering, Circular Economy, Climate Change, Cultural Heritage, Education and Learning Processes, Energy, Environment, Economy, Geoinformatics, Human Modelling, Industrial Symbiosis, Management and Quality Control, Material Science and Engineering, Naval Coastal and Maritime Design Engineering and

Planning, Spatial Planning, Sustainable Development, Systems' and Processes Engineering, Technology, Transportation, Processes, among others, and the thematic areas will be dynamically adjusted and determined taking into account both the progress of Science and Engineering, as well as future trends and the trending concerns and needs of Society.

Information for Volume Editors and Authors

Moreover, conferences, in which TCG is either co-organizing or participating in their Organizing and Scientific Committee, will be able to submit a request to publish their Proceedings (in either Greek or English language) always through the "e-Publishing" mechanism, as long as the request has been submitted to TCG and has the approval of TCG's Governing Bodies, either six months before the conference date *(in cases where the proceedings are to be published prior to the conference initiation)*, or three months before the conference date *(in cases where the proceedings are to be issued after the Conference)*.

The Governing Committee of the TCG assigned the responsibility of the publication to the Editorial Board and the Scientific Board of the Journal; the list of members of each board is herein attached.

Antonia Moropoulou · Haris Doukas · Maria Loizidou ·
Christos Akratos · Konstantinos Moustakas

ISSUE
Sustainable Waste Management

Editors

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The Technical Chamber of Greece (TCG) decided to republish in English a Scientific International Open Access e-Journal. The "Technical Annals" - a journal which was counting decades of life following T.C.G. activities – will be edited by the T.C.G. through e-Publishing Platform at the EKT (National Documentation Centre) and will concern all the advancements in Engineering, referring to the disciplines:

- Civil Engineering
- Architect Engineering
- Mechanical Engineering
- Electrical & Computer Engineering
- Rural & Surveying Engineering
- Chemical Engineering
- Mining & Metallurgical Engineering
- Naval Architecture & Marine Engineering
- Electronic Engineering
- Engineering of Urban Planning & Regional Development
- Environmental Engineering
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- Production & Management Engineering

Referring also to interdisciplinary Thematic Areas at the forefront of Research and Innovation such as: Agricultural Engineering and Food Processing, Artificial Intelligence, Aerodynamics, Bioengineering, Circular Economy, Climate Change, Cultural Heritage, Education and Learning Processes, Energy, Environment, Economy, Geoinformatics, Human Modelling, Industrial Symbiosis, Management and Quality Control, Material Science and Engineering, Naval Coastal and Maritime Design Engineering and Planning, Spatial Planning, Sustainable Development, Systems' and Processes Engineering, Technology, Transportation, Processes, et al as dynamically will be defined by the progress of science and engineering, the future trends and the social needs.

Through the e-journal, TCG is aiming to publish at least three volumes per year, to connect Greek Engineers with the International Community of Engineering Science and Innovation, for the benefit of the public interest and the promotion of science through research, innovation, and development, in compliance with its constitutional targets.

Technical Annals is a peer-reviewed journal.

Preface

The conference series of Sustainable Solid Waste Management was initiated with the first conference event in Athens in June 2012 (ATHENS 2012).

After this conference event (https://athens2012.uest.gr), the following conference events took place:

- ATHENS 2014 2nd International Conference on Sustainable Solid Waste Management (https://athens2014.biowaste.gr)
- TINOS 2015 3rd International Conference on Sustainable Solid Waste Management (https://tinos2015.uest.gr)
- CYPRUS 2016 4th International Conference on Sustainable Solid Waste Management (https://cyprus2016.uest.gr)
- ATHENS 2017 5th International Conference on Sustainable Solid Waste Management (https://athens2017.uest.gr)
- NAXOS 2018 6th International Conference on Sustainable Solid Waste Management (https://naxos2018.uest.gr)
- HERAKLION 2019 7th International Conference on Sustainable Solid Waste Management (https://heraklion2019.uest.gr)
- THESSALONIKI 2021 8th International Conference on Sustainable Solid Waste Management (https://thessaloniki2021.uest.gr)
- CORFU 2022 9th International Conference on Sustainable Solid Waste Management (https://corfu2022.uest.gr)

The first conference events took place because there was an obligation to host a conference event at the end of a LIFE project, where the project results had to be presented and disseminated to a large audience. More specifically, the 1st conference took place in the framework of the LIFE DRYWASTE project, the 2nd conference in the framework of the LIFE ATHENS-BIOWASTE project, the 3rd conference in the framework of the LIFE ISWM-TINOS project the 4th conference in the framework of the LIFE INTER-WASTE project, etc. In the first events even no registration fee was applied, but that become inevitable with the increasing number of participants.

It is true that a lot of effort and hard work was necessary in order to make the conference events larger year by year. The conference topics included all aspects related to waste management including waste prevention and separation at source, waste valorisation, advances in biological treatment methods (anaerobic digestion, as well as composting), waste-to-energy, biotechnology and biorefineries, management of specific waste streams, such as construction and demolition waste, waste from electrical and electronic equipment, batteries and accumulators, etc, circular economy, symbiosis networks, recycling and resource recovery, food waste management, sludge management and recovery of materials from wastewater and sludge, tools in the field of waste management, waste management experiences in islands and isolated areas, etc.

Furthermore, it is our intention to put emphasis on the scientific and academic character of the conference, but at the same time keep the inter-disciplinary character of the conference series and also include the presence of the private and public sector, local authorities, businesses, financial institutions, policy makers and society and present the latest developments and achievements in the field of solid waste management with special emphasis on municipal solid waste.

In addition, starting from the NAXOS 2018 Conference, we also organize a two-day summer school for MSc Students and PhD Candidates from all over the world and members of the working teams of local authorities, but the summer school can also target at larger audience to strengthen their qualification in the field of solid waste management and circular economy and bioeconomy. This summer school takes place prior to the conference event every year and preferably not at the same venue as the conference itself.

We also decided to host the conference at a different area of Greece (or in the neighbouring Cyprus) every year so that the participants can get familiar with the beauties of our country, especially in the Greek islands and also the Greek traditions, cuisine and summer, since all conference events take place within June.

Our upmost attempt is to build a conference family, not just a common conference audience and be able to promote additional networking opportunities with the development of new innovative project ideas. The role of social events is also crucial for developing stronger relationships and bonds between the conference participants. That is also the reason that we encourage physical presence and virtual participation is just an opportunity when the travel is not possible.

As in the cases of the previous international conferences, the **CHANIA 2023 10th International Conference on Sustainable Solid Waste Management** that took place from 21st to 24th June 2023 aimed to make a further step forward in the field of solid waste management through the promotion of innovative technologies and effective practices. The conference had about 1,000 participants including both virtual participants and those traveling to the beautiful island of Crete. It was the 2nd time that a conference of this series was hosted in Crete, after the successful conference in Heraklion in June 2019, the last conference before COVID-19.

Efforts were made to achieve high quality services for the conference participants. It is also important to mention the introduction for the 5th time of the summer school prior to the conference. More than 50 participants attended the summer school in June 2023, and our aim is also to continue and keep it in all our future conferences giving emphasis to different research fields every year.

Waste prevention, source separation, recycling and production of secondary materials, biological Treatment (aerobic & anaerobic), the treatment at central facilities constituted priority subjects of the conference agenda. Attention was drawn to bioprocesses, biorefineries in waste management to close the loops, circular economy and bioeconomy and of course WASTEtoENERGY with the contribution of the Waste-to-Energy Research and Technology Council, that was a co-organiser of this conference, with the active involvement of Prof. Nickolas Themelis, the father of the Council.

Emphasis was placed on circular economy in all key action areas (production, consumption, waste management, secondary raw materials, innovation, investment & monitoring) and all priority sectors (food waste, plastics, biomass and bio-based-products, construction & demolition waste, critical raw materials, textiles, etc.).

The Conference provided an opportunity to bring together scientists & professionals from government departments, industries, Municipalities, private institutions, research & education institutions, being a forum for the exchange of the most recent ideas, techniques & experiences in a broad area of waste management.

A special Session focused on solid waste management and the role of Local Authorities & Municipalities for taking advantage of both recyclable materials and biowaste and minimize residues for landfilling. The Conference agenda was rich and dense, offering a considerable variety of topics presented through more than 550 presentations within the twenty-six different oral sessions and an extensive poster session with more than 200 posters.

In addition, it was our intention to increase the conference benefits by including parallel sessions and events of ongoing projects within the conference agenda. The agenda included this year the final event of the H2020 Project “WaysTUP!: Value chains for disruptive transformation of urban biowaste into biobased products in the city context” Friday morning on 23rd June, while the Launching event of the LIFE CO2toCH4 project with title “Demonstration of a mobile unit for hybrid energy storage based on CO2 capture and renewable energy sources" was scheduled on Thursday 22nd June. Lastly, a LIFE networking session was included in the conference agenda on Thursday organized by the new capacity building project Greek Life Task Force plus (LIFE21-CAP-EL-GRLTFplus) of the Green Fund in collaboration with ELMEN-EEIG, the external LIFE project monitoring team.

We would like to thank the co-organisers, the Waste-to-Energy Research & Technology Council, the Region of Crete, the Municipality of Chania, the DEDISA that is responsible for municipal waste management in Chania and the sponsors for supporting the CHANIA 2023 conference. At the end we had the feeling that the participants found the CHANIA 2023 Conference interesting, useful and up to their expectations. After the hybrid conference in Corfu in June 2022, we were happy that more speakers joined with physical presence.

The fourth volume of the Technical Annals – International Scientific Journal in advances in Engineering by the Technical Camber of Greece (T.C.G.) included twelve (12) papers from the CHANIA 2023 Conference.

The 1st paper of this issue deals with the design of an innovative system for the detoxification of pharmaceutical wastewater, while the 2nd paper presents a work on nanofiltration and selective crystallisation for the recovery of bio-based fertilizing products from seawater desalination brine.

Next, the following paper (3rd) refers to food industry biowaste as substrate for biosolvents production focusing on lactic acid and ethyl lactate, while the fourth one is a review on metal-organic frameworks (MOFs) as novel adsorbents for alternative fuel gas storage.

Advances in corrosion mitigation for Waste-to-Energy systems is the subject of the fifth paper with emphasis on evaluating coatings and application techniques. The next paper (6th paper) caters for the sustainability analysis for scandium recovery from secondary sources. The exploration of the feasibility of solar and wind energy utilization in Poland is the topic of the 7th paper involving a hybrid energy mapping approach. Furthermore, the 8th paper is a review of contemporary sewage sludge treatment and management methods in European countries with an emphasis on Greece.

Next, the 9th paper of the Issue deals with the implementation of an sludge model to simulate Thriasio wastewater treatment plant operation in West Attica, Greece, while the comparison of three (3) analytical techniques for theextraction and determination of five possible contaminants in food contact recycled materials is the title of the 10th paper.

The last two papers of the Issue refer to the sustainable management of end-of-life creosotetreated wood poles sawdust into red ceramics for environmental and health protection (11th paper) and lessons learnt and lessons from EU Best Practices in relation to the Greek Legal Framework on Waste Management within the Circular Economy Context (12th paper) respectively.

This edition would not have been possible without the commitment and support from the editors of this issue (Antonia Moropoulou, Haris Doukas, Maria Loizidou, Christos Akratos, Konstantinos Moustakas); as well as the valuable assistance of the editing team at Technical Annals managing by Mrs Lilly Athini (Fotini Kyritsi, Eleni Bairaktari, Evridiki Karathanasi, PanagiotisVrelos, Maria Sinigalia, Manolis Erotokritos, Isabella Tsavari, Dimitris Psarris, George Trachanas), to whom we are most grateful

November 2023 Maria Loizidou, Member of the Scientific Council of Technical Annals

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Circular Economy

Comparison of 3 analytical techniques for the extraction and determination of 5 possible contaminants in food contact recycled materials

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Abstract. Climate change and ecological crises have become pressing matters in Europe and the world. In an attempt to put a halt to the massive production of packaging waste, the European Standardization Organisation (CENELEC) has developed harmonized standards to promote reuse, recycling, and other forms of recovering packaging waste. However, when implemented in the food and beverage industry, possible contaminants present in these recycled packaging materials could compromise public health. The present study is part of an ongoing research aiming to develop fast, simple, and reliable analytical methods to identify such contaminants in recycled materials intended to come in contact with foodstuffs. To this end, three extraction methods were developed and assessed regarding their effectiveness and accuracy in isolating a mixture of five possible contaminants [Benzophenone (BP), 2,6-Diisopropylnaphthalene (2,6-DiPN), 2,7-Diisopropylnaphthalene (2,7-DiPN), o-Terphenyl (o-TPH), and m-Terphenyl (m-TPH)] in samples of recycled paperboard materials: the Soxtec Extraction (SE), the Ultrasound-Assisted Extraction (UAE), and the Head Space Solid Phase Micro Extraction (HS-SPME). The average recovery rates (ARRs) of the contaminants were satisfactory; the substances were recovered at rates between 61-100% using the SE method, at 100-120% using the UAE method, and at 98-107% using the HS-SPME method. All methods performed well in terms of precision; all produced an overall repeatability relative standard deviation (RSD) of below 2.5% and all HorRat values were well within the acceptable limits, ranging from 0.04 to about 0.1. However, taking into consideration the ANOVA analysis, the method that stood out and altogether demonstrated the best analytical results was the HS-SPME.

Keywords: contaminants; recycled paperboard; extraction techniques; GC/MS

1 Introduction

In recent years, EU waste legislation has actuated considerable improvements in waste management. Full implementation of that legislation, however, is of the highest importance if the EU is to reap the environmental and economic benefits of the circular economy; the transition to such an economy calls for extensive modifications from product design, production, and supply, to novel business and market models. In addition, the rise of environmental awareness has inevitably prompted industries to increase their demand for and development of alternative packaging materials, including fiber-based packaging, aiming to encourage consumers to make more eco-friendly choices. In the circular economy, “waste” from one process becomes the input for another and so new ways of turning waste into resources and prolonging the life of products are being implemented throughout the supply chain. Recovered fibers constitute a significant source of raw materials for the paper industry given the fact that paper packaging is largely manufactured with the use of recycled paper. In 2020, around 74% of all paper and board consumed in Europe was recycled. However, due to the Covid-19 crisis, among other factors, the consumption and recycling of paper and board seem to have recently taken a heavy drop. More specifically, in comparison to the base year of the Declaration (2015), the amount of paper and board collected and recycled decreased by 3.1 million tonnes [1].

As highlighted in several studies, recycling flaunts both environmental and economic assets in terms of technological and system-level perspectives [2–7]. However, when it comes to the production of packaging designated for food contact, the use of recovered fibers must be carefully assessed. Recycled paper and board have been used primarily as outer packaging of food products as they are infamous sources of non-volatile compounds and external contaminants. The basic source of these contaminants is usually the “raw” recovered material, which, during the recycling process, is being treated with various chemicals, many of which are not intended to come into contact with foodstuff and can exceed acceptable levels. Such well-known migrants include mineral oils, photoinitiators, phthalates, and per- and polyfluorinated substances [8–12]. Under appropriate conditions, these contaminants could migrate from and through the packaging into the food [13]. Even though the recycling of paper and board is essential for a greener future, the safe use of paper and board for food contact materials (FCM) remains a challenge; the migration of substances should be restricted to quantities harmless to human health [14]. To this end, in Europe, as well as the US, the same level of safety for chemicals migrating into foods is considered a requisite for all recycled and virgin materials alike [15–18]. In an attempt to minimize the risks, many food companies either discontinued using recycled paper/paperboard and retracted to virgin fibers or utilized additional functional barriers in an attempt to curb the migration from recycled materials into foodstuff [8, 19].

Numerous studies have been carried out on the migration of substances from packaging materials to foods. By and large, the results of these studies demonstrate that the interaction between the packaging and food products is influenced by a lot of factors, such as the structure of the packaging samples, the chemical nature of the migrants, and the time and temperature conditions of the migration tests [12, 14, 18, 20–36]. Consequently, a cautious selection of packaging materials is entailed in order to avoid any adverse effects on the quality, safety, and shelf stability of foodstuffs. To this end, the Committee of Ministers of the Council of Europe adopted in October 2020 new, updated guidelines known as “Resolution CM/Res (2020) 9 on the safety and quality of materials and articles for contact with food". These guidelines, in conjunction with the supplementary Technical Guide, supersede the previously in force "Policy statement concerning paper and board materials and articles intended to come into contact with foodstuffs" (Version 4 dated 12.02.2009) [37–39].

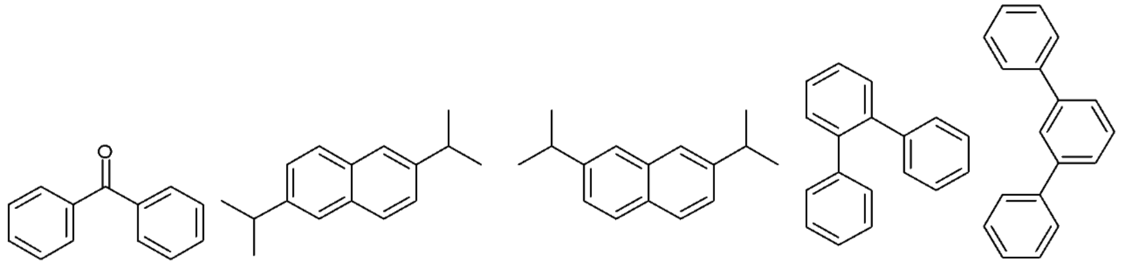
To extensively promote manufacturing and policy decisions favoring harmless alternatives over hazardous chemicals in food packaging, all concerning substances, as well as the amounts thereof, should be identified. So far, studies on determining contaminants in food packaging have focused mainly on monomers and a few additives used in high concentrations, such as phthalate plasticizers [34, 36, 40]. However, even low amounts of these hazardous substances in food contact materials (FCMs) could cause health damage, even though the material as such complies with all legal requirements. Prior to being identified, the substances in question should first be efficiently extracted from the packaging material. The most common extraction and clean-up techniques that have been tested on paper and board FCMs; include HS-SPME [41–46], Soxhlet extraction [43, 47, 48], reflux distillation [49–52], and UAE [53]. The choice of extraction method is of utmost significance in order to achieve accurate and reliable results.

The current study focuses on evaluating the extraction efficiency of three commonly used techniques to determine five potential contaminants present as residues in commercially recycled paperboards intended for food packaging. The selection of the contaminants was based on their prospective presence and frequency in materials containing recycled fibers. The main objective was to identify the most appropriate technique meeting the criteria of being rapid, straightforward, and sensitive for extracting and determining these compounds at low concentrations.

2 Experimental procedures

2.1 Chemicals

All chemicals used were of high analytical grade and purchased from Sigma-Aldrich, Fluka, Supelco, and Merck. Standard solutions were prepared of the five following possible contaminants: Benzophenone (BP), 2,6-Diisopropylnaphthalene (2,6-DiPN), 2,7-Diisopropylnaphthalene (2,7-DiPN), o-Terphenyl (o-TPH), and m-Terphenyl (m-TPH) (Scheme 1). A mixture of these substances was used as the standard solution for the contamination of the paperboards.



1 Benzophenone **BP**

2 2,6-Diisopropylnaphthalene **2,6DiPN**

3 2,7-Diisopropylnaphthalene **2,7DiPN**

4 *o*-Terphenyl ***o*-TPH**

5 *m*-Terphenyl ***m*-TPH**

The initial concentrations of the selected substances were 1 g L-1, from which two final standard solutions of 10 mg L-1 and 1 mg L-1 of all substances were prepared.

2.2 Paper samples

The paper samples used in this study were the same as in previous work [46, 54]. Three of them were made of 100% recycled pulp matter (R1, R2, R3) and one was of 0% recycled material (V). The absorption capacity of each type of paperboard is expected to vary therefore known volumes of the standard solution were used during contamination as a correction factor.

More specifically, the materials used were:

R1: “Triplex R Kraft”, Basis Weight: 440 g/m^2, thickness: 541 μm.

R2: “Duplex R”, Basis Weight: 400 g/m^2, thickness: 485 μm.

R3: “Triplex BR”, Basis Weight: 440 g/m^2, thickness: 541 μm.

V: “Bl. Kraft + CTMP”, Basis Weight: 273 g/m^2, thickness: 486 μm.

2.3 Analytical Methods

Three commonly used extraction methods were optimized and evaluated in this study: the Soxtec extraction (SE), the ultrasound-assisted extraction (UAE), and the headspace solid phase microextraction (HS-SPME). A gas chromatography-mass spectrometry (GC/MS) analysis superseded each extraction to determine the contaminants.

For the identification and quantification of the selected substances, as well as the assessment of their recovery rates, several contamination tests were conducted on the paperboard samples. The ones consisting of recycled material were thoroughly cleansed beforehand with dichloromethane in ultrasonic baths. All four paperboard samples were then thoroughly saturated with a range of solutions of the standard substances (20-20.000 μg/l) and standard reference curves were plotted for each contaminant.

2.4 Soxtec Extraction (SE)

The contaminants were extracted from the paperboard samples with the use of a semi-automatic solvent extractor (SER 148, VELP Scientifica Srl, Italy). Prior to the analysis, all parameters were optimized through testing according to previous work [54]. The paperboard samples, each weighing 1.0 g, were consecutively placed in extraction thimbles and treated with 50 ml dichloromethane (DCM) at 110ºC for 2h. The thimbles were then set in rinse position for an extra 1.5h and, after the samples were dried with the use of synthetic air, they were redissolved in 1.0 ml of acetonitrile. An aliquot of 1.0 μl of the final solution was transferred into the GC/MS injection port. All analyses were performed in triplicate.

2.5 Ultrasound-Assisted Extraction (UAE)

An Elmasonic S10 H ultrasonic bath (Elma GmbH, Singen, Germany) was utilized for this analysis. The parameters of the liquid-phase extraction were the same as in previous work [53].

2.6 Head Space – Solid Phase Micro Extraction (HS-SPME)

For the identification and quantification of the substances under study, paperboard samples were steeped in 1 ml of the 1 mg L-1 standard solution. Approximately 100 mg of the saturated paperboard samples were weighed, cut into pieces (5 x 5 mm), and placed in glass vials of 10 ml volume.

The extraction of volatile compounds from the headspace was performed using a 65 μm Polydimethylsiloxane / Divinylbenzene (PDMS/DVB) fiber (Supelco, USA) [41]. The vials were placed in an oil bath at 135°C (higher bath temperatures produced adverse recovery results) for 15 minutes until equilibrium and after that, the PDMS/DVB fiber was inserted and exposed to the headspace for 30 minutes. The fiber was then transferred to the GC instrument for the analysis of the substances. All experimental tests were carried out in triplicate.

Additionally, all samples were saturated with aliquots ranging from 30 to 750 μg kg-1 of the standard solutions of the contaminants and subjected to HS-SPME analysis under the same conditions as described above in order to plot the necessary reference curves.

2.7 GC/MS

All chromatographic analyses were conducted on a HP 6890 GC system coupled to a HP 5973MS detector. Additional components consisted of a nonpolar HP-5 (5%-phenyl)-methylpolysiloxane column (60 m × 0.25 mm i.d., with 1 μm film thickness) (J&W Scientific, Folsom, USA) and high purity He (carrier gas) released at a flow rate of 0.8 mL/min. The temperature programming used was the same as in previous work [54]. Finally, the identification of the compounds was performed using a mass spectral library (Wiley 7, NIST 2005) and through comparing the linear retention indices (Kovats indices) to reference standards and/or published data [55, 56].

3 Statistics

The software used for all statistical analyses was the SAS 9.4 (SAS Institute Inc., Cary, NC, USA).

4 Results and discussion

4.1 Recoveries

According to the updated SANTE Directive [57] the recovery rates of the substances should span from 70 to 120% in all contaminated samples and the relative standard deviations should not surpass 20%. The limits of detection (LODs) for the standard solutions of the 5 contaminants were determined at a signal-to-noise ratio of 3. The LODs and the limits of quantification (LOQs) for the concentrations tested ranged from 0.005 to 0.5 mg kg-1, and from 0.1 to 1 mg kg-1, respectively.

Soxtec Extraction (SE)

The SE method recovery rates for all concentrations of the 5 substances ranged between ~53% and ~100%, whilst the average recovery rates (ARRs) ranged from ~61% and ~100% (Table 1). In addition, the standard deviation values (SD) were all well below 20% in all cases. Even though the RRs of o-TPH were found to be a bit lower than the acceptable lower limits (<70%), all in all the SE can be considered a reliable method for the analysis of these contaminants that may be present in recycled paperboard.

Table 1. Paper recovery rates (RRs) and standard deviation (SD) of the 5 contaminants at three concentrations (125 μg kg^{-1}, 300 μg kg$^{-1,}$ and 500 μg kg^{-1}) using the SE method.

Contaminant	**Recovery**							
	125μg kg^{-1}		300μg kg^{-1}		500μg kg^{-1}		ARR* (%)	SD (%)
	RR (%)	SD (%)	RR (%)	SD (%)	RR (%)	SD (%)		
BP	73.24%	1.46%	62.68%	0.89%	73.17%	0.91%	69.70%	6.07%
2,6-DiPN	86.52%	1.58%	83.50%	1.35%	100.29%	1.14%	90.10%	8.95%
2,7-DiPN	84.16%	1.53%	78.20%	1.38%	99.10%	1.25%	87.15%	10.76%
o-TPH	53.36%	1.38%	60.59%	1.42%	68.55%	1.39%	60.83%	7.60%
m-TPH	69.88%	0.79%	75.90%	0.72%	86.31%	0.77%	77.36%	8.31%

*ARR: Average Recovery Rate

Ultrasound – Assisted Extraction (UAE)

The UAE method recovery rates for all concentrations of the 5 substances ranged between ~94% and ~126%, while the average recovery rates (ARRs) ranged from ~100% and ~120% (Table 2). In addition, the standard deviation values (SD) were all well below 20% in all cases. Therefore, the UAE constitutes a reliable method for the analysis of these contaminants that may be present in recycled paperboard.

Table 2. Paper recovery rates (RRs) and standard deviation (SD) of the 5 contaminants at three concentration levels (125 μg kg^{-1}, 300 μg kg$^{-1,}$ and 500 μg kg^{-1}) using the UAE method.

Contaminant	**Recovery**							
	125μg kg^{-1}		300μg kg^{-1}		500μg kg^{-1}		ARR* (%)	SD (%)
	RR (%)	SD (%)	RR (%)	SD (%)	RR (%)	SD (%)		
BP	122.30%	1.72%	109.50%	1.32%	94.56%	1.29%	108.79%	13.88%
2,6-DiPN	100.40%	1.56%	99.54%	1.35%	99.02%	1.21%	99.65%	0.70%
2,7-DiPN	102.20%	1.60%	101.55%	1.58%	100.61%	1.15%	101.45%	0.80%
o-TPH	120.60%	1.82%	116.17%	1.79%	113.75%	1.47%	116.84%	3.48%
m-TPH	125.50%	2.20%	118.09%	1.54%	116.33%	1.11%	119.97%	4.87%

*ARR: Average Recovery Rate

Head Space – Solid Phase Extraction (HS-SPME)

The HS-SPME method recovery rates for all concentrations of the 5 substances ranged between ~96% and ~110% (Table 3). Even though at concentrations 125 and 300 μg kg-1 the contaminant o-TPH was not recovered, it was completely recovered at concentration 500 μg kg-1. According to the results, the HS-SPME method can be reliably used for the recovery of all 5 contaminants.

Table 3. Paper recovery rates (RRs) and standard deviation (SD) of the 5 contaminants at three concentration levels (125 µg kg^{-1}, 300 µg kg$^{-1,}$ and 500 µg kg^{-1}) using the HS-SPME extraction method.

Contaminant	Recovery							
	125µg kg^{-1} RR (%)	SD (%)	300µg kg^{-1} RR (%)	SD (%)	500µ kg^{-1} RR (%)	SD (%)	ARR* (%)	SD (%)
BP	98.26%	0.98%	99.35%	0.95%	96.54%	2.04%	98.05%	0.62%
2,6-DiPN	105.38%	1.25%	106.44%	1.26%	105.83%	2.39%	105.88%	0.65%
2,7-DiPN	100.73%	0.98%	100.86%	1.09%	97.26%	2.60%	99.62%	0.90%
o-TPH	n.d.	n.d.	n.d.	n.d.	104.23%	2.86%	104.23%	2.86%
m-TPH	106.13%	1.07%	109.53%	1.36%	106.40%	2.87%	107.35%	0.97%

*ARR: Average Recovery Rate

4.2 Accuracy of methods

The accuracy of the methods was expressed as approximate trueness since Certified Reference Materials (CRMs) were not used in this study. The concentrations were greater than 10 µg kg-1, so the acceptable range was from -20% to + 10%. The trueness of the methods was evaluated at 125 µg kg-1. Altogether, twenty trials were performed. The results of the tests are given in Table 4. In bold are the acceptable values.

Table 4. Approximate values of the trials at 125 µg kg^{-1} for each extraction technique.

Contaminant	UAE	SE	HS-SPME
	125µg kg^{-1}	125µg kg^{-1}	125µg kg^{-1}
BP	153	92	**122.83**
2,6-DiPN	**126**	**108**	**131.72**
2,7-DiPN	**128**	**105**	**125.91**
o-TPH	151	67	-
m-TPH	157	87	**132.66**

According to the results, of the three methods, the HS-SMPE has the highest accuracy at 125 µg kg-1 as 4 out of 5 contaminants are within limits, while in the UAE and SE methods, only two out of 5 are within limits.

4.3 Precision of methods

The methods' precision was evaluated using the Horwitz Ratio (HorRat) equation [58]. This equation is a precision assessment criterion that finds wide applicability in certifications and international standards such as ISO 17025. For a method to be considered precise, it should meet the following criteria:

- HorRat ≤ 0.5: excellent precision
- HorRat ≥ 2: unacceptable precision

A method can be accepted for values between these limits with appropriate substantiation.

HorRat values of each method were calculated by assessing the relative standard deviation (RSD) at a concentration of 125 µg kg-1. The maximum theoretically calculated RSD at said concentration was estimated to be RSD= 21,88. The experimental %RSD and HorRat values are given in Table 5.

Table 5. Experimental %RSD and HorRat values for the UAE, SE, and HS-SPME methods at a concentration of 125μg kg^{-1}.

	RSD			**HorRat**		
	UAE	**SE**	**HS-SPME**	**UAE**	**SE**	**HS-SPME**
BP	1.51	2.05	1.08	0.07	0.09	0.05
2,6-DiPN	1.50	1.92	1.08	0.07	0.09	0.05
2,7-DiPN	1.68	1.76	0.97	0.08	0.08	0.04
o-TPH	1.61	2.43	-	0.07	0.11	-
m-TPH	1.83	1.19	1.03	0.08	0.05	0.05

The RSD and HorRat values indicate that the HS-SPME method produced more precise results than the other two methods tested.

4.4 ANOVA analysis

The analysis of variance (ANOVA) was performed on a total of 20 spiked samples to assess the aberration between the average values of the 4 out of 5 studied compounds at a concentration of 125 μg kg-1.

For the BP compound, the HS-SPME method almost coincided with the theoretical approach; 99% of HS-SPME values appeared to be better distributed than the corresponding distribution of the range of 25% of the theoretical values. The UAE and Soxtec methods showed statistically significant differences but had better distribution than the theoretical.

For the 2,6-DiPN compound, the UAE seems to coincide with the theoretical approach; 99% of the UAE values appeared to be better distributed than the corresponding distribution of the range of 25% of its prices theoretical. HS-SPME has a small price range, which is almost within the range of 25% of the theoretical values. The means are significantly different prices and intermediaries. Although SE shows statistically significant differences from the theoretical, it seems that the price distribution is better. The range of 99% of SE is within the 99% distribution range of theoretical values.

For the 2,7-DiPN compound, the UAE and HS-SPME seem to coincide statistically with the theoretical approach; 99% of the values of the two methods seem to be better distributed than the corresponding distribution of the range of 25% of the theoretical values. However, the SE analysis presented statistically significant differences.

For the m-TPH compound, none of the methods is grouped by the theoretical approach. Only the HS-SPME method seemed to demonstrate the smallest statistical differences. The value distribution range is very small and is almost within the distribution range of 25% of the theoretical prices, which is also the case for the SE method.

The statistical approaches confirmed that the most reliable results were obtained when using the HS-SMPE method.

5 Conclusions

All methods tested performed well in terms of precision; all showed an overall repeatability relative standard deviation (RSD) of below 2.5%. Additionally, the HorRat values of all methods were within the limits for performance acceptability, ranging from 0.04 to about 0.1. However, taking into consideration the ANOVA analysis, the method that stood out and altogether demonstrated the best analytical results was the HS-SPME.

The proposed method could be used for the determination of these compounds as undesirable impurities in paperboards classified as food-grade materials. The HS-SMPE analysis, coupled with the GC/MS method, is not only simple and rapid but also sensitive. It is therefore suitable for the routine analysis of the most common organic compounds found in recycled paperboard. The integration of such a simple and reliable analytical technique in the line of food packaging production could be an important asset to both the producers and the promotion of circular economy in general. Not only could the proposed HS-SMPE analysis be used to identify and prevent potential risks prior to the formation of the final packaging products, it would also ensure the distribution of safe food packaging without putting financial strain on the producers. Finally, acknowledging the risk-free products, consumers would feel more open to the use of recycled materials in food packaging and together with the producers they could fully embrace the benefits of circular economy.

5.1 Correction factors

After determining that HS-SPME was the most reliable for this specific procedure, correction factors were computed so as to attain optimal accuracy of the results. The said factors were calculated for each individual contaminant by estimating the mean value of 20 spiked samples at a concentration of 125 μg kg-1 and then dividing the resulting value by the value of the concentration (Table 6).

Table 6. Correction factors estimated at a concentration of 125 μg kg^{-1}.

Contaminant	Correction factor
BP	1.02
2,6-DiPN	0.95
2,7-DiPN	0.99
o-TPH	-
m-TPH	0.94

In addition, three commercial food-grade paperboard samples were tested (R1, R2, R3) in order to verify the applicability of the method for the simultaneous determination of all 5 contaminants. The corrected values of the contaminants were evaluated by multiplying their concentrations by the corrected factors estimated above (Table 7). As seen in Table 7, the deviation of the corrected value of the contaminants' concentration compared to the one obtained using the proposed methods is low, which indicates the high accuracy of the methods. However, by implementing the said correction factors to all contaminants the overall accuracy of the methods, as well as the reliability of the results are increased.

Table 7. Concentrations found in three commercial food-grade paperboard samples and their corrected values.

Contaminant	**R1**			**R2**			**R3**		
	Found (μg kg^{-1})	**SD**	**Corrected (μg kg^{-1})**	**Found (μg kg^{-1})**	**SD**	**Corrected (μg kg^{-1})**	**Found (μg kg^{-1})**	**SD**	**Corrected (μg kg^{-1})**
BP	23	1	24	48	1	49	21	1	21
2,6-DiPN	250	1	238	420	17	399	174	3	165
2,7-DiPN	141	2	140	202	3	200	93	3	92
o-TPH	11	2		33	1		11	2	
m-TPH	18	2	17	13	1	12	12	2	12

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Research involving human participants and/or animals This article does not contain any studies with human or animal subjects.

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Advances in Corrosion Mitigation for Waste-to-Energy Systems: Evaluating Coatings and Application Techniques

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Abstract. Waste-to-Energy (WTE) systems, utilizing post-recycled municipal solid waste (MSW) and other biomass materials, have been proven as alternatives to landfilling for sustainable waste management. These processes have offered benefits such as reduced landfill space, decreased methane emissions, and minimized waste volume. However, operational challenges, specifically high-temperature corrosion (HTC) of superheater tubes, have hindered their efficiency due to the presence of chlorine, alkaline salts, and sulfates. To address this issue, a range of coating techniques have been developed, with thermal spray techniques, particularly high velocity oxy-fuel (HVOF) spray, proving to be the most effective for protecting superheater tubes. A comparative analysis of experimental data from multiple studies has indicated that coatings with Alloy 625, Alloy C-276, Colmonoy 88, FeCr, IN625, NiCr, NiCrTi, and A625 offer high corrosion resistance at relatively low material costs, with corrosion rates below 1 mm/year. High chromium, nickel, and molybdenum content coatings have performed exceptionally well under high-temperature and high-chlorine conditions. Notably, T92 and P91, due to their low cost and high corrosion resistance, emerged as strong candidates for superheater tubes operating at 550°C. While A625 has demonstrated excellent corrosion resistance, its high cost has limited its practicality. Ultimately, the selection of suitable coatings has depended on the specific WTE plant design and operating experience. The additional cost of applying these coatings has been a minor fraction of the overall financial gains, as it extends the superheater tubes' lifetime and reduces plant downtime for tube repair or replacement.

Keywords: High-temperature corrosion (HTC), Protective coatings, Superheater tubes, Thermal spray techniques, Waste-to-Energy (WTE)

1 Introduction

Globally, approximately 2.01 billion tons of municipal solid waste (MSW) are generated annually, with a growing interest in utilizing waste-to-energy (WTE) technologies for post-recycling MSW management [1]. In addition to MSW, biomass combustion for energy production is gaining traction as a sustainable and renewable energy source. For instance, bioenergy with carbon capture and storage (BECCS) is a technology supported by combustion processes, offering a promising approach to achieve negative carbon emissions [2, 3]. However, the combustion of MSW and biomass presents different challenges due to their distinct compositions. MSW, which contains natural organic compounds and chlorinated plastics (mostly polyvinylchloride, PVC), results in high chlorine concentrations (0.47-0.72 wt%) in the gas passing through the boiler [4,5]. In contrast, biomass materials generally have varying chlorine content depending on their specific composition, with some feedstocks exhibiting lower concentrations than MSW [4]. Regardless of the feedstock, high temperatures inside boilers, along with the presence of alkaline metals (Na, K, etc.), heavy metals (Pb, Zn, etc.), and sulfates during combustion, can lead to severe high-temperature corrosion (HTC) issues. The problem is particularly critical for superheater tubes (SHT), which are affected by ash deposits that melt at 300-550°C [5, 6].

Superheater tube corrosion in combustion systems is a result of four simultaneous mechanisms. The first mechanism involves corrosion driven by gaseous phase chlorine, such as HCl and Cl2. The second mechanism is attributed to the condensation of alkali and heavy metal chlorides and/or sulfates on the tube surfaces. The third mechanism comprises corrosion induced by deposits and the sulfidation of condensed chlorides. Finally, the fourth mechanism entails the dissolution of protective oxide layers and tube metal caused by molten salt eutectics. Superheater tube corrosion can lead to material wastage, tube leakages, reduced tube lifetimes, and unplanned boiler shutdowns in waste-to-energy and biomass combustion plants. The corrosion rate of these tubes can be as high as several millimeters per year [4-7].

In many WTE plants, steam conditions are maintained at 400-450°C and 2.9-5.8 MPa to ensure stable operation and minimize corrosion of superheater tubes [5, 7]. Reducing steam temperature can enhance the stabilization of protective oxide layers on superheater tubes. However, the demand for higher efficiency in power and heat generation necessitates increased steam temperatures. For instance, raising the temperature from 400°C to 500°C can result in a 20% increase in power generation [7,8]. Nevertheless, elevating the steam temperature to such levels requires flue gas surrounding the superheater tubes to reach temperatures above 650°C, which significantly exacerbates corrosion on the tubes [4, 8].

Frequent replacement of superheater tubes has become a common practice for WTE plants operating at higher steam temperatures, which improves the thermal efficiency of the plant but also increases operational costs [4, 5,7]. Consequently, finding effective methods to prevent HTC and extend the lifetime of superheater tubes is a pressing issue [10].

To mitigate HTC problems various approaches have been adopted [7-10]. Early methods included adding refractory coatings (e.g., SiC) and metal shields, reducing soot blowing pressure and frequency, installing baffles, relocating superheater tubes to lower temperature zones, and upgrading the metals used for superheater tubes. Subsequently, weld overlays, laser claddings, fused coatings, and thermal spray coatings emerged as more effective solutions for addressing HTC issues in waste-to-energy and biomass combustion boilers.

Thermal spray coating techniques, such as flame spray, electric arc spray, plasma spray, high-velocity oxy-fuel spray, high-velocity air-fuel spray, and detonation spray, have demonstrated success in European WtE plants for protecting superheater tubes and extending their lifetimes [9, 11]. These methods allow the application of various materials, resulting in high-quality coatings characterized by low porosity and high hardness. The process involves using a spray gun to melt the selected coating material, in powder or wire form, and depositing the molten particles onto the target surface with a high-velocity gas jet. Advantages of thermal spray techniques include the ability to create relatively thin layers (100-800µm), a wide range of coating materials, and the flexibility for on-site or off-site application, all at an affordable cost. As a result, thermal spray techniques offer an effective solution for addressing corrosion issues in superheater tubes [9, 11].

Original contributions: The primary contributions of this study lie in its comprehensive technical and economic analysis of various thermal spray techniques and coating materials used for prolonging the life of superheater tubes in waste-to-energy and biomass combustion plants. By employing case studies and drawing on the existing body of research, this study provides a holistic understanding of the factors influencing the effectiveness of different coating materials and their corresponding thermal spray techniques. Furthermore, this research offers valuable insights and guidance to industry professionals and engaged stakeholders in making informed decisions regarding the selection of appropriate thermal spray techniques and coating materials to enhance superheater tube performance. By identifying the most suitable coatings and application methods, this study aims to contribute to the long-term sustainability and economic viability of waste-to-energy and biomass combustion plants.

2 Materials and Methods

2.1 Coating techniques considered

This study considers various thermal spray techniques. These techniques are known for their distinct advantages and limitations in terms of cost, application, porosity, bond strength, and coating quality [7, 11-25]. A summary is provided below:

i. Flame Spray: A low-cost and flexible technique that uses either powder, wire, or rod form feedstock materials. The feedstock is melted by a combustion gas and then sprayed onto the substrate using high-speed compressed air. However, coatings produced by this method have high porosity (10-20%), low density, and low bond strength compared to other techniques [7, 11, 12]

ii. Electric Arc Spray: This technique uses wire-form feedstock materials and creates an electric arc between two metallic wires, melting them. The molten particles are accelerated towards the substrate by a compressed gas stream. Electric arc spray offers low heat input, high bond strength, denser coating, and lower operating costs compared to flame spray. However, it is limited to metal wire feedstock materials and generates significant fumes and dust during operation [12]

iii. Plasma Spray: This method involves ionizing plasma-forming gas between two electrodes, heating it to extremely high temperatures, and using the resulting plasma jet to propel molten particles onto the coated surface. Plasma spray, including atmospheric and vacuum variants, provides low porosity levels and does not degrade the substrate's mechanical properties. However, this technique has a relatively high cost and complexity [7, 11, 21]
iv. Detonation Spray: The first high-velocity thermal spray process, in which fuel gas and coating materials are ignited in a water-cooled gun barrel, creating molten particles that are accelerated towards the substrate at supersonic velocities. This method results in coatings with low porosity, high density, and excellent mechanical properties. However, it is unsuitable for low-density spray materials, has high noise levels, and is expensive [13, 14]
v. Warm Spray: A variant of high-velocity oxy-fuel spray that uses a mixing chamber to control temperature and speed, ensuring coatings maintain their original characteristics without thermal deterioration. This technique is relatively new, and thus has fewer applications in WTE boilers [15-17]
vi. High Velocity Oxy-Fuel (HVOF) and High Velocity Air-Fuel (HVAF) Spray: Both techniques use a mixture of fuel and oxygen (HVOF) or air (HVAF) to create high-pressure flames that melt and propel feedstock particles onto the substrate. These methods produce thicker coatings with strong adhesion and low porosity. However, they have a relatively low deposition rate and higher equipment costs. HVOF spray is the most prevalent technique in WTE applications due to its ability to produce high-quality coatings [18-20, 22-25]

2.2 Coating and tube materials considered

Numerous laboratory tests have been conducted on different coating and tube materials (Tables 1- 3), providing crucial data such as material composition, and corrosion rates and contributing to a better understanding of the interactions and performance under different conditions [5, 9, 20, 22-25]. To comprehensively analyze this data, the following assumptions were made:

i. All test environments exert an equal corrosion effect on the selected coating and tube materials [5, 12]
ii. Technical parameters, aside from the chosen thermal spray technique, do not influence coating quality [5, 12]
iii. The sample superheater tube's unit length is assumed to be one meter [5, 7]
iv. The sample superheater tube's outside diameter is 3.81 cm (1.5 in), and the wall thickness is 0.4572 cm (0.18 in) [5, 7, 12]
v. The WTE plant's operating time is 8,000 hours per year (90% availability) [26].
vi. Coating materials are composed of pure metal elements [11, 12]
vii. The coated superheater tubes' lifetime will be extended by five years, during which only the tube coatings will corrode [9]

viii. Corrosion rates are uniform around the tube [5, 9]. Thus, the volume loss due to corrosion of the superheater tube in each unit period equals the corrosion rate multiplied by the time and the tube's surface area

ix. Only the costs of tube or coating materials are considered, excluding equipment costs. The cost of metal is a fraction of the total cost for thermally coating one square meter of superheater tubes' surface (Supplementary materials) [12]

x. Experimental coating data obtained at temperatures above 550°C were excluded, as WTE superheater tubes do not operate at higher temperatures [26]

Based on the information provided in the research studies listed in Tables 1-3, the density and price/cost of materials can be calculated [27, 28]. A sample calculation is provided in the supplementary materials. In addition, supplementary materials contain complete data for each coating and tube material, the calculated costs of applying coatings to a one-meter-long superheater tube for a presumed five-year-lifetime extension, and the costs of manufacturing one meter of superheater tubes using the selected materials for each research study listed in Table 1.

2.3 Summary of formulas used

In our investigation, we utilized a series of mathematical formulas to analyze and calculate various aspects of our study [12, 18, 23, 25].

1. **Corrosion Rate:** The rate of corrosion was determined by calculating the thickness lost over the test time. The formula used was:
   Corrosion Rate = Thickness Lost / Test Time
2. **Loss of Volume per Year:** This was calculated by multiplying the corrosion rate by the operation time and the surface area of the superheater tube. The formula used was:
   Loss of Volume per Year = Corrosion Rate × Operation Time × Surface Area of Superheater Tube
3. **Loss of Mass per Year:** This was calculated by multiplying the loss of volume per year by the density. The formula used was:
   Loss of Mass per Year = Loss of Volume per Year × Density
4. **Cost for Superheater Tubes' Five-Year-Lifetime Extension:** This was calculated by multiplying the loss of mass per year, the price of the coating material, and the duration of five years. The formula used was:
   Cost for Superheater Tubes' Five-Year-Lifetime Extension = Loss of Mass per Year × Price of Coating Material × 5 Years
5. **Volume of Superheater Tubes:** This was calculated by multiplying the cross-sectional area of the tube by the length of the tube. The formula used was:
   Volume of Superheater Tubes = Cross Section Area of the Tube × Length of the Tube
6. **Cost for Certain Length of Superheater Tube:** This was calculated by multiplying the volume of the tube by the price of the tube material. The formula used was:
   Cost for Certain Length of Superheater Tube = Volume of the Tube × Price of Tube Material

2.4 Effect of thermal conductivity on superheater tube efficiency

Thermal conductivity signifies a material's ability to conduct heat [29]. To gain a general understanding of whether coatings will impact the efficiency of superheater tubes, the following calculations and analysis are performed:

Conductance of a metal material = k / l

Here, k represents the thermal conductivity of materials, usually expressed in units of W/(m·K), and l denotes the thickness of materials, typically measured in millimeters (mm).

2.5 Cost and Benefit Analysis

The cost and benefit analysis (CBA) is based on a specific WTE plant with the following characteristics [26]:

i. Number of Units: Three
ii. Maximum Continuous Rating (MCR) a. Solid Waste Capacity per Unit: 600 tons/day b. Fuel Design HHV: 5,500 Btu/lb
iii. Design Date (MCR) a. Continuous Steam Output: 171,121 lb/hr b. Steam Pressure (at superheater non-return valve outlet): 865 psig c. Steam Temperature (at superheater non-return valve outlet): 830°F d. Feedwater Temperature: 300°F
iv. Heat Loss: 28.65%
v. Heating Surface Summary (Circumferential) Superheater III: 5,278 ft^2 Superheater II: 5,372 ft^2 Superheater I: 11,027 ft^2 Total Heating Surface of Superheater: 21,677 ft^2 (2,014 m^2)
vi. The efficiency of the turbine inside the plant is assumed to be 28%, and the price for electricity produced by the plant is assumed to be $50/MWh.

Therefore, the daily electricity production for this three-unit plant can be calculated as follows:

$$3\ Units \times \frac{600\ ton\ MSW}{day-unit} \times \frac{5{,}500\ Btu}{lb} \times \frac{2204.62\ lb}{ton} \times \frac{0.293071\ Wh}{Btu} \times \frac{MWh}{10^6\ Wh} = 6{,}396.5\ \text{MWh/day}$$

Considering the heat loss, the net daily electricity production is:

6,396.5 MWh/day * (1 - 28.65%) * 28% = 1,277.9 MWh/day

With an electricity price of $50/MWh, the plant's daily earnings amount to:

(1,277.9 MWh/day) * ($50/MWh) = $63,894.5/day

3 Results and Discussion

3.1 Selection of Superheater Tube materials

For the future selection of superheater tube materials, it is essential to prioritize those with low corrosion rates and reasonable costs. As illustrated in Figure 1, Alloy 625 demonstrates commendable performance at 525°C and 625°C, while Alloy 263 exhibits relatively low corrosion rates at 575°C, 625°C, and 750°C. Additionally, P91 provides corrosion rates below 5 mm/year at 525°C and 625°C. Furthermore, T92, Sanicro 28, Hastelloy C-2000, and HCM12A display low corrosion rates (<5mm/year) at the tested temperatures [13-25].

Although Alloy 625 presents the best corrosion resistance performance among all examined tube materials, its high price (Figure 1) is a significant drawback. Similarly, Alloy 263 performs well in WTE environments at 525°C and 625°C but is also associated with a high cost. Due to their elevated costs, Alloys 263 and 625 are not ideal choices for superheater tubes. Nevertheless, these substances may be appropriate for use as coating materials, which will be explored further in the subsequent discussion [5, 22, 25].

On the other hand, P91 emerges as a viable choice for tube material, considering its relatively better corrosion resistance at 525°C and 625°C, along with its lower cost compared to other tube materials. Besides P91, T92 also possesses a relatively low price and exhibits good performance in high-temperature-corrosion environments [5, 24].

3.2 Comparison of Corrosion Resistance of Coating Materials

Figure 2 compares the corrosion resistance of the coating materials tested in the cases listed in Table 1. For the sake of clarity, some coating materials are labeled differently to distinguish between various cases. The following coating materials demonstrate relatively low corrosion rates, i.e., less than 1 mm per year:

(a) NiCr sprayed by HVOF,
(b) Alloy C-276 sprayed by HVOF,
(c) IN625 sprayed by HVOF,
(d) NiCrTi sprayed by electric arc,
(e) Tube material A625 (potential coating material),
(f) Colmonoy 88 sprayed HVOF (at 450°C and 500°C),
(g) FeCr sprayed by HVOF,
(h) NiCrBSiFe sprayed by HVOF, and
(i) Alloy 625 sprayed by HVOF.

Alloy 718 and Colmonoy 88 tested at 550°C also exhibit good corrosion resistance, with rates less than 1.5 mm per year. SW 1641 tested at 450°C demonstrates a corrosion rate of around 6 mm per year. In contrast, the remaining tested coating materials display relatively high corrosion rates, i.e., more than 10 mm per year [13-25].

High-chromium, high-nickel, and nickel-chromium alloys have demonstrated high resistance to high-temperature oxidation and corrosion, making them suitable for thermally sprayed coatings in WTE boilers [34 & 35]. Increasing molybdenum content in nickel-based alloy coatings has been found to improve corrosion resistance in chlorine-rich and chlorine-oxidizing waste incineration environments. Several materials have been tested under WTE conditions for 6000 hours, with corrosion rates decreasing as the [Cr+Ni+Mo] concentration in the alloy increased, regardless of the coating temperature (450 or 550°C). Ceramic coatings have also shown good durability on superheater tubes inside WTE boilers, but their application remains limited [7].

To identify the best choice of coating materials, those with relatively high corrosion rates are excluded from the subsequent analysis.

3.3 Comparison of Cost for Coating Materials and Lifetime Extension

Figure 3 compares the cost of applying each coating material to an assumed one-meter-long superheater tube to achieve a five-year-lifetime extension. To differentiate between various cases, some of the coating materials are labeled with different names, as was done for Figure 3. Among the coating materials with lower corrosion rates in Figure 1, NiCr sprayed by HVOF, NiCrTi sprayed by electric arc spray technique, Alloy C-276 sprayed by HVOF, IN625 sprayed by HVOF with DJ, the tube material A625 (potential coating material), FeCr sprayed by HVOF with CJS, and Colmonoy 88 by HVOF (at 450°C, 500°C, and 550°C) exhibit both better corrosion resistance and lower cost. Coating materials SW1641, SW1600, and NiCrBSiFe are excluded due to their high costs, but their data can be found in Supplementary materials [5, 13-25].

Figure 4 features coating materials with corrosion rates of less than 1 mm/year and costs of less than \$100 for coating the assumed one-meter-long superheater tube. Some less attractive materials are not included in Figure 4 but can be found in Supplementary materials. NiCr sprayed by HVOF offers both better corrosion resistance and lower cost compared to other potential coating materials. Additionally, Alloy C-276 coating sprayed by HVOF exhibits excellent performance at 525°C and has a relatively low cost [12]. IN625 sprayed by HVOF with DJ demonstrates a very low corrosion rate and cost at its test temperature of 550°C. NiCrTi sprayed by electric arc spray technique shows outstanding performance under high-temperature-corrosion environments, and its cost is low [5].

Although the metal cost for spraying Colmonoy 88 is relatively low (<\$50), its corrosion rate is high at the test temperature of 500°C compared to other coating materials; however, it is still less than 1 mm per year. FeCr sprayed by HVOF with CJS has a relatively high corrosion rate but is low-cost compared to other coating materials. As such, it could be considered for superheater tube coating in high steam temperature applications [12, 23, 25].

The tube alloy, A625, provides both an acceptably low corrosion rate and cost at a test temperature of 525°C. All the coating materials presented in Figure 4 offer outstanding corrosion resistance (corrosion rate < 1mm/year). Furthermore, the cost of thermal deposition is at best about \$200, for example, for NiCr deposit. When compared to the fabricated NiCr alloy tube price of approximately \$30/kilogram, it is evident that thermal coating should only be applied for maintenance purposes. Therefore, WTE companies should evaluate the relative costs of applying these materials in specific WTE applications and choose the one that provides the best overall cost performance.

3.4 Effect of thermal conductivity on superheater tube efficiency

Since the thermal conductivity of metals, in general, is close to 30 W/m K [53], and the thickness of the analyzed superheater tubes is approximately 0.5 cm (0.005 m), the conductance of metals in general is calculated to be 6,000 W/m^2 K. A typical value for the conductance of gas is around 200 W/m^2 K [28]. Given that the conductance of metals is generally greater than that of gas, it can be concluded that the overall heat transfer through the tube wall is not controlled by metals. This principle will always hold true since the thickness of the tube wall with coatings cannot be as extensive as several centimeters, ensuring that the conductance of metals will always surpass that of gas. Consequently, applying additional coatings onto superheater tubes will not affect their efficiency.

3.5 Cost-Benefit Analysis of Superheater Tube Coatings

Figure 5 illustrates the cost of selected coating materials for the assumed five-year-lifetime extension. Detailed data on their cost can be found in supplementary materials.

Annually, WTE units undergo approximately 15 days of shutdown for periodic maintenance. Coatings can help reduce maintenance time for superheater tubes, allowing the saved time to be used for continued energy production. It is crucial that the cost of adding coatings does not surpass the revenue generated by the plant during the time saved by extending the lifetime of superheater tubes [4, 26].

As depicted in Figure 5, the metal costs for spraying Colmonoy 88 by HVOF are about 12 times greater than the daily revenue earned by the plant. This means that using Colmonoy 88 as a coating material at 550°C in the assumed five-year period will not result in a loss of profit only if the total superheater tube maintenance time exceeds 13 days. WTE plants generally spend around two weeks on whole-plant maintenance [26]. Consequently, it is unlikely that many days are dedicated solely to superheater tube maintenance; hence, applying very costly coating materials may not be a reasonable choice.

This analysis demonstrated that Alloy 625 sprayed by HVOF can be used as SHT coating materials without affecting the plant's profit if the current downtime for superheater tube maintenance is more than four days in the assumed five-year period. Colmonoy 88 sprayed by HVOF, FeCr sprayed by HVOF with CJS, and A625 will be suitable coatings when the maintenance time for superheater tubes is more than two days in the assumed five-year period. The remaining selected coating materials could be used when the downtime for superheater tube maintenance is more than one day in total over an assumed five-year period. Some of them would be a good choice even when the maintenance time is only more than half a day.

In summary, when selecting coating materials and application methods, it is essential to consider the SHT unit corrosion rate and cost, and to compare the estimated cost with the revenue that can be earned during the number of days saved by using SHT coatings that prolong the lifetime of superheater tubes.

4 Conclusions and Future Research Directions

4.1 Conclusions and Recommendations for Superheater Tube Coatings in WTE Plants

High-temperature combustion and the presence of corrosive components in MSW cause severe high-temperature corrosion (HTC) in superheater tubes. This study found that adding coatings to superheater tubes using thermal spray techniques, especially high-velocity oxy-fuel (HVOF) spray, can effectively extend their lifespan and reduce maintenance issues.

Coatings with high chromium, nickel, and molybdenum content demonstrate outstanding corrosion resistance under high-temperature-high-chlorine conditions. Several coating materials and alloys, including NiCr, NiCrTi, Alloy C-276, IN625, FeCr, Colmonoy 88, and Alloy 625, exhibited corrosion rates of less than 1 mm/year and reasonable application costs. Combining these coatings with better alloy tubes (e.g., P91 and T92) in the initial manufacturing of superheater tube bundles and refurbishing high corrosion areas after a year's operation is recommended for minimum cost and maximum plant availability.

Ultimately, the choice of coating material should consider each plant's specific conditions, as the additional cost for applying coatings should not exceed the revenue generated from extending the superheater tubes' lifetime and reducing maintenance time.

4.2 Future Research Directions

For a more precise evaluation of thermal spray techniques and coating materials, further studies should consider:

i. The impact of pressure on superheater tube thickness and corrosion conditions
ii. Testing each selected coating material in WTE environments under the same temperatures
iii. Accounting for parameters influencing the quality of coatings, such as spray distance, powder feed rate, fuel ratio, selection of guns and nozzles, and powdered materials' particle size
iv. Applying different coatings to different portions of superheater tubes, considering the varying temperature and corrosion effects along their positions
v. Including additional costs, such as instrument cost, for a more comprehensive analysis

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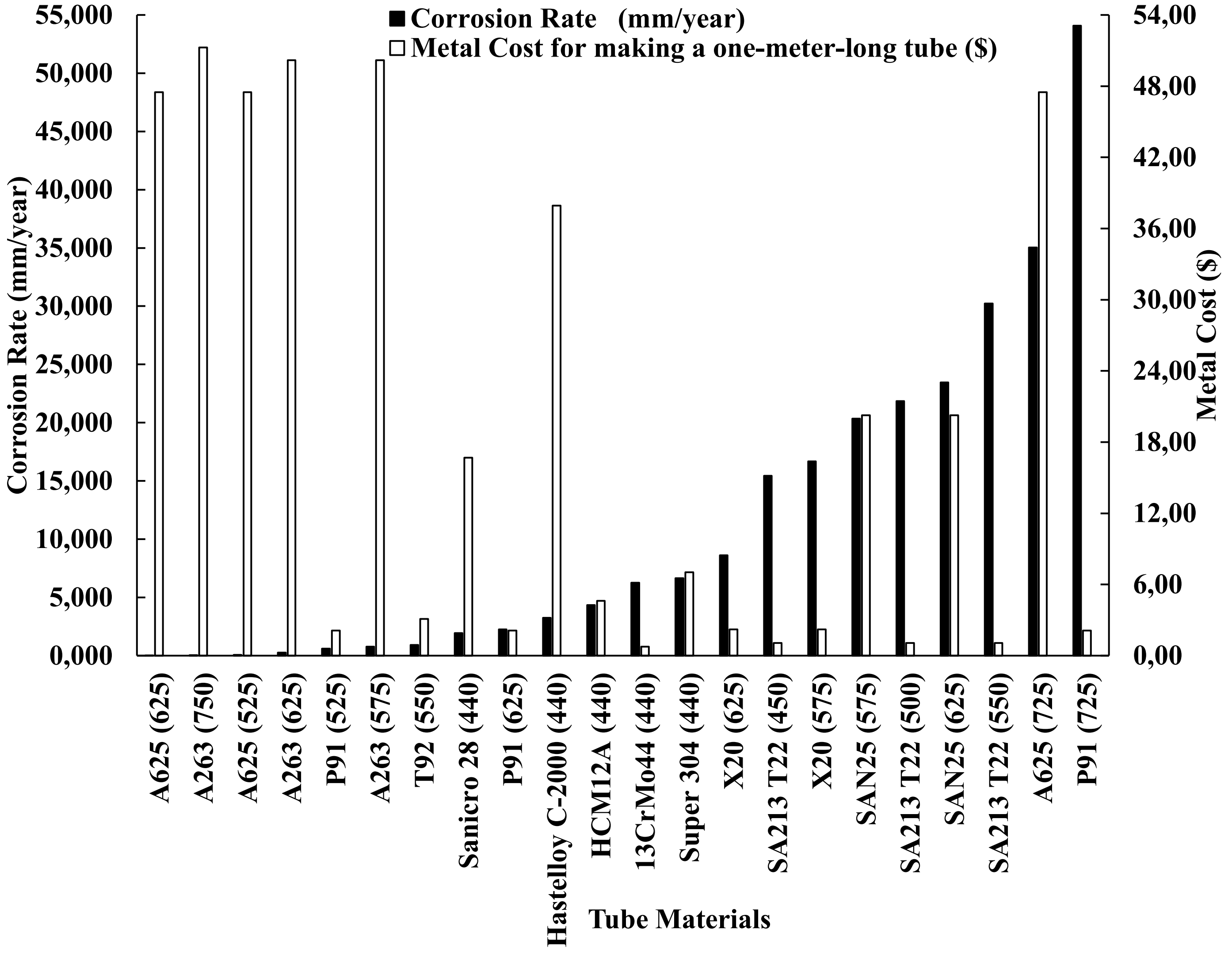

Fig 1. Corrosion Rate and Metal Cost for a One-Meter Superheater Tube
(Test Temperatures Indicated in Parentheses)

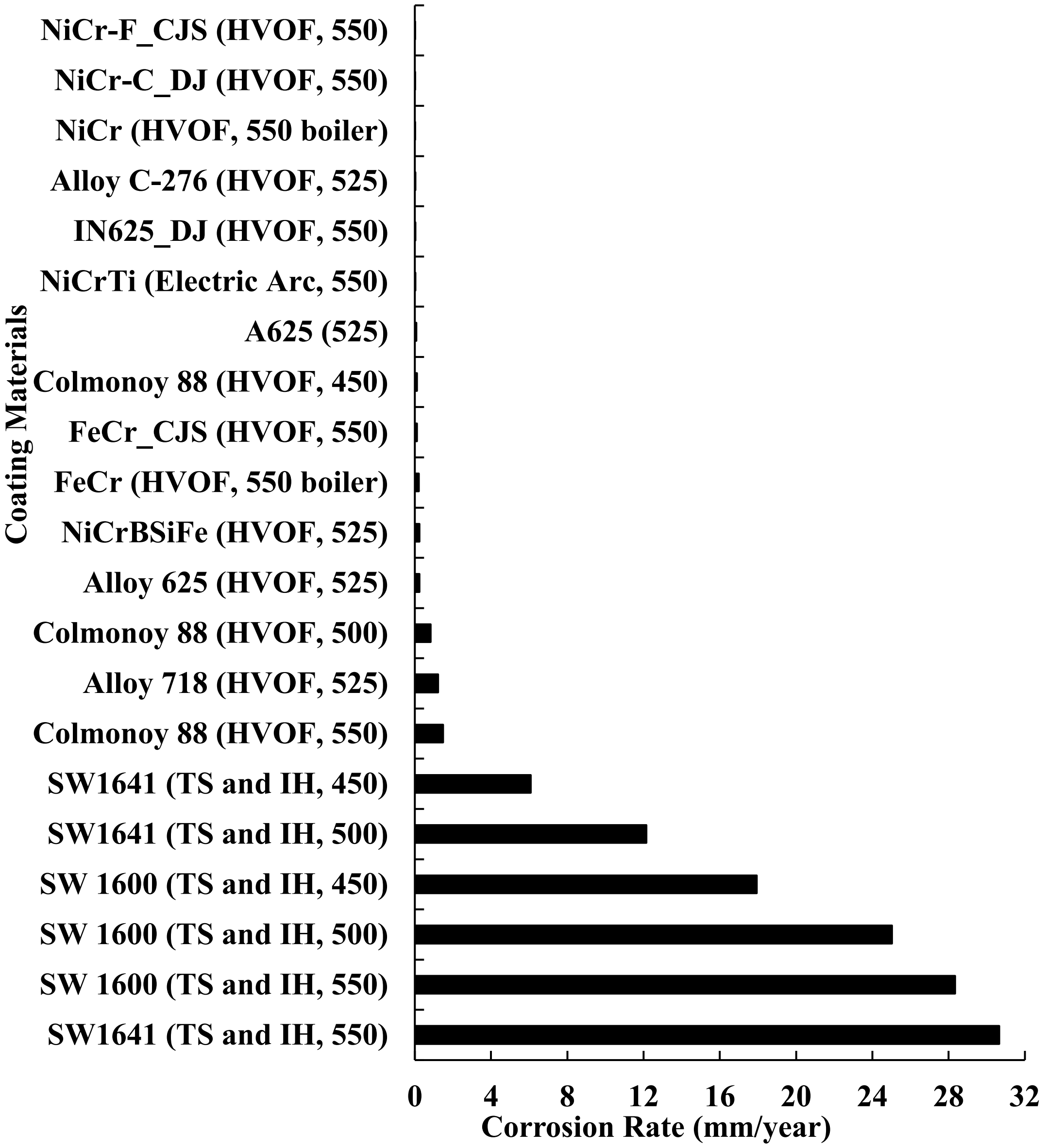

Fig 2. Estimated Corrosion Rate for Coating Materials (Test Temperatures and Techniques Shown in Parentheses; "F" in "NiCr-F" Represents "Fine" Powder, "C" in "NiCr-C" Represents "Coarse" Powder; "TS and IH" Denotes "Thermal Spray and Induction Heating")

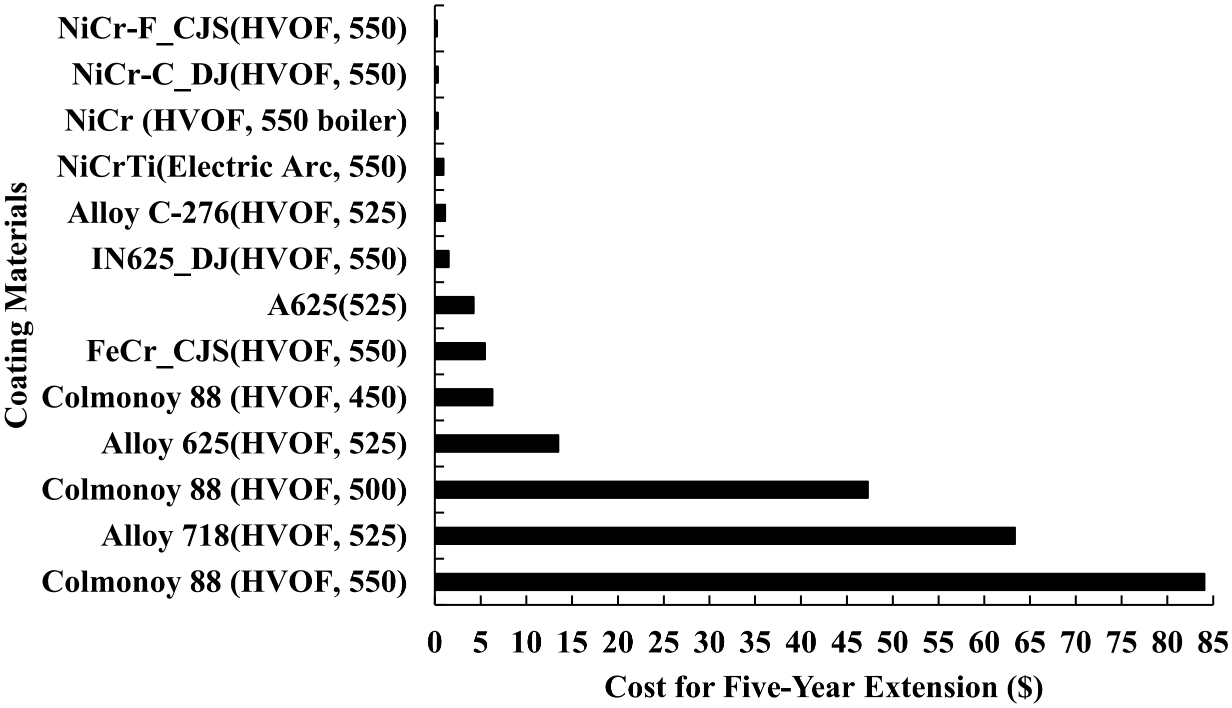

Fig 3. Metal cost for spraying coating materials onto a one-meter-long superheater tube for five-year-lifetime extension. The test temperature and technique used for each coating material are shown in parentheses. "F" in "NiCr-F" indicates the use of fine powder, while "C" in "NiCr-C" indicates the use of coarse powder. The estimated cost includes the material cost and the labor cost of applying the coating

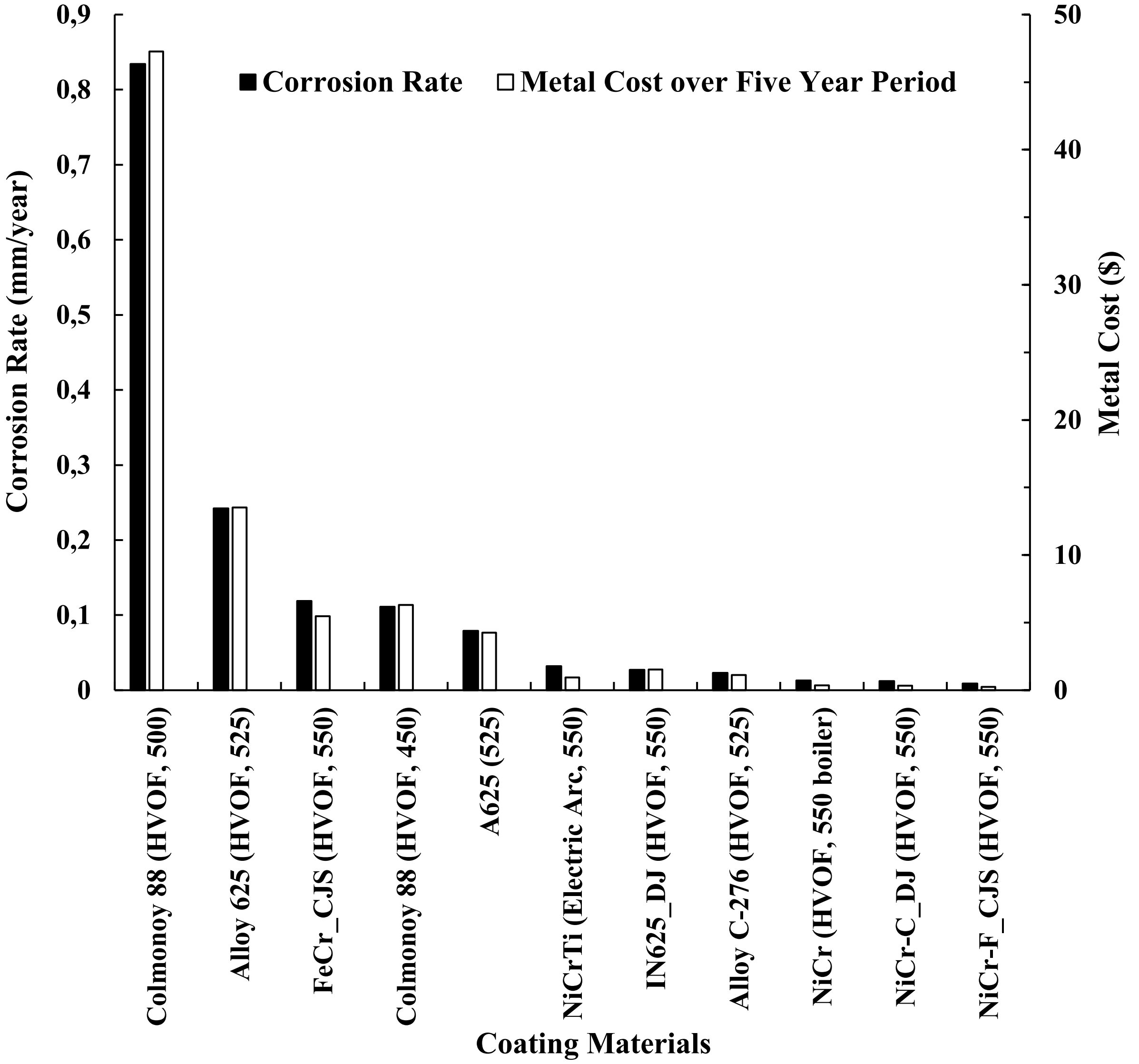

Fig 4. Estimated corrosion rates (<1 mm/year) and metal costs (<$100) for coating materials sprayed using various techniques and temperatures for a five-year-lifetime extension of super-heater tubes. The techniques and temperatures used for testing are shown in parentheses. "F" in "NiCr-F" denotes fine powder, while "C" in "NiCr-C" denotes coarse powder

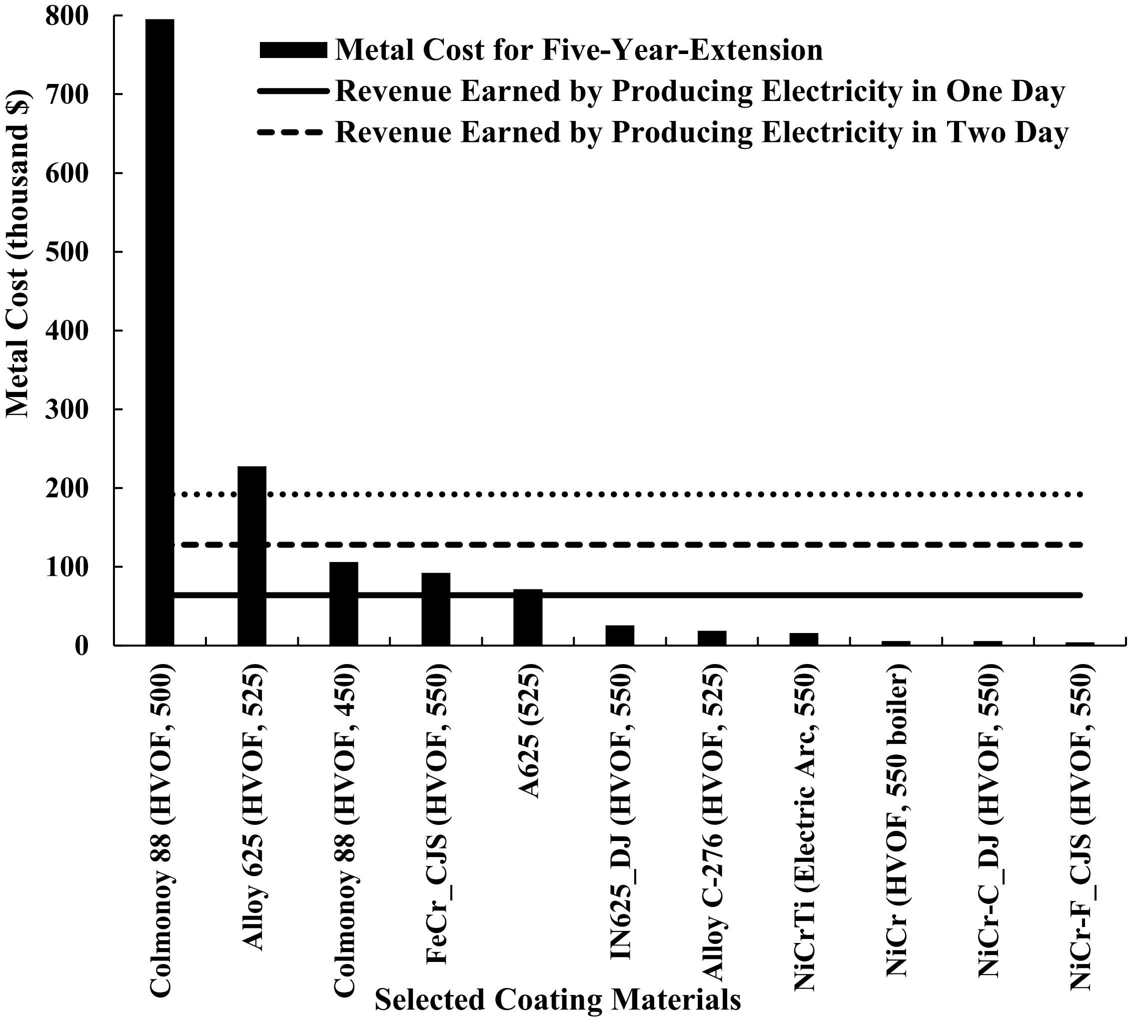

Fig 5. Metal cost for adding selected coating materials for five-year-lifetime extension (test temperature and techniques used are shown in parentheses; “F”in “NiCr-F” stands for “fine”, which means that fine powder was used for the test, “C” in “NiCr-C” stands for “coarse”, which means that coarse powder was used for the test.) The cost is estimated for a one-meter-long superheater tube

Table 1. Case Studies for Potential Coating Materials and Tube Materials

Case	Technique	Coating Materials	Tube Materials	Test Environment	Temperature	Test Duration	Ref.
1	HVOF (Carbide Jet Spray and Diamond Jet Hybrid guns)	NiCr, IN625, Diamalloy 4006 (Ni-21Cr-10W-9Mo-4Cu), and iron-based partly amorphous alloy SHS9172 (Fe-25Cr-15W-12Nb-6Mo)	X20, Alloy 263, and Sanicro 25	NaCl-KCl-Na2SO4 salt with controlled H2O atmosphere (10% H2O with 6.5 wt.% NaCl, 59 wt.% Na2SO4, and 34.5 wt.% KCl)	525 and 625	168h	9
2	HVOF (Carbide Jet Spray and Diamond Jet Hybrid guns) and Electric Arc Spray	NiCr, IN625, FeCr, and NiCrTi	T92 and A263	In a circulating fluidized bed boiler	550 and 750	5900h	22
3	HVOFGF (gas-fueled) and HVOFLF (liquid-fueled) system. Gas-fueled Diamond Jet (DJ) Hybrid 2600 and liquid-fueled Carbide Jet Spray (CJS). Nozzles 2702 and 2701 were applied with DJ spraying.	NiCr(51Ni-46Cr-2Si-1Fe) and FeCr (Fe-19Cr-9W-7Nb-4Mo-5B-2C-2Si-1Mn) powder		In laboratory exposures simulating biomass boiler conditions (the coated specimens were installed into a superheater area of the boiler with a probe measurement device) and in an actual power plant boiler exposure (with NaCl-Na2SO4-KCl molten salt in water vapor atmosphere).	575 and 625 for lab; 550 and 750 for the actual boiler	168h for lab; 1300/300/5900h for the actual boiler	23
4			13CrMo44, HCM12A, Super 304, Sanicro 28, and Hastelloy C-2000	In the waste-fired power plant, Müllverwertung Borsigstrasse, MVB, in Hanburg, Germany	440	1500h	24
5	Kerosene-fuel-led TAFA-JP5000 HVOF system	NiCrBSiFe, Alloy 718, Alloy 625, and Alloy C-276	P91, A625	45% K2SO4-KCl mixture and gaseous HCl-H2O-O2 containing environments.	525, 625, and 725	168h	25
6	HVOF (Thermal Spray and Induction Heating)	Colmonoy 88, SW 1600, SW1641	SA213 T22	NaCl salt, 8% O2, 12% CO2, 800ppmv HCl, 100 ppmv SO2 with a balance of N2	450, 500, and 550	24h	5

Table 2. Composition for each coating material

Ref	**Material**	**Ni**	**Fe**	**Cr**	**Mo**	**Al**	**Nb**	**Ti**	**W**	**C**	**B**	**Mn**	**Si**	**Cu**	**Co**	**V**	**P**	**S**
20	Alloy 625	63.79	5	21.2	8.3	0.5	1.2	0.01										
9	NiCr	51.8	1.1	45	…		…		…	…	…	…	2.1	…				
9	IN625	63	2.5	21.5	9		3.7		…	…	…	0.1	0.2	…				
9	Diamal-loy4006	54	1	20.5	9		…		10	0.75	0.75	…	…	4				
9	SHS9172	…	28	25	6		12		15	4	5	3	2	…				
22	NiCr	51.3	…	46.5	…		…	…	…				2.2		…			
22	IN625	66.5	…	21	8.8		3.5	…	…				0.2		…			
22	FeCr	…	60.1	19	3.6		7.1	…	8.6				1.6		…			
22	NiCrTi	55.25	…	44	…		…	0.75	…				…		…			
23	NiCr	50.2	1.1	46.5	…		…		…	0.1	…	…	2.1					
23	FeCr	…	52.3	18.6	3.6		7.1		8.6	2.1	5	1.1	1.6					
25	NiCrBSiFe	70.6	4.6	17.2	…	…	…	…	…	0.8	3.1	…	3.7			…	…	…
25	Alloy 718	53.24	17.9	18.78	3.04	0.48	5.26	…	…	0.03	0.004	0.01	0.1			…	0.004	0.002
25	Alloy 625	67.209	0.081	21	8	…	3.48	…	…	0.03	…	0.1	0.1			…	…	…
25	Alloy C-276	58.976	5.09	15.55	16.48	…	…	…	3.81	0.004	…	0.06	0.03			…	…	…
5	Colmonoy 88	56	10.9	15					17.3	0.8								
5	SW 1600	75.1		15	2.5						3.1		4.3					
5	SW1641	52.9		37.1	3						3.6		3.4					

Table 3. Composition for each tube material

Ref	Material	Ni	Fe	Cr	Mo	Al	Nb	Ti	W	C	B	Mn	Si	Cu	Co	V	P	S
9	X20	0.55	85.2	11.25	1	…	…	…	…	0.2		1	0.5	…	…	0.3		
9	A263	49.44	0.7	20	5.85	0.6	…	2.15	…	0.06		0.6	0.4	0.2	20	…		
9	SAN25	25	43.1	22.5	…	…	0.5	…	3.6	0.1		0.5	0.2	3	1.5	…		
22	T92	…	87.9	9	0.6			…	2				0.5		…			
22	A263	51.5	0.5	20	5.8		…	2.2	…						20			
24	13CrMo44	0.1	97.73	0.85	0.5					0.12		0.5	0.2					
24	HCM12A	0.5	84.335	11.3	0.5				2	0.11	0.005	0.5	0.5			0.25		
24	Super 304	9	68.57	18	…		0.4			0.03		0.8	0.2	3				
24	Sanicro 28	30.6	36.41	26.6	3.3					0.09		1.6	0.5	0.9				
24	Hastelloy C-2000	58.893	1.2	22.5	15.7					0.007		0.2	…	1.5				
25	P91	0.33	88.615	8.9	0.96	0.01	0.08	0.005	0.05	0.12	…	0.48	0.23			0.2	0.015	0.005
25	A625	61.537	3.76	21.5	9.12	0.1	3.52	0.24	…	0.024	…	0.14	0.05			…	0.008	0.001
5	SA213 T22		96.65	2.25	1					0.1								

Nanofiltration and selective crystallisation for the recovery of bio-based fertilizing products from seawater desalination brine

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Abstract. The majority of companies that operate desalination units produce significant quantities of brine, a hypersaline product whose disposal in the sea contributes to the degradation of local fauna and flora. The proposed framework for the valorisation of seawater brine in its entity and recovery of high purity water unveils a sustainable zero liquid discharge strategy consisting of two precipitation steps for the recovery of $Mg\ (OH)_2$ and $CaCO_3$. After pH conditioning, the brine (without Mg^{2+} and Ca^{2+}) is led to nanofiltration unit for Na_2SO_4 separation from the NaCl - KCl rich stream. Monovalent salt stream is further concentrated by multiple effect distillation evaporator and crystallizer and KCl is separated from NaCl by flotation using sodium dodecyl sulfate as floating agent. The outcomes of this exploratory effort validate that the process upscaling is feasible. The aforementioned micronutrients have readily been tested for their part in enhancing the agronomic performance of fertilising products, so they possess market potential to support local/national/European fertilisation purposes. Last but not least, such a nutrient recovery approach can ensure capital recovery within the expected time limitations of an investment and in some cases offset completely the treatment cost.

Keywords: nutrient recovery, seawater desalination brine

Table 1. List of abbreviations

Abbreviation	Name	Abbreviation	Name
BBFs	Bio-based fertilisers	N	nitrogen
Ca	calcium	NR	nutrient recovery
$CaCO_3$	calcium carbonate	C	organic
KCl	potassium chloride	P	phosphorus
$Mg\ (OH)_2$	magnesium hydroxide	K	potassium
MED	multiple effect distillation	RO	reverse osmosis
NF	nanofiltration	WW	waste water

1 Introduction

Climate change, climate immigrants, and the global population growth challenge the future of crop production [1] by intensification [2] and compliance with strict environmental rules at a local/national/international level [3]. This trend demands that mineral-based fertilizers be replaced because of variations in nutrient availability across different regions, intermittent restrictions on nutrient transfer, and growing awareness of ore depletion [4].

To both combat these challenges and make agriculture sustainable and greener, several organisations are currently committed to the application of nutrient recovery (NR) strategies for the production of fertilising products [4]. The nutrients in solid waste and waste water (WW) streams are considered as raw material for obtaining Bio-based fertilisers (BBFs) to replace mineral-based fertilisers. The feedstock [5] can be anything from solid (all ashes with phosphorus (P) content >7%, precipitated phosphate salts (struvite [6] (after calcining to remove organic contaminants, with ammonia recovery), calcium phosphate), food waste, food industrial by-products (food processing wastes) or bone meal, secondary materials e.g. wood chips, organic fibres, biomass ash, sewage sludge digestates, ashes from sewage sludge incineration or liquid waste streams, thought attempts have shifted towards the valorisation of nutrient-based, commercially significant products found in WW streams. The WW feedstock candidates for NR practices can be liquors with a high ammonium concentration, and food industrial WW, any type of industrial WW (paper, food processing, bottle water and cosmetics), urban WW, as well as brine, the target of the presented work.

Currently, NR technologies involve the recovery of both P and nitrogen (N) and there are cases in which micronutrients are also recovered from the input streams. As an example of crystallization as calcium silicate-hydrate, mono or diammonium phosphate can be recovered by precipitation with phosphoric acid by reacting with ammonia gas [7]. Other examples of process technologies can include microbial fuel cells [8] or any kind of hybrid systems of photoautotrophic and heterotrophic microalgal cultivation [9], nanofiltration (NF), multiple effect distillation (MED). In order to validate the market of recovered nutrients and the nutrient recovery technologies, SuSPhos® 'has built and validated a kilogram-scale prototype reactor and is now ready for the compilation of the industrial pilot' [10]. Using a hollow fibre liquid-liquid membrane contactor (HF-LLMC) is a promising technology capable of transforming recovered nitrogen into several ready-to-use fertilisers (ammonium salts). This technology is capable to produce ammonium salts in solution with a concentration like conventional fertilisers present in market [11].

Regarding the recovered products, they should be part in the fertilisers market either by replacing an existing product or by complementing its performance. In some countries, struvite from NR practices, already has an EU 2003/2003 fertiliser validation and an end-of-waste status [7]. The market share for organic and mineral fertilisers could be complemented by a BBF with an organic (C) and mineral (N, P) base. A substitute for nitrate fertilisers could be a BBF with a mineral base and a high N content. A BBF enriched in Ca/P with better properties (organic content) than mineral fertilisers of phosphate origin has the capacity to share the market for phosphate fertilisers. Another example of WW-based NR product is Ammonium salts with plant growth promoting bacteria. These fertilisers can provide the inorganic nutrients required by the plant while the organic part can act as a bio-stimulant [12].

Any series of recovered micro-nutrients that are proven to complement plant growth can increase the yield of BBFs or replace micronutrient fertilisers on the market. A mixture of inorganic (N) and organic components could compete with products that are currently present in the market of organic and inorganic fertilisers. Hence, the relevance of the positioning in the market of this type of products is of utmost importance [13]. All in all, it has to be kept in mind that NR and the production of bio-based fertilisers, and WW-based fertilisers, in particular, are innovative practices [14]. The valorisation however of bio-based input streams (Urban WW, sewage sludge, food, Industrial WW and brine) into marketable fertilizing products or components is urgent and is guided and directed by accurate legislation for such products to enter the EU market. Still, the market for products from practices of recovery remains scarce [15].

Desalination of seawater is widely used to produce high-purity water to deal with water scarcity throughout Europe and the other continents. It is carried out in specialized plants using different techniques. The principal method for high-purity water production is reverse osmosis (RO). The application of this method results in fresh water and brine; a hypersaline by-product considered waste with a high concentration of minerals and metals [16]. Since seawater brine represents a potential alternative source for raw materials production and some salts are already being recovered, the development of suitable technologies for the selective recovery of a broad spectrum of salts as marketable products is imperative. Membrane-based separation processes, bioprocesses along with electrochemical and other hybrid processes represent technologies that have shown potential for metals recovery/removal [17]. The precipitation of minerals from brine reduces the fresh water production cost as well as minimises the brine disposal problem [18]. Despite their encouraging performance in lab-scale studies, these processes have not reached commercialisation yet, due to several associated challenges.

Current practice in countries using large-scale desalination plants is to reject brine back to the sea, leading to the degradation of local fauna and flora. However, further processing of brine could result in the recovery of economically prime important materials such as magnesium, calcium, and potassium salts and high-purity water. Brine treatment can contribute to the minimization of the environmental footprint of desalination plant [19].

Given its limited geological sources, Mg^{2+} has been qualified as a critical raw material by the European Union Commission [20]. Thus, its recovery from brine could be an alternative source. Another salt with an increasing consumption rate is KCl. It is estimated that under current consumption, world stocks of KCl will last until 2111. KCl is another salt that can be recovered from seawater desalination brine, as mentioned in the previous paragraph.

Due to its low cost and higher potassium (K) content than most other sources (50–52 % K, 60–63 % K_2O and 45–47 % Cl^-), potassium chloride (KCl) is the most often used K fertilizer [21]. In addition to achieving a sustainable circular economy, recovery and reuse of potassium are necessary since its current consumption rate will soon lead to the depletion of its reserves.

The aim of this study is to investigate the process parameters for the optimization of $Mg(OH)_2$, limestone calcium carbonate $CaCO_3$ and KCl recovery in terms of valorization of brine as a wastewater stream from the desalination plants. The main targets are the recovery of high purity water and salts. This work is the predecessor of the design of a pilot system for the treatment of the waste stream produced from a RO desalination plant. These salts are economically prime important nutrient resource-based micro and macro nutrients to be valorised in/as Bio-based fertilisers. Potassium can be reused as a primary macronutrient, while Mg^{2+} and Ca^{2+} as micronutrients for the manufacturing of bio-based fertilizers [22, 23]. The parameters examined are reagents quantity and stirring time to optimize the purity and quantity of the recovered salts that are obtained as marketable ingredients of BBFs. The experiments are analyzed and organized through a 2^2 factorial design [24] in order to make a statistical evaluation of the tests and results.

2 Methodological approach

2.1 Brine sampling

Brine samples were collected during three different periods of time from the outlet of a small-scale desalination plant applying reverse osmosis (RO) of a hotel in Sounio, south-east Athens. The samples were stored at ambient conditions.

2.2 Brine characterisation

Analyses were performed according to standard methods (APHA). Every experimental measurement is preceded by the analysis of a brine sample, from the same day as the experiment. The results of seawater desalination brine applying reverse osmosis (RO) and seawater (inlet of RO) characterisation are presented in **Table 8**. There are variations depending on the local composition of brine, therefore the measured ion concentrations are likely to slightly vary in different brine samples.

2.2.1 Materials

Sodium hydroxide-NaOH(2M), calcium hydroxide-$Ca(OH)_{2(s)}$, nitric acid-HNO_3 1.5%, sodium carbonate-$Na_2CO_{3(s)}$, potassium chloride-KCl, NaCl, sodium dodecyl sulfate-$CH_3(CH_2)_{11}OSO_3Na$ and hexadecyl trimethyl ammonium bromide were all supplied by Sigma Aldrich (Merck).

2.2.2 Methods

A Spectroquant® UV-VIS spectrophotometer Pharo 300 was used to measure the chlorides (Cl^-), the sulfate ions (SO_4^{2-}), the nitrates (NO_3^-) and the phosphates (PO_4^{3-}).

The concentration of K^+, Na^+, Ca^{2+} and Mg^{2+} in the brine samples was measured using the Agilent Technologies® 200 Series AA 240 FS AA flame atomic absorption spectrometer (FAAS). All samples were analysed in triplicate. The setting for the examples was: wavelength 248.3 nm, slit width 0.2 nm, flame type: acetylene-air with a flow of 2.0 L/min with 13.5 L/min flow of air. The calibration curve, with deuterium used for the background correction, ranges between 0.1–10 mg/L. The limit of detection (LOD) is 0.002 mg/L and 0.007 mg/L and the limit of quantification (LOQ) is 0.005 mg/L and 0.025 mg/L for the instrument and the method, respectively.

Bicarbonate ions (HCO^{3-}) were measured with titration and neutralization up to pH=4.4.

Analyses on recovered dried samples with X-ray Diffraction (XRD) were performed using a Cu X-ray tube (λ=1.5418 Å) BRUKER D8-ADVANCE (twin/twin) diffractometer (40kV, 40 mA). The recorded range of angles was 2θ=10-60 ° and the recording speed 0.02 °/sec.

2.3 Brine treatment process

The first step of the brine treatment train is the precipitation of Mg^{2+} in the form of $Mg(OH)_2$. The addition of two reagents NaOH and $Ca(OH)_2$ for Mg^{2+} recovery is studied. Two series of experiments are carried out under different values of stirring time and quantity of reagent to recover the best combination regarding the highest quantity and purity of Mg^{2+} recovery. Na_2CO_3 is added to the brine after Mg^{2+} removal for $CaCO_3$ precipitation. As in the former experiments series, stirring time and quantity of the reagent are the two parameters examined to achieve maximum recovery of $CaCO_3$. After pH conditioning, the brine (without Mg^{2+} and Ca^{2+}) is led to NF unit for Na_2SO_4 separation. The stream rich in monovalent ions such as Na^+, K^+, and Cl^- is further concentrated by a rotary evaporator for the reclamation of high-purity water. Then, KCl is separated from the mixed salt of NaCl-KCl using a flotation technique. Sodium dodecyl sulfate and hexadecyl trimethyl ammonium bromide are used as flotation agents. The efficiency of each floating agent is examined in terms of KCl recovery and purity. The bench-scale experiments of the proposed seawater brine treatment are described in **Fig.1.**

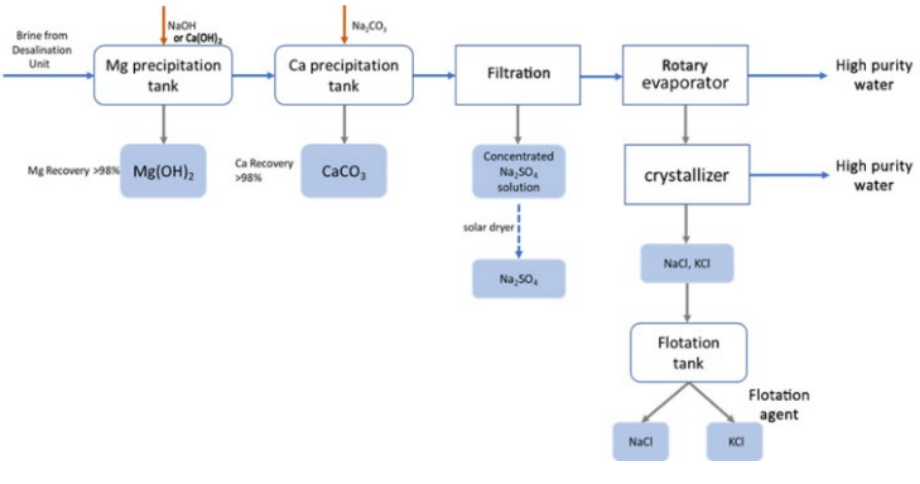

Fig. 1. Process flow diagram of the proposed seawater brine treatment

2.3.1 Mg^{2+} Removal

For the Mg^{2+} removal, samples of 200ml characterized brine are used. Chemical precipitation of Mg^{2+} is realised by using two different reagents. The first one is NaOH (2M) solution and the second one is solid $Ca(OH)_2$. Firstly, in every experimental series, the reagent is added under magnetic stirring. Different quantities of the reagent and different reaction times are examined. Sedimentation curves for magnesium hydroxide precipitation are also examined between 0-24 h. After the reaction, solid $Mg(OH)_2$ is separated through centrifugation (10min, 3500rpm) and then the liquid samples are collected. Liquid brine samples are diluted with nitric acid 1.5% and then are analyzed through AAS method to measure the final concentration of Mg^{2+} and calculate its removal percentage (%). Solid is washed out with deionized water, then collected in a crucible and left at 105 °C until dry. Finally, the dry solid is weighted, ground and analyzed through XRD method to determine its composition.

2.3.2 Ca^{2+} Removal

Solid sodium carbonate (Na_2CO_3) is added to brine samples without Mg^{2+} and the mixture is stirred. As a product of the reaction, a new solid is produced, $CaCO_3$, which is separated from the liquid solution through centrifugation (10min, 3500rpm). The liquid solution is filtered and then diluted with nitric acid 1,5% to be analyzed using AAS method. Through this analysis the concentration of Ca^{2+} is measured and the percentage (%) of Ca^{2+} removal is calculated. Solid $CaCO_3$ is washout out with deionized water. Finally, it is left at 105° C to dry and is analysed through XRD method.

After pH conditioning, the brine (without Mg^{2+} and Ca^{2+}) is led to a rotary evaporator for water and salt recovery. Recovered salt is led to flotation for the separation of KCl from NaCl.

2.3.2.1 Factorial experimental design

Recovery of Mg^{2+} and Ca^{2+} is designed through a 2^2 factorial experiment of two parameters (reagent's quantity and stirring time). Experiments are realized under various conditions and combinations of the upper and lower levels of the parameters. The experiments with the conditions that refer to level 0 were repeated 4 times for statistical evaluation. The parameters selected are quantity of the reagent and different reaction times; a series of experiments are carried out under different conditions and combinations of the two parameters. X_1 refers to reagent's quantity and X_2 to stirring time. Stoichiometric quantity of the reagent is used as centre of the factorial design and based on the symmetry are defined the upper and lower extreme values of the levels. Specifically, at the upper level (+1) 110% of reagent‘s quantity is added with a stirring time of 45 min while at the lower (-1), 90% of the stoichiometric quantity is added with 15 min stirring time (**Table 2**).

Table 2: Parameters and levels of the factorial design

Factorial parameters			Factorial levels		
	unit		-1	0	1
Reagent's quantity	g/ml	X_1	90% of stoichiometry	stoichiometry	110% of stoichiometry
Stirring time	min	X_2	15	30	45

2.3.2.2 *Factorial design for the recovery of Mg^{2+} from brine using NaOH (2M) as reagent*

Experiments for the recovery of Mg^{2+}, using NaOH (2M) as reagent are based on the chemical reaction (1):

$Mg^{2+}_{(aq)} + 2\ NaOH_{(aq)} = Mg(OH)_{2\,(s)} + 2\ Na^{+}_{(aq)}$ (1)

The initial sample is 200ml brine with 2,74g/L concentration in magnesium. Based on the above reaction, the stoichiometric quantity of NaOH (2M) for the precipitation of magnesium is 22.5ml; mixing time for this level is settled at 30'. Conducting all possible combinations of the levels of the two parameters (**Table 3**), resulted in 12 experiments in total. For the upper and lower level, 4 trials take place with two replicates for each level. As for the center, 4 replicates are realized for statistical validation.

Table 3. Factorial design for Mg^{2+} recovery from brine using NaOH (2M) as reagent

Experiments A/A	Quantity NaOH (2M) (ml)	Mixing time (min)
1	20.25	15
2	20.25	15
3	24.75	45
4	24.75	45
5	20.25	45
6	20.25	45
7	24.75	15
8	24.75	15
9	22.50	30
10	22.50	30
11	22.50	30
12	22.50	30

2.3.2.3 *Factorial design for the recovery of Mg^{2+} from brine using $Ca(OH)_2$ as reagent*

Experiments for the recovery of Mg^{2+}, using $Ca(OH)_2$ as reagent are based on the chemical reaction (2):

$Mg^{2+}_{(aq)} + 2\ Ca(OH)_{2\,(s)} = Mg(OH)_{2\,(s)} + Ca^{2+}_{(aq)}$ (2)

Similarly to the latter process, 200ml of brine sample are used and based on the stoichiometry of the reaction, the quantity of $Ca(OH)_2$ for the $Mg(OH)_2$ precipitation is 1.356g under 30 min stirring time; these values are considered the center of the experimental design. Conducting all possible combinations of the levels of the two parameters (**Table 4**), resulted in 12 experiments.

Table 4. Factorial design for Mg^{2+} recovery from brine using $Ca(OH)_2$ as reagent

Experiments A/A	Quantity $Ca(OH)_2$ (g)	Mixing time (min)
1	1.220	15
2	1.220	15
3	1.492	45
4	1.492	45
5	1.220	45
6	1.220	45
7	1.492	15
8	1.492	15
9	1.356	30
10	1.356	30
11	1.356	30
12	1.356	30

2.3.2.4 Factorial design for the recovery of Ca^{2+} from brine

Experiments for the recovery of Ca^{2+}, using Na_2CO_3 as reagent are based on the chemical reaction (3):

$Ca^{2+}_{(aq)} + Na_2CO_{3\,(s)} \rightarrow CaCO_{3\,(s)} + 2Na^{+}_{(aq)}$ (3)

Using 200ml of brine sample and based on the stoichiometry of the reaction (3), the quantity for the $CaCO_3$ precipitation is 0.48g Na_2CO_3 by stirring the mixture for 30’; these values are considered the center of the experimental design. Conducting all possible combinations of the levels of the two parameters (Table 5), resulted in 12 experiments.

Table 5. Factorial design for Ca^{2+} recovery from brine

Experiments A/A	Quantity Na2CO3 (g)	Mixing time (min)
1	0.43	15
2	0.43	15
3	0.53	45
4	0.53	45
5	0.43	45
6	0.43	45
7	0.53	15
8	0.53	15
9	0.48	30
10	0.48	30
11	0.48	30
12	0.48	30

2.3.3 KCl recovery from brine

After magnesium and calcium removal and pH conditioning from 10.5 to 7, the resulting brine is forwarded to a rotary evaporator for concentration and then to the oven for salt crystallization. KCl is more soluble at high temperatures than NaCl, so every 2 min, brine is separated from the crystallized salt. The separated brine is expected to be more enriched in KCl, upon full evaporation. Three types of salt resulted and are named A, B and C; C is expected to be the most KCl-rich, while A is the least KCl-rich fraction. Mixed (NaCl-KCl) salt is led to a flotation cell for the separation of KCl from NaCl. For this purpose, a saturated solution of KCl and NaCl is prepared by dissolving 342g KCl and 514g NaCl in 2L of deionized water. In every flotation trial, 10g of the mixed salts are added into 40 ml of the saturated solution and then Sodium Dodecyl Sulfate 1% is used as flotation agent. The mixture is stirred for 10 min and air is provided through a pipe to create froth; KCl crystals are attached on bubbles and then are collected. Finally, crystals are left to dry. A quantity of salts is diluted with nitric acid 1.5% for further qualitative analysis through AAS method. XRD analysis is performed for each kind of salt, to study their composition qualitatively. The results obtained are given in **Fig. 2** to **Fig.4**.

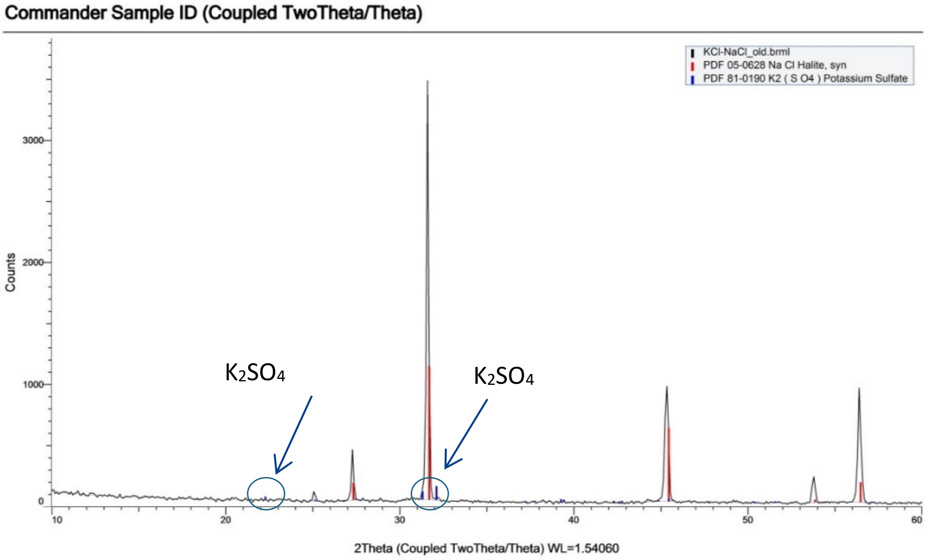

Fig. 2: Mixed salt A XRD analysis

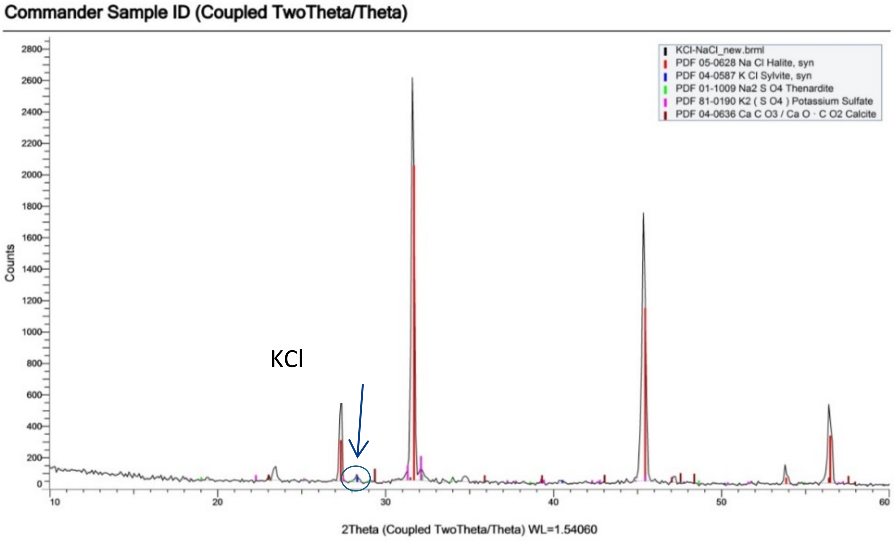

Fig. 3. Mixed salt B XRD analysis

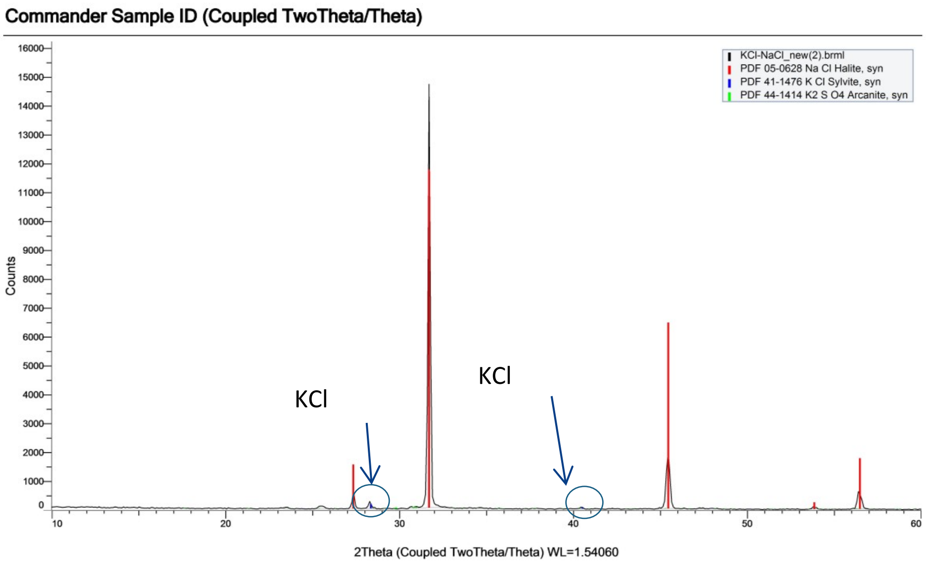

Fig. 4. Mixed salt C XRD analysis

Peaks corresponding to NaCl in the form of halite (red peaks) are visible in all three plots. In **Fig.2**, which corresponds to salt A, some smaller peaks appear which are probably due to K_2SO_4 presence, while no peaks corresponding to KCl are found, due to the very low concentration of KCl in salt A. However, in **Fig. 3** and in **Fig. 4** (mixed salt B and C) a small peak (blue in color) is visible due to the presence of KCl (sylvite). Other peaks probably correspond to the compounds K_2SO_4, Na_2SO_4 and $CaCO_3$.

To achieve a quantitative estimate of the composition of mixed salt, the analytical AAS is used (**Table 6**).

Table 6. Mixed salt analysis using AAS

K (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)
0.034	1.724	0.208	0.012	0.028

The concentration measured for potassium corresponds to 1.63 % KCl in salt B. There are also small concentrations of Mg^{2+} and Ca^{2+} which are probably not completely removed in the previous stages of the experiment. A total of 195 g of salt is collected where 52 g is salt A (less rich in K), 100 g salt B and 43 g salt C (richest in K). For the recovery of potassium by flotation method, 17 experiments are carried out where 10 g of salt are used for each one. The effect of the flotation agent addition is mainly studied keeping the amount of saturated KCl – NaCl solution constant; 40 mL are used in every experiment. In addition, tests are performed on how flotation time, mass of added salt and granulometry of the salt affect the recovered amount of KCl and its purity. **Table 7** shows the conditions for each experiment [25] and the recovered mass of solid.

Table 7. Conditions of the flotation experiments and the recovered solid mass

Experiments	Pre-treatment time (min)	Flotation time (min)	Concentrated solution volume (mL)	Added salt (g)	Floating agent volume (mL)	Granulometry (μm)	Recovered solid (mg)
A1	5	5	40	10	5.0	-	360
A2	5	5	40	10	5.0	-	150
A3	5	5	40	10	2.5	-	200
A4	5	5	40	10	2.5	-	80
A5	5	5	40	10	1.0	-	70
B1	5	5	40	10	1.0	-	110
B2	5	5	40	10	5.0	-	180
B3	5	5	40	10	0.5	-	140
B4	5	5	40	10	0.5	-	80
B5	5	5	40	10	1.0	<180	60
B6	5	5	40	10	1.0	<180	60
B7	5	5	40	10	1.0	>180 & <1000	80
B8	5	5	40	10	1.0	>180 & <1000	100
C1	5	5	40	10	0.5	-	180
C2	5	5	40	10	0.5	-	130
C3	5	5	40	10	1.0	-	70
C4	5	5	40	10	1.0	-	100

As resulted from **Table 7**, recovered KCl quantity ranges from 60 mg to 200 mg with one single experiment providing 360 mg solid. According to the table, increasing the volume of the added flotation agent increases the recovered solid (**Fig. 5**) as more froth is collected [26].

Fig. 5. Recovered KCl crystals

3 Results and discussion

3.1 Feedstock characterization

Table 8 shows the concentration of main anions and cations contained in the three brine samples treated in this work and in seawater.

Table 8. Ions concentration in seawater and brine

Ions concentration (mg/L)	Brine (1st sample)	Brine 2nd sample	Brine 3rd sample	Seawater
K^+	813	874	906	380
Na	19674	17781	18230	8026
Ca^{2+}	1552	1472	1523	450
Mg^{2+}	2736	2225	2200	1314
Cl^-	35400	44000	43800	27000
SO_4^{2-}	3820	5700	4730	4400
HCO_3^-	238	107	221	140
PO_4^{3}	0.08	0.42	0.23	-
NO_3^-	0.01	1.10	0.80	-
TDS	6.85 g/100ml	7.43 g/100ml	7.48 g/ 100ml	3.45 g/ 100ml
Electrical conductivity	64.2 mS/cm^2	64.2 mS/cm^2	64.2 mS/cm^2	50.000 uS/cm
pH	7.77	7.70	7.80	7.50-8.40

3.2 Results from the factorial design

3.2.1 Mg^{2+} recovery with NaOH (2M) addition

According to **Table 9**, the maximum Mg^{2+} removal and minimum Ca^{2+} removal have occurred on experiments 5 and 6. In these cases, 90% of reagent's stoichiometric quantity is mixed with brine sample for 45 min.

Table 9. $Mg(OH)_2$ recovery through brine reaction with NaOH (2M)

N/N	Experiments A/A	Quantity NaOH (2M) (ml)	Mixing time (min)	%Mg^{2+} removal	%Ca^{2+} removal	Mg^{2+}/Ca^{2+}	Recovered $Mg(OH)_2$ mass (g)
N1	1	20.25	15	86.50	67.20	1.49	0.76
	2	20.25	15	86.70	59.10	1.69	0.87
N2	3	24.75	45	99.00	82.30	1.22	0.90
	4	24.75	45	99.90	70.80	1.41	1.10
N3	5	20.25	45	89.90	48.80	2.05	0.60
	6	20.25	45	89.70	53.60	1.89	1.07
N4	7	24.75	15	98.80	69.20	1.43	0.97
	8	24.75	15	100.00	65.90	1.52	0.83
				Centre			
Centre	9	22.25	30	92.00	54.60	1.68	0.84
	10	22.25	30	96.50	49.70	1.74	0.93
	11	22.25	30	95.50	50.50	1.79	0.85
	12	22.25	30	94.70	51.20	1.75	0.87
	13	Maximum Mg^{2+} removal based on stoichiometry		100.00	0.00	100.00	1.276

Fig. 6. shows that experiments with maximum amount of reagent and maximum stirring time (N2) result in largest amount of salts recovery

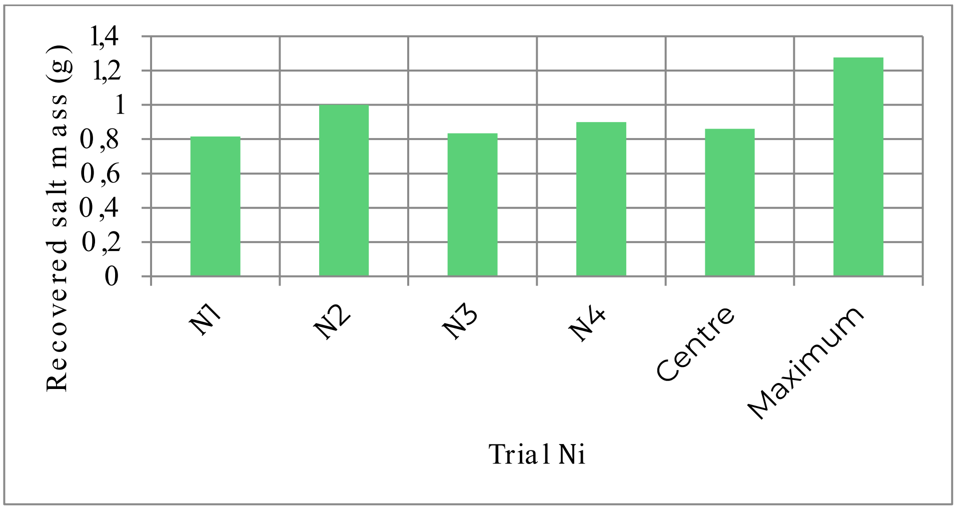

Fig. 6. Mass of recovered $Mg(OH)_2$ for every trial

Table 10. $Mg(OH)_2$ recovery through brine reaction with NaOH (2M)

A/A	Quantity of NaOH (2M) (ml)	Stirring time (min)
N1	20.25	15
N2	24.75	45
N3	20.25	45
N4	24.75	15
Centre	22.25	30
Maximum	Stoichiometry	

After processing the factorial experimental results (**Table 10**) [24, 27], the following model is developed, correlating the $Mg(OH)_2$ recovery from brine (Y, %) with the selected controlling parameters:

Y = -2.228 + 0.102 * (NaOH (2M) addition) + 0.077 * (stirring time) – 0.003 * (NaOH (2M) addition) * (stirring time) (4)

Equation 4 shows that all parameters are statistically important including their interaction. Furthermore, both mathematical models proved to be adequate according to the Fisher criterion [25, 28, 29, 30, 31].

3.2.2 Mg^{2+} recovery with $Ca(OH)_2$ addition

According to **Table 11**, maximum Mg removal has occurred with higher reagent dosage.

Table 11. $Mg(OH)_2$ recovery through brine reaction with $Ca(OH)_2$

N/N	Experiments No	Quantity $Ca(OH)_2$ (g)	Mixing time (min)	%Mg removal	Recovered $Mg(OH)_2$ mass (g)
N1	1	1.220	15	86.88	0.936
	2	1.220	15	87.46	0.881
N2	3	1.492	45	99.98	1.652
	4	1.492	45	99.62	1.716
N3	5	1.220	45	86.91	1.145
	6	1.220	45	86.64	1.195
N4	7	1.492	15	99.98	1.030
	8	1.492	15	99.18	0.940
		Centre			
Centre	9	1.356	30	94.39	1.390
	10	1.356	30	94.48	1.444
	11	1.356	30	95.30	1.368
	12	1.356	30	96.67	1.240
	13	Maximum Mg^{2+} removal based on stoichiometry		100.00	1.067

Fig. 7. shows that experiments of N_2 trials provide the highest amount of salts recovery.

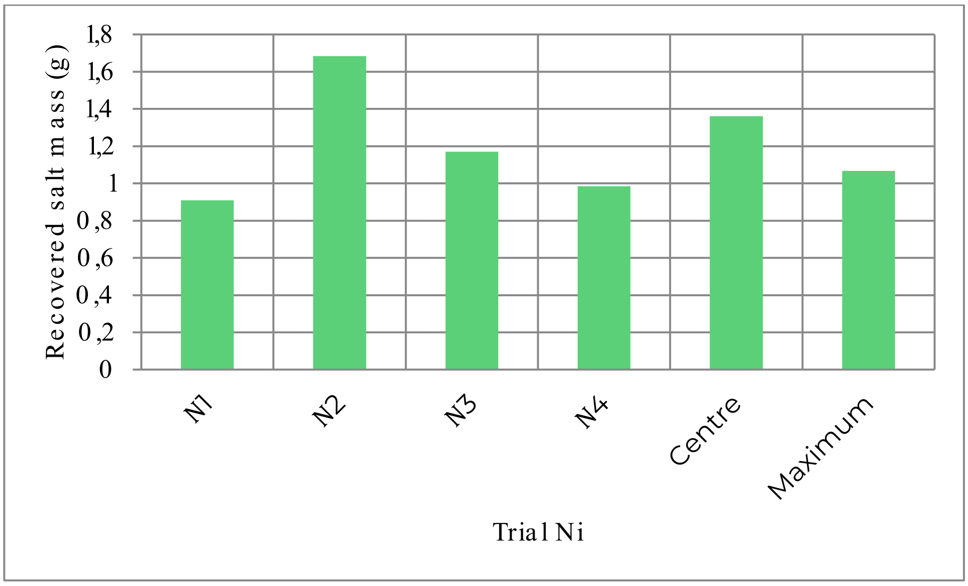

Fig. 7. Mass of recovered $CaCO_3$ for every trial

First degree equation 5 shows that the most important parameter for Mg^{2+} recovery through $Ca(OH)_2$ addition is reagent's quantity, whereas reaction time is not considered as a factor that can affect the results.

$Y = 0.295 + 0.47 * (Ca(OH)_2 \text{ addition})$ (5)

3.2.3 Ca^{2+} recovery with Na_2CO_3 addition

Table 12 shows that all different experiments result in an average class rate of 99% $CaCO_3$ recovery.

Table 12. $CaCO_3$ recovery through brine reaction with Na_2CO_3

N/N	Experiment No	Quantity Na_2CO_3 (g)	Mixing time (min)	%Ca removal	Recovered $CaCO_3$ mass (g)
N1	1	0.432	15	97.00	0.33
	2	0.432	15	98.00	0.35
N2	3	0.528	45	99.00	0.39
	4	0.528	45	98.00	0.34
N3	5	0.432	45	99.00	0.37
	6	0.432	45	99.00	0.38
N4	7	0.528	15	99.00	0.33
	8	0.528	15	99.00	0.37
		Centre			
Centre	9	0.48	30	98.00	0.32
	10	0.48	30	99.00	0.35
	11	0.48	30	98.00	0.33
	12	0.48	30	99.00	0.37
	13	Maximum Mg^{2+} removal based on stoichiometry		100.00	0.45

Equation (6) shows that Ca^{2+} removal increases both with Na_2CO_3 addition and stirring time. However, reagent's addition has a greater effect on Ca^{2+} removal because of its greater coefficient.

$Y = 0.9372 + 0.0081 * (Na_2CO_3 \text{ addition}) + 0.0002 * (\text{stirring time})$ (6)

3.3 Nanofiltration simulation model

According to the experimental process flow diagram (**Fig. 1**) the brine after Mg^{2+} and Ca^{2+} removal will enter the NF unit. The occupation of the NF unit is necessary for the removal of SO_4^{2-}ions from the seawater desalination brine. Regarding the NF process unit the separation efficiency was set as the main optimization parameter. Since only small volumes of brine (200ml and 50 L) have been treated during the lab-scale experiments, it was not possible to implement NF step. Thus, it was decided to run a simulation model for the treatment of 0.5 m^3/day of brine (raw feed composition is presented in **Table 13**) using the water application value engine (WAVE) software.

Table 13. Concentrations of brine ions and TDS before and after NF process

	Raw Feed (mg/L)	Concentrate (mg/L)	Permeate (mg/L)
K	912.60	1,588	729.80
Na	21,974	37,701	17,718
Mg	11.60	30.57	6.46
Ca	17.40	45.98	9.66
SO_4^{2-}	3,416	15,046	271.30
TDS	58,688	103,304	46,616

After many runs with different types of NF membranes the most appropriate seems to be the membrane NF270-2540 in terms of SO_4^{-2} removal. This membrane seems to be more appropriate (large pore diameter: 270 μm) because the stream is very dense and would create fouling and scaling issues [32]. The removal efficiency results in the brine salts & TDS removal percentages are described in **Table 14**. The simulation was performed under pH=7. For this type of membrane and aforementioned conditions no special comments were derived from the wave simulation model regarding fouling or scaling issues.

Table 14. NF % removal of brine ions & TDS

	% removal of major ions
K	20
Na	19
Mg	44
Ca	44
SO_4^{2-}	92
TDS	21

To conclude with, the simulation of the NF process using membrane NF270-2540 implied a 92% removal (Table 14) of SO42- from the brine inlet. The resulting effluent streams will be used for the optimisation of the downstream processes.

4 Conclusions

Summing up, in the first part of the experimental process, the salts are recovered by precipitation as $Mg(OH)_2$ and $CaCO_3$ after the addition of NaOH or $Ca(OH)_2$ and Na_2CO_3. Then, the divalent SO_4^2 are separated from the brine using nanofiltration (NF). The next part of the process targets brine concentration and the recovery of a mixed salt of NaCl and KCl applying thermal crystallization. In the final stage, KCl is collected from the mixed salt by flotation.

The main achievement of this work is the proof that macro and micronutrients can be recovered from the brine produced by an RO desalination plant. The acquisition of such end-products adds high value to the existing desalination plants, contributing to the alignment with EU Water Framework Directive, Circular Economy Package and sustainability in the agricultural sector. Furthermore, this work contributes to the definition of the main design of a system parameters and their values.

To achieve the recovery of water and salts from RO desalination brine next steps should be followed:

- $Mg(OH)_2$ recovery (precipitation)
- $CaCO_3$ recovery (precipitation)
- Separation of the divalent SO_4^2 from the brine (nanofiltration).
- Brine concentration (water evaporation)
- Recovery of a mixed salt of NaCl and KCl
- Separation of KCl from the mixed NaCl-KCl salt (flotation).

A sustainable brine treatment leads to avoidance of its disposal in the sea and decreases its impact on the environment and aquatic life. Also, recovery of nutrients from brine could reduce the CO_2 emissions in comparison with the conventional methods of nutrients production. Moreover, this technology facilitates compliance with proposed regional/EU-27 regulations towards replacing the production of fossil-based fertilizers. The introduced seawater brine technology framework outlines a sustainable, competitive zero liquid discharge approach to completely convert brine into reclaimed water and salts of commercial value. Last but not least, the results of this preliminary work justify the feasibility of the process upscaling.

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Energy

Exploring the Feasibility of Solar and Wind Energy Utilization in Poland: A Hybrid Energy Mapping Approach

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Abstract. Poland is obliged to reach the target of 21% share of renewable energy sources in gross final energy consumption by 2030. Thus, it makes it necessary and obligatory for the country to expand its wind and solar power generation. This research presents the preliminary process of creating the hybrid energy map for the country that would make it simpler both for the government and the enterprises to choose the available siting location. Geodata is assessed along with the siting constraints in a spatial analysis by using Geographic Information System (GIS), encompassing infrastructural constraints, land use, and renewable energy resources. The final outcome of the paper is the visual hybrid energy map of Poland showing the available space for both wind and solar farms.

Keywords: hybrid energy map, Poland, GIS, wind power, solar power.

1 Introduction

1.1 Problem background

Nowadays, climate issues are one of the most important topics being discussed worldwide. The problems with energy supply and use are not only just related to global warming, but also to environmental concerns such as air-pollution, forest destruction, and ozone depletion [1]. It is a serious problem, and it requires a massive transformation of the world's energy infrastructure - ideally to 100% clean, renewable energy (RE) producing zero emissions, as suggested by Jacobsen et al [2]. It is extremely clear that faster expansion of renewable energy systems is a necessary requirement for a sustainable energy future [3]. That is why there are currently five main support mechanisms of electricity from renewable energy sources (RES) in the EU that are implemented: investment subsidies, fixed price mechanisms, fixed premium mechanisms, quota system based on auctions or tradeable green certificates [4]. As a result, the EU introduced a renewable energy directive EU 2018/2001/EU.

Due to the before mentioned directive from EU 2018/2001/EU, Poland received a new bidding RE target of 21% share of RES in gross final energy consumption by 2030 (EU, 2018). The gross final energy consumption includes the aggregate consumption in the electricity sector, heating, and cooling sector, as well as for transport purposes. The target for 2020 is 15% [6]. According to Główny Urząd Statystyczny, Poland has reached 12.18% share of RES in 2019 [7]. However, Figure 1 shows that the total installed capacity of RES in 2019 was 20.1% including biomass and biogas.

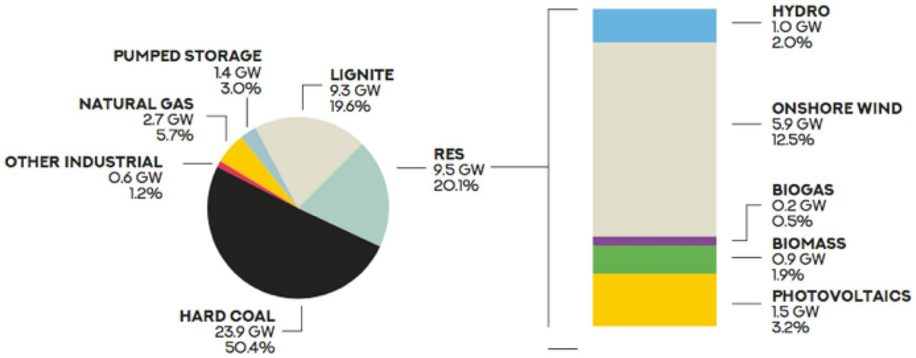

Fig. 1. Installed Capacity in the Polish system at the end of 2019 [8]

The focus of this study is based on Poland which has an area of 306 230 square kilometres and almost 38 million inhabitants [9]. It is a rather low-lying country with 91% of its territory lying below 300m above sea level [10]. Poland is the 9th largest country in Europe and has a variety of geographical characteristics. Its coastline measures approximately 1,000km and is located in the north part of the country. Most of the country consists of many lakes and low hills. However, to the south of central lowlands the terrain rises slowly and becomes dominated by highlands. Along the southern border stretches the mountains. Only 3% of Polish territory is elevated higher than 500m above the sea level [10].

Figure 1 illustrates an overview of the installed capacity in the Polish system in 2019. According to the Główny Urząd Statystyczny, at the end of 2019 there has been a total installed capacity of 47,378 MW. It can be clearly seen that Poland remains dependent on thermals. Hard coal and lignite account for almost 70% of the total capacity. As this study focuses on wind and solar systems it is worth to take a look at them. Onshore wind installations account for 12.5% and photovoltaics to 3.2%. The current situation in Poland moves towards more renewable solutions but regrettably the hard coal and lignite are still the biggest players.

1.2 Problem formulation and research questions

The problem formulation and research questions justify the existence of this paper. In order for the reader to clearly understand and recognise the drive and the motivation of this report the problem formulation and research questions should be as detailed as possible.

Poland needs to create an energy infrastructure that has to comply with the EU directive and help the country reach its target of 21% share of RES by 2030. That can be done by developing the renewable energy sources. The main challenge identified by the author was to preliminary recognise the potential and available onshore wind power and solar power unit locations in Poland with consideration of possible constraints.

What are the prime locations in Poland with the greatest potential for wind and solar power generation?

Analysing the potential space for hybrid uses of solar and wind energy in Poland.

The main research question aims to identify the most suitable locations through geodata. In order to answer this question geodata will be collected and a map will be created with the use of GIS. The desired goal of the research is a hybrid energy map of Poland, where the available space for wind and solar farms siting is shown. In order to reach the outcome other sub questions shall be answered. The following research questions will narrow down the study and help answering the main problem.

1. What is the current status of renewable energy in Poland?
2. What are the advantages of utilizing hybrid resources, specifically wind and solar, such as a hybrid energy map for Poland?
3. Which constraints, including infrastructural elements like roads, railways, and water bodies, as well as land use factors such as buildings, were considered in mapping the potential areas suitable for hybrid energy use in Poland?

1.3 Methodology

This section's purpose is to outline and argue for the methodological choices, techniques and considerations that form the foundation of the report and its results. This paper uses both quantitative and qualitative data and is a combination of a theoretical research and data analysis. As a starting point, quantitative data is being collected and analysed using a numerical analysis. Furthermore, it is supported by desk research, gathering open-source, and free geodata.

The selection of mixed-method approach has been made to enable the researcher to answer the research questions in a more reliable way [11]. Hybrid solar-wind map has been conducted within the use of QGIS tool and previously collected geodata. In the following section a short introduction to Geographical Information System is given as it is the main application used in this paper.

1.4 Use of Geographical Information System

Use of QGIS software is the base of this report. It is used to collect and analyse geodata and visualise the developed artefact, the hybrid energy map of Poland. Thus, this section will explain how Geographical Information System (GIS) will enable the researchers to accomplish it.

According to (ERIS, 2020), GIS is a framework used by thousands of organizations in virtually every field. It helps them to make various maps that can communicate, perform analysis and share information around the world. There are obviously different ways to use GIS in many different areas and industries. However, this paper will aim to use GIS to create the final artefact by overlaying different constraint layers on top of each other in order to end up with one single map [12]. The software is able to differentiate between two types of data formats: raster and vector. Raster data (also called as grid data) represents the surfaces and it is cell-based [13]. Vector formats can be split into three types: points, lines and polygon data. Vector data can be used for example to store GIS data with firm borders such as roads. There are many different software tools available, but this paper uses the free and open-source QGIS tool, which is widely used and familiar to many researchers.

Poland is the second-largest coal-mining country in Europe and the ninth-largest coal producer in the world [14]. Coal is regrettably the most important primary energy fuel in the country and plays a big role in electricity production. Throughout the 90s, it delivered annually around 95% of total electricity production. Luckily, the share of other fuels (biofuel, gas, wind and solar) grew since mid-2000s and partially replaced coal [15]. This change happened as a result of EU climate and energy policies which enforced the use of renewables [16].

Nevertheless, this rather poor energy mix influences renewable development in Poland and traditional coal use is one of the barriers for renewables [17]. Additionally, there are many various factors that have impacted on the development of renewables in Poland, such as lack of long experience in renewables utilisation, low stability and unpredictable political framework [17].

Wind, biomass and waste were the largest source of RE in Poland [18]. Solar power is still at the last place of RES in Poland, but it has observed a drastic growth in the recent years. Wind energy has been intensively growing until it was halted in 201. Undoubtedly, it is an effect of unfavourable legal solutions for wind energy, in particular the Wind Farms Investment Act of May 2016 [17]. The most important output from this act is the distance in which wind farms can be located and built and it is to be around 1,5 – 2 km from housing regardless of the opinion of local residents [17].

The rationale behind selecting QGIS as the GIS tool for this study lies in its versatility, accessibility, and compatibility with the objectives of the research. QGIS, being an open-source software, provides a cost-effective solution for data collection, analysis, and visualization, aligning well with the aim of utilizing free and open sources for gathering geodata. Its robust functionality allows for the integration of diverse data formats, including shapefiles and TIFF files, which were the primary formats used in this study. Additionally, QGIS offers a user-friendly interface and a wide range of geospatial analysis tools, making it suitable for both qualitative and quantitative analysis required for this research. Furthermore, QGIS has gained popularity among researchers and practitioners in the field of GIS, ensuring ample resources and support for troubleshooting and implementation. Hence, QGIS emerged as the preferred choice over other software options due to its compatibility with the study's methodology, cost-effectiveness, versatility, and user-friendliness.

2 Theoretical background

This section will analyse the theoretical background of current renewable energy situation in Poland, with focus on wind and solar, and the hybrid renewable energy system. Furthermore, the use of GIS will be described and analysed.

This part will focus on the theoretical knowledge about the hybrid renewable energy systems and wind-solar energy systems. In order to see the benefits of creating a hybrid energy map, the theoretical background is going to be briefly discussed. Obviously, each system can be a standalone structure. However, there are advantages of considering implementation of a hybrid solution. This section aims to describe the use of hybridization of processes.

Hybrid renewable energy system (HRES) is, according to Khare, et al. [19], a combination of renewable and conventional energy source. Nevertheless, it can also combine two or more renewable energy sources that work in standalone or grid-connected mode.

Wind and solar energy are intermittent resources and are dependent on geographical and weather conditions [20]. Although each of the systems can work independently, none of them will generate accessible energy for noticeable portion of the year. Therefore, according to Abu-Hamdeh and Alnefaie, hybridization of wind and solar energy systems for electricity are usually more reliable and less expensive compared to standalone system. An example of the hybrid system will be shown in order to get the general understanding of the concept.

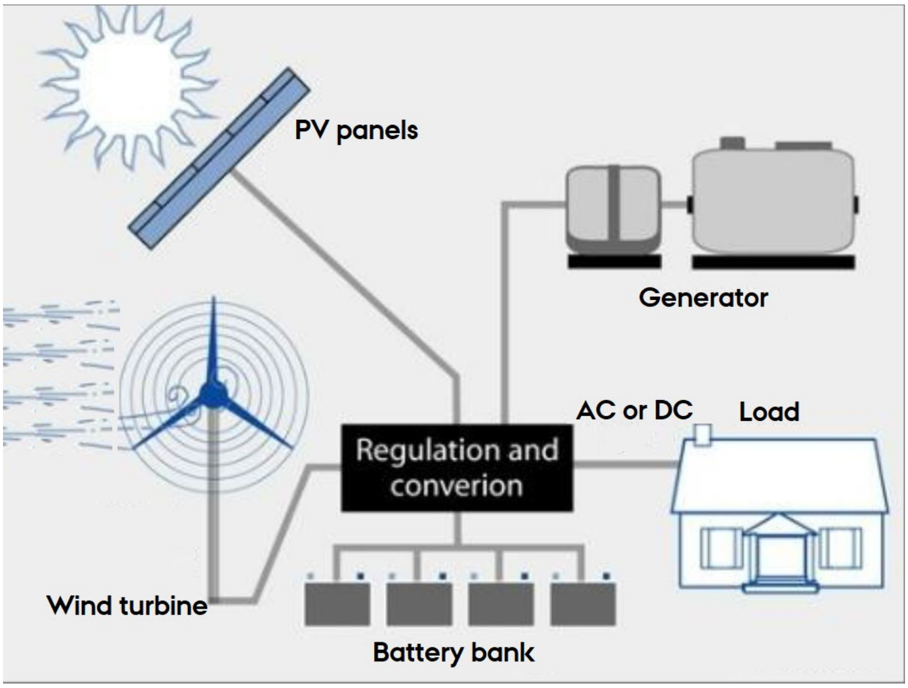

Fig. 2. A Schematic form of a hybrid power system [21]

Figure 2 shows the schematic of solar-wind hybrid system. As it can be seen the solar panels are being used to collect light and convert it to energy along with the wind turbines that collect energy from wind. In this case there is only one solar wind inverter that has inputs for two sources. It includes required AC to DC transformer to supply charge to batteries from AC generators. Eventually, the power from the solar panels and the wind turbines is filtered and stored in the battery bank [22].

The HRSE that combines both solar and wind energy key resources can operate in two modes: simultaneous and sequential. The difference between both is that the first one produces energy concurrently while the latter produces energy alternatively [19].

Taking into consideration the current situation of energy mix in Poland it is worth to notice that one of the main advantages of hybrid wind-solar system is generating approximately twice as much as solar or wind only systems.

Many different researchers have carried out on the development and assessment of the wind-solar hybrid systems. Ramli et al. [23] has presented a case study model based on the wind-solar system on the techno-economic energy analysis in Saudi Arabia. Furthermore, Khare et al. [19] presented a research study focused on different issues related to HRSE such as optimum sizing, feasibility analysis and control aspects.

There is a lot of research and studies conducted on that matter, however, this paper aims to describe the concept briefly to have the common understanding of the reader. To conclude, the solar-wind hybrid RE system is increasing day by day and has shown great development in the recent years for electricity production all over the world. Next section of the research will focus on the practical application of GIS in order to show the potential for solar-wind system implementation.

3 GIS mapping analysis

In order to answer the problem of this paper and the research questions, various data is required. The aim of this report was to utilise the free and open sources, such as Diva GIS, Geofabrik, Open Street Maps and GADM [24]. Afterwards, the acquired geodata was split based on the scope of the layers.

3.1 Data sources

The objective of this paper is to create a visualization of a hybrid energy map for Poland. In order to fulfil it and answer the research questions various data are required. Data were collected from numerous free and open sources. The base of the map was the wind and solar atlas. Wind map for Poland has been collected from Global Wind Atlas [25] and respectively, solar map for the same territory was collected from Global Solar Atlas [26]. Furthermore, other geodata required for the constraints have been collected from Diva and Geofabrik.

The infrastructural category includes layers that are the constraints such as roads, railways and waterbodies [27]. The next category includes only the land use, in this case – buildings. The last category consists of two main resources – wind speed and solar power. Table 1 summarizes all of the categories and criteria.

Diva-gis.org and Geodata.de are some of the most reliable and free geodata available in the market and thus, most of the data has been collected from there.

All the geodata gathered for this paper was collected in two formats, namely Shape files or TIFF files. These are the main formats used in this paper. Shapefiles are able to support point, line and area features. TIFF format is used for georeferenced raster imagery. It is mostly used for satellite or aerial photography [28].

Table 1. Collected geodata

Category	Criteria	Source	Requirements
Infrastructure	Roads	Diva-gis.org	
	Railways	Diva-gis.org	
	Waterways/waterbodies	Diva-gis.org	
	Borders	GADM.org	
Land use	Buildings	Geofabrik.de	
Resource Based Data	Wind speed	Global Wind Atlas	above 6m/s
	Solar speed	Global Solar Atlas	above 1,100 kWh/kW

In detail, regarding the GIS mapping process, the following steps were followed:

- Preprocessing the Data:
  - The first step involved gathering geospatial data from various sources such as the Global Wind Atlas, Global Solar Atlas, Diva-gis.org, and Geofabrik.de.
  - Data collected included wind and solar maps for Poland, as well as infrastructure data such as roads, railways, water bodies, and land use data like buildings.
  - The data collected were in different formats, including shapefiles and TIFF files, and needed to be organized and imported into QGIS.
- Spatial Analysis:
  - Once the data were imported and organized, spatial analysis was conducted to identify areas suitable for wind and solar power generation.
  - For wind power analysis, a raster function in QGIS was used to calculate areas with wind speeds greater than or equal to 6 meters per second (m/s), which is optimal for large-scale wind energy projects.
  - Similarly, for solar power analysis, areas with solar radiation exceeding 1,100 kilowatt-hours per kilowatt (kWh/kW) were identified as suitable for solar power generation.
  - Constraints such as roads, railways, water bodies, and buildings were overlaid on the wind and solar maps to identify feasible locations for hybrid energy generation.
- Visualization of Results:
  - After conducting spatial analysis, the results were visualized using QGIS to create the hybrid energy map of Poland.
  - The final map displayed areas with sufficient wind speed and solar radiation, indicating potential locations for hybrid energy generation.

- Areas that did not meet the criteria for wind and solar power generation were left out.
- The visualization provided a clear depiction of prime locations with the greatest potential for hybrid wind-solar energy generation in Poland, aiding decision-making for future renewable energy projects.

Based on the above information it is natural to conclude that the resource-based data layers are TIFF files as wind and solar data are difficult to present as point or lines. They are represented in raster format. All the other data layers for infrastructure and land use category are shape files as they are represented by point, line or polygon. Data format has a crucial impact on the reliability of the final outcome and therefore, it is significant to find the layers in the required formats.

3.2 Organising the data

Once all the required data was collected the next step of the analysis was to import it to QGIS and organise it. As a starting point, the coordinate reference system (CRS) has been set. CRS refers to the way in which spatial data that represents the earth's surface are flattened. In this project meters are used for defining the location of features instead of meridian of latitudinal or longitudinal. Therefore, Universal Transverse Mercator (UTM) zones have been selected for CRS of this papers, namely WGS 84/ UTM zone 33N. After setting the right CRS for the whole project, the same must be done for each layer in order to make sure that the features on the map are represented accurately.

3.3 Calculations

After gathering the data and setting up the CRS the calculations could be done. The process of calculating and creating the final map consists of 3 main steps with different sub-tasks and can be seen in Figure 3.

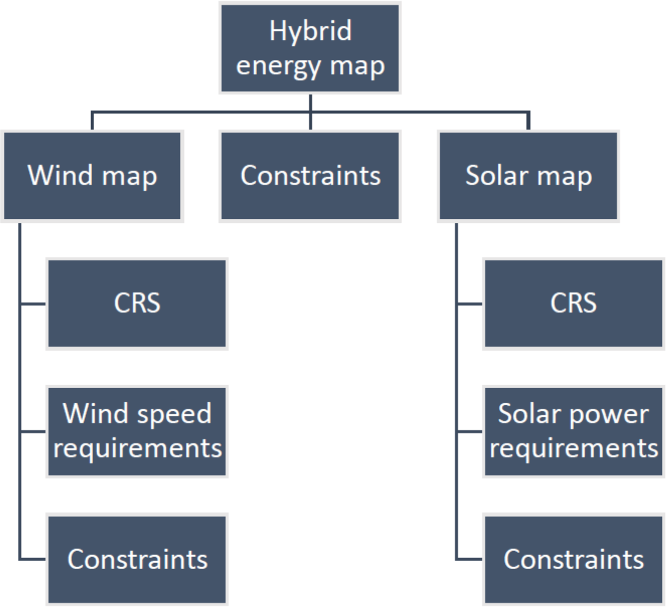

Fig. 3. Mapping Process

The wind map has been taken into consideration. The first thing was to set the correct CRS for all the layers as mentioned in the previous section.

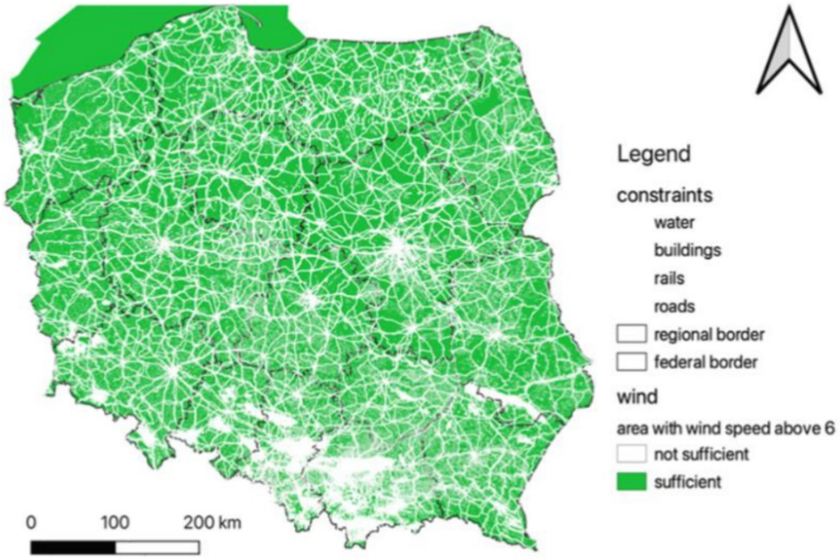

Fig. 4. Wind map with wind resource above 6m/s

As stated in Table 1, the requirement for wind speed is 6s/m in order to be optimal for large scale projects implementations. It has been done with use of raster function in QGIS, where the wind map at 100m has been calculated as >= 6, since below 6 m/s or 6.5 m/s it is very hard to find a viable approach on the long terms for any wind energy project [29]. Afterwards, the software has automatically shown the area that meets these requirements together with other constraints.

Figure 4 shows a map of Poland with available potential area (green) with wind speed equal or bigger than 6s/m. It means that theoretically the wind farms could be installed in the green points, and it would not interfere with the constraints chosen for this paper, namely: roads, railways, waterbodies and buildings. It is worth noticing that the map takes into consideration the offshore area of Poland. By clipping the area accordingly to the federal borders, the offshore space could not be clipped as the northern border of the country crosses the sea.

Afterwards, the same process has been performed for the solar map. The requirement chosen for the solar power was 1,100 kWh/kW. The purpose of choosing this value was to show the potential space available for rather big industrial PV installations. The outcome has been surprising as the potential area with solar power equal or bigger than 1,100 kWh/kW is more limited than the wind range. Figure 5 shows the final outcome of the solar map above 1,100 kWh/kW.

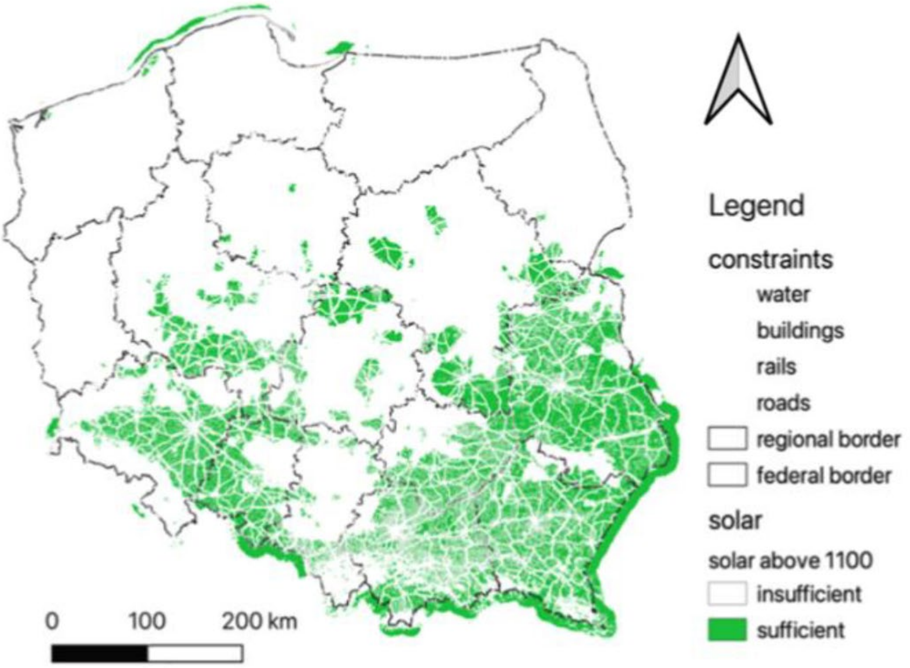

Fig. 5. Solar map with solar resource above 1,100 kWh/kW

3.4 Outcome

The outcome of the two maps has been calculated through raster function as follows: (wind map >=6) *1 AND (solar map >=1,100)*1

By using this function, QGIS tool showed only the area that was meeting the requirements of wind speed above 6s/m and solar power of 1,100 kWh/kW. It can be clearly seen that the space shrank radically from only wind potential area, then solar that was already limited to the final one.

Figure 6 shows the final visual outcome of the hybrid energy map of Poland, where green is the area with sufficient wind speed and solar power, and white is the insufficient area.

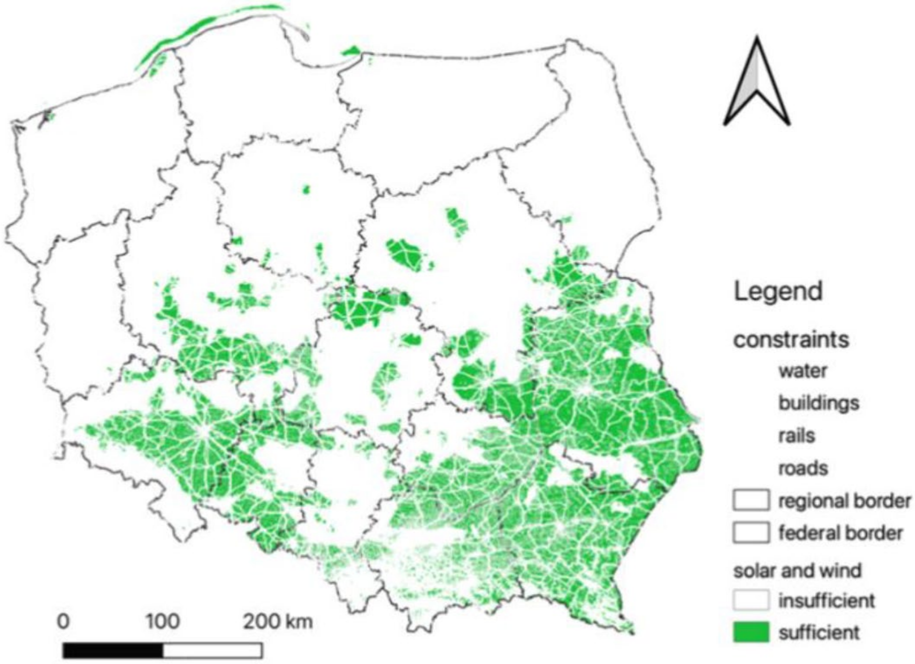

Fig. 6. Hybrid wind-solar power map of Poland

4 Discussion

The final outcome of this paper can lead to many different discussions. The current energy mix in Poland shows the need for renewable energy implementation in order to limit the use of hard coal and lignite and eventually eliminate it completely. As mentioned earlier in the paper, Poland is obliged by EU to reach 21% share of RES in gross final energy consumption by 2030. The preliminary hybrid energy map of Poland that is the outcome of this paper can serve as an aid for the companies as well as for the government to decide on the location of the future wind and solar farms. It can be seen which areas are worth to research further in order to use the hybrid renewable system.

Furthermore, the final visual outcome of this report can ease the decision on either to even consider use of hybrid renewable system or proceed with the single renewable source, e.g. wind farm. It can be clearly noticed that south-eastern part of Poland has higher potential for hybrid wind-solar use than the rest of the country.

The hybrid energy map for Poland presents policymakers with crucial insights into the distribution of renewable resources, guiding strategic decisions for sustainable energy development. By identifying regions ripe for wind-solar hybrid projects, policymakers can craft effective policies to incentivize investment and meet renewable energy targets. Investors benefit from clear guidance on optimal deployment areas, while collaboration with local communities and grid modernization efforts can address regulatory and infrastructure challenges. Overcoming barriers such as financing constraints and regulatory hurdles requires a concerted effort from stakeholders. Ultimately, leveraging the hybrid energy map's findings can drive Poland towards a greener and more resilient energy future.

The paper introduces a hybrid energy map designed specifically for Poland, focusing on the viability of wind and solar power generation. This map is crafted utilizing Geographic Information System (GIS) software along with geodata, which undergoes evaluation alongside various siting constraints. The objective of the study is to pinpoint the most promising locations for wind and solar power generation within Poland, taking into account infrastructural limitations, land usage, and the availability of renewable energy resources. Furthermore, the paper delves into an analysis of the current state of renewable energy in Poland, the benefits of employing hybrid resources, and the constraints integrated into the mapping process to identify suitable areas for hybrid energy utilization.

In contrast to prior studies, this paper adopts a comprehensive approach to identify potential sites for wind and solar power generation in Poland [31]. Leveraging GIS and geodata facilitates a meticulous examination of the country's constraints and resources [32]. Furthermore, the paper underscores the significance of renewable energy sources in fulfilling the EU's renewable energy objectives [33].

One limitation of the study lies in its exclusive focus on wind and solar power generation, potentially overlooking the broader spectrum of renewable energy sources in Poland. Moreover, the paper could enhance its impact by providing a more nuanced discussion on the policy ramifications of the hybrid energy map [34].

Future research endeavors could explore the potential of alternative renewable energy sources in Poland, such as hydropower and geothermal energy. Additionally, further scrutiny could be directed towards assessing the prospective ramifications of the hybrid energy map on the Polish energy market and the environment.

Last but not least, taking aside all the advantages of the hybrid wind-solar installations, it is worth discussing if the country has actually the prerequisites for that. The preliminary wind map shows that there is a lot of available space with sufficient wind speed in Poland, therefore, it could mean that the main focus should be on the wind farms and the hybrid installations should be implemented only if possible (in the area available in the hybrid energy map of this paper).

5 Conclusions

This section will aim to give a brief summary of the paper and answer the research questions. Next, the criticism of this report will be formulated and suggestions for further research are presented.

The research questions will be answered and finally the results to the main question will be presented. The aim of this research was to describe the current situation of renewable energy in Poland in order to give the reader a common understanding of the position the country is currently in. Briefly, Poland is still a country of coal, where the hard coal accounts for more than 50% of the total installed capacity in 2020. As Poland is a member of EU, it is obliged to develop the RES constantly. Currently, the obligation is 21% by 2030. However, the national laws and directives do not help to reach that goal [30].

Furthermore, the hybrid renewable energy system has been introduced together with its benefits. One of the main advantages of hybrid wind-solar system is generating approximately twice as much as solar or wind only systems, which in case of Poland's energy mix can be very beneficial and move things forward.

Last research question was regarding the constraints taken into consideration while mapping the available space. In this paper only the buildings, roads, railways and water have been taken into consideration. All the above helped answering the main problem of this paper, namely:

What are the prime locations in Poland with the greatest potential for wind and solar power generation?

The problem has been answered only visually in Figure 6. It shows clearly that the southern part of Poland has better potential for hybrid energy use and that is where the focus should be.

Every research or study faces difficulties and limits of certain elements and so does this one. Naturally, there are internal and external factors that limit the study. Therefore, this section aims to formulate the criticism of the report. Due to limited scope of the project, several assumptions had to be made. The wind map and solar map have been used in different units of measurement, which is a big limitation to the final outcome and requires further research. The wind speed has been indicated at 100m in m/s, whereas the solar power has been specified in kWh/kW. Moreover, the map is preliminary and thus, the buffers have not been included, since the researchers were aiming to show the big picture; after all a detailed analysis including all the buffer zones for the whole country, would have required a huge computing capacity, which was not available at the moment. Due to the above-mentioned, only the visual outcome has been delivered as the time and resource limitations did not allow the researcher to go more in depth with the further calculations.

There are many different ways to continue with this study, especially, as mentioned before, this is research for a preliminary hybrid energy map of Poland.

First of all, more detailed map in terms of constraints could be one of the topics to continue further with. This said, the constraints could include ecological constrains such as NATURA200 and other projects that limit the space available. Furthermore, as mentioned in the limitations section, the buffers could be added to the buildings, airports, etc. Once this is done, the wind map and solar map could be presented in the same units of measurements, e.g. kWh/kW. Furthermore, more detailed calculations in terms of the available space could be conducted. That would result in the percentage of the country that is available for the hybrid wind-solar system. Last but not least, once the before mentioned would be studied, there would be another very interesting topic for further study. Namely, verifying how many wind turbines and solar panels could be installed in the available space in Poland and what would be the outcome of it.

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Environment

Analyzing the Greek Legal Framework on Waste Management within the Circular Economy Context: Lessons learnt and lessons from EU Best Practices

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Abstract. The shift towards a circular economy is an essential goal of contemporary environmental policy, focusing on reducing waste generation, enhancing resource efficiency, and encouraging sustainable growth. This paper examines waste management approaches in the context of the national circular economy strategy, emphasizing regulatory structures, technological progress, and optimal methods for waste prevention, reuse, and recycling. Important policy tools, including extended producer responsibility (EPR), economic instruments, such as DRS and Pay as you Throw, as well as eco-design guidelines, and market incentives for recycled materials, are analyzed for their effectiveness and efficiency in minimizing environmental effects. The study additionally evaluates the impact of digital tools, data-informed decision-making, and cutting-edge waste treatment methods, such as mechanical-biological treatment (MBT), anaerobic digestion, and chemical recycling. Additionally, it addresses the socio-economic effects of moving to circular waste management systems, emphasizing the significance of involving stakeholders, raising public awareness, and fostering industry partnerships. Through the analysis of case studies and national progress indicators, this research uncovers obstacles and possibilities for enhancing waste management practices in accordance with circular economy principles. Results show that cohesive policy frameworks, investment in infrastructure, and shifts in behavior among consumers and businesses are crucial for realizing long-term sustainability objectives. The study concludes by providing strategic suggestions for policymakers, businesses, and researchers to enhance waste valorization, increase resource efficiency, and speed up the national circular economy transition. These insights enhance the overall comprehension of waste management as a crucial facilitator of a sustainable and resilient economy.

Keywords: Circular Economy, Waste Management, Resource efficiency, Reuse and Recycling, Extended Producer Responsibility (EPR)

1 Introduction

The shift towards a circular economy signifies a significant change in environmental policy, seeking to minimize waste, improve resource efficiency, and promote economic sustainability [1]. In contrast to the conventional linear economic model—founded on the "take, make, dispose" approach—the circular economy emphasizes closed-loop systems that involve continual reuse, refurbishment, or recycling of materials and products [2]. This model corresponds with the wider sustainability aims of the European Union (EU), as detailed in the European Green Deal and the Circular Economy Action Plan (CEAP) 2020, which highlight waste reduction, eco-friendly design, and separating economic growth from resource use [3,4].

As a member state of the EU, Greece has worked to harmonize its waste management policies with European directives, especially by incorporating the Waste Framework Directive (2008/98/EC), as amended, the Landfill Directive (1999/31/EC), and the Packaging and Packaging Waste Directive (94/62/EC) into its national laws [5,6,7]. The implementation of Law 4819/2021 and the National Waste Management Plan (NWMP) 2020–2030 demonstrates Greece's dedication to meeting EU waste reduction goals and advancing principles of a circular economy [8,9]. These actions involve improving separate waste collection, applying Extended Producer Responsibility (EPR) programs, and limiting single-use plastics [10].

Nonetheless, in spite of these legal progressions, considerable obstacles persist in achieving effective execution. Greece still displays one of the highest reliance rates on landfills in the EU, as more than 75% of its municipal waste ends up in landfills—significantly higher than the EU average of 23.4% [11,12]. Recycling rates continue to be low, affected by poor waste separation at the origin, insufficient investment in advanced waste management facilities, and a lack of public awareness [13,14, 15]. Additionally, regional differences in waste management capabilities worsen these issues, as islands and rural regions find it difficult to adhere to EU waste regulations [16].

Analyzing Greece’s waste management approaches alongside best practices from top EU countries exposes significant policy deficiencies. Member States like Germany, the Netherlands, and Sweden have effectively adopted high-performance circular economy models by enforcing strict landfill prohibitions, utilizing sophisticated digital waste monitoring systems, and providing economic incentives for material recovery [17,18]. Germany, for example, has reached a recycling rate surpassing 67% by implementing extensive EPR policies and utilizing Pay-As-You-Throw (PAYT) programs, which economically encourage households to reduce waste [19,20]. The Netherlands has launched industrial symbiosis initiatives via its Circular Economy Program 2050, promoting businesses to use each other’s waste as raw materials [21]. Through the implementation of comparable strategies, Greece could improve its waste management effectiveness and hasten its shift towards a sustainable circular economy.

This paper rigorously analyzes Greece's waste management legal framework, examining its compliance with EU directives and pinpointing systemic obstacles that impede its efficiency. Through the examination of effective patterns from other EU countries, this study seeks to offer data-driven policy suggestions to strengthen Greece's regulatory framework, upgrade waste management infrastructure, and promote a more robust circular economy.

2 Legal Framework on Waste Management in Greece

Greece's legal framework for waste management is mainly influenced by EU law, especially the Waste Framework Directive (Directive 2008/98/EC) and the Circular Economy Action Plan (European Commission, 2020). These instruments create a legal framework for sustainable waste management by focusing on waste reduction, re-use, recycling, and efficient resource use.

Three critical regulatory mechanisms governing waste management at the EU and national levels are the Extended Producer Responsibility (EPR), the Eco-Design Regulations, and the Waste Treatment Hierarchy Compliance. These frameworks ensure that producers and consumers take responsibility for minimizing waste generation, enhancing product sustainability, and complying with EU waste reduction targets.

At the national level, Greece has integrated these policies via legislative actions such as Law 4819/2021, the National Waste Management Plan (NWMP) for 2020–2030, and rules that implement the circular economy concept. Such rules are enshrined in the Greek National Plan on Circular Economy which outlines a strategic framework aimed at transitioning the country's economic model from a linear to a circular paradigm, promoting sustainable development and resource efficiency. It foresees 71 actions and initiatives covering the full spectrum of circular economy including all the waste streams concerned. Rooted in the principles of reducing waste, reusing materials, and recycling resources, the plan emphasizes the integration of circular economy practices across key sectors, including agriculture, manufacturing, construction, and tourism. It aligns with the European Green Deal and the EU Circular Economy Action Plan, setting ambitious targets for reducing environmental impacts, enhancing competitiveness, and fostering innovation. The plan also focuses on legislative reforms, incentives for green investments, public-private partnerships, and awareness-raising initiatives to support systemic change. By embedding circular economy principles in national policy, Greece aims to improve environmental performance, strengthen economic resilience, and contribute to climate neutrality goals.

The main tools of the Greek policy and legal framework consist of:

2.1 The Extended Producer Responsibility (EPR):

The Extended Producer Responsibility (EPR) is an environmental policy framework that shifts the responsibility of waste management from municipalities to producers. It mandates that producers manage their products throughout their entire life cycle, including post-consumer waste collection, recycling, and disposal [22]. The main objectives of EPR is to enhance waste collection and recycling rates by requiring producers to establish or finance waste management systems, to promote eco-design by incentivizing manufacturers to produce more durable, repairable, and recyclable products [23], to reduce landfill dependency by ensuring proper waste segregation, treatment, and recovery of materials [24] and to implement the "polluter pays" principle, making producers accountable for the environmental impact of their products [25]. The OECD framework on EPR defines it as a policy instrument that extends a producer's responsibility beyond production and sale to post-consumer waste management (OECD, 2016).

The legal foundation of EPR in the EU is primarily based on:

- The Waste Framework Directive (Directive 2008/98/EC, as amended) – Establishes the principles of EPR and mandates that member states implement policies requiring producers to manage post-consumer waste [25]
- The Packaging and Packaging Waste Directive (Directive 94/62/EC, amended by Directive (EU) 2018/852) – Requires manufacturers to take financial and operational responsibility for the collection, sorting, and recycling of packaging materials [26]
- The Directive 2012/19/EU on Waste Electrical and Electronic Equipment (WEEE Directive) – Imposes recycling obligations on producers of electrical and electronic goods [27]
- The Directive 2000/53/EC on End-of-Life Vehicles (ELV Directive) – Regulates the collection and recycling of vehicles, ensuring proper disposal of hazardous waste [28]

Greece has incorporated EPR principles into its national framework through Law 4819/2021, mandating producer responsibility in packaging, electronics, batteries, and end-of-life vehicles [29]. However, implementation challenges persist due to weak enforcement mechanisms, lack of financial incentives for producers, and inadequate monitoring systems [30]. Compared to Germany and France, which have well-developed EPR programs with strict compliance monitoring, Greece struggles with producer non-compliance and inefficient collection systems [31].

2.2 The Eco-Design Legal Framework

Eco-design regulations refer to legislative measures aimed at improving the sustainability of products throughout their life cycle. These regulations mandate energy efficiency, resource conservation, and recyclability standards in product design, ensuring that manufacturers minimize environmental impact [32].

The EU has developed comprehensive legislation to enforce eco-design principles, primarily through:

- Eco-Design Directive (Directive 2009/125/EC) – Establishes minimum environmental standards for energy-related products, reducing their energy consumption and environmental footprint [33]
- EU Circular Economy Action Plan (COM/2020/98) – Promotes sustainable product design, durability, and repairability, focusing on extending product lifecycles and reducing waste generation [34]
- Directive 2018/851 amending the Waste Framework Directive – Requires waste prevention measures in product design, prioritizing reuse, repair, and recyclability [35]

- Single-Use Plastics Directive (Directive (EU) 2019/904) – Imposes design restrictions on plastic products, banning non-recyclable single-use plastics [36]

Greece has transposed the Eco-Design Directive into national law, requiring manufacturers to comply with EU energy efficiency and recyclability criteria [37]. However, enforcement remains weak, with low compliance rates among Greek manufacturers compared to countries like Sweden and Denmark [38]. Key challenges include the lack of financial incentives for companies to adopt eco-friendly designs, the weak market surveillance mechanisms, resulting in non-compliant products and the limited consumer awareness regarding sustainable product choices [39].

2.3 Waste Treatment Hierarchy Compliance

The waste treatment hierarchy is a legally binding principle that dictates the preferred order of waste management strategies, ensuring that waste prevention, reuse, and recycling take precedence over landfill disposal [40]. The hierarchy prioritizes the Prevention – Avoiding waste generation, the Reuse – Extending the life of products and materials, the Recycling – Processing materials into new products, the Energy Recovery – Converting non-recyclable waste into energy and the Disposal (Landfill/Incineration) – The least preferred option [41].

The EU has established a strong legislative foundation for waste hierarchy compliance through:

- the Waste Framework Directive (2008/98/EC, Article 4) – Legally enforces the waste treatment hierarchy and obliges member states to prioritize waste prevention and recycling [42]
- the Landfill Directive (1999/31/EC) – Restricts landfilling of biodegradable municipal waste and mandates pre-treatment of waste before disposal [43]
- the Revised EU Waste Targets (Directive 2018/851) – Establishes recycling targets: 55% by 2025, 60% by 2030, and 65% by 2035 [44]
- the EU Circular Economy Package (2018) – Introduces restrictions on landfill usage and requires separate waste collection systems [45]

Greece continues to struggle with landfill dependency, with 75% of municipal waste still being landfilled, far exceeding the EU average of 23.4% [46]. Compliance failures have led to multiple EU infringement cases against Greece due to illegal landfill operations and poor waste management infrastructure [47].

Although there is a detailed legislative framework, considerable obstacles remain in the successful implementation of waste management policies in Greece. Administrative inefficiencies continue to be a significant obstacle, frequently associated with bureaucratic fragmentation, insufficient cooperation between national and local authorities, and uneven regulatory enforcement [48]. Research indicates that a lack of enforcement measures leads to significant non-compliance, especially in areas where obligations for waste separation and recycling are inadequately supervised [49]. Moreover, the restricted public knowledge and involvement in sustainable waste management practices impede the effectiveness of policy initiatives. Studies show that public engagement in recycling initiatives is minimal because of insufficient information sharing and the lack of incentives encouraging waste minimization and appropriate disposal [50]. This problem is worsened by infrastructure shortcomings, including a lack of recycling facilities and poor waste collection systems, which further restrict the effectiveness of waste reduction strategies [51]. Tackling these implementation gaps necessitates a comprehensive strategy, incorporating improved regulatory supervision, investment in waste management facilities, and focused educational initiatives to boost public engagement [52]. Enhancing governance systems and guaranteeing the efficient distribution of EU funds may significantly contribute to addressing these challenges and fulfilling Greece's circular economy goals [53].

Fig.1. The figure is visualizing the key challenges in Greece's waste management implementation. It highlights the severity of administrative inefficiencies, enforcement gaps, public awareness issues, and infrastructure deficiencies, based on recent studies and EU reports [54, 55, 56, 57]

3 EU Best Practices in Waste Management

To identify effective strategies for enhancing Greece's waste management system, this article analyzes successful initiatives implemented by EU member states, focusing on best practices in policy frameworks, innovative recycling technologies, circular economy approaches, and community-driven sustainability programs:

- Germany's Dual System (Duales System Deutschland, DSD) is an EPR-based waste collection and recycling scheme that has significantly enhanced packaging waste recovery and minimized landfill dependency. Under this system, producers and retailers finance the collection, sorting, and recycling of packaging waste through the Green Dot (Der Grüne Punkt) licensing fee, which incentivizes eco-friendly packaging design [58].
  The system operates alongside municipal waste collection services, ensuring separate collection streams for recyclables, organics, and residual waste. Since

its introduction in the 1990s, the recycling rate for packaging waste in Germany has surpassed 70%, one of the highest in Europe [59]. The success of this model lies in market-driven mechanisms, competitive waste management companies, and strict government oversight [60]. However, challenges such as over-complexity in sorting, contamination of recycling streams, and increasing plastic waste volumes require continuous adaptation [61]. Lessons for Greece include the adoption of EPR schemes for packaging, enhanced consumer participation in source separation, and improved waste-sorting infrastructure.

- Sweden's Waste-to-Energy Model: Near-Zero Landfilling. Sweden is globally recognized for its highly advanced Waste-to-Energy (WtE) system, which enables the country to achieve near-zero landfill dependency [62]. Approximately 99% of Sweden's municipal waste is either recycled or used for energy recovery, with only 1% ending up in landfills [63]. This success is attributed to a well-integrated waste hierarchy, where non-recyclable waste is converted into electricity and district heating through state-of-the-art incineration plants [64].
  Sweden's WtE incinerators use advanced flue gas treatment technologies, reducing harmful emissions while maximizing energy recovery efficiency. The country also imports waste from neighboring countries, such as Norway and the UK, demonstrating the economic viability of WtE solutions [65]. However, critics argue that over-reliance on incineration can discourage higher waste prevention and recycling rates [66].
  For Greece, where landfill dependency remains high (~80%), investing in modern WtE facilities (gasification or pyrolysis), combined with strict waste sorting policies, could significantly reduce waste volumes while producing renewable energy.

- The Netherlands has established itself as a leader in circular economy initiatives, focusing on waste prevention, material recovery, and industrial symbiosis (10). The Dutch government has set an ambitious goal of achieving a 50% reduction in primary raw material consumption by 2030 and transitioning to a fully circular economy by 2050 [67].
  Key strategies include the Mandatory Extended Producer Responsibility (EPR) schemes for packaging, electronics, and textiles, the High landfill taxation and bans on landfilling recyclable materials to promote reuse and recycling [68], the Material recovery hubs in industrial zones, where waste from one industry serves as input for another (industrial symbiosis) [69], the consumer awareness programs and sustainable product design incentives to foster responsible consumption [70]. The Netherlands has also been pioneering chemical recycling, which breaks down plastics into their molecular components, enabling higher-quality recycling outcomes [71].
  Greece can learn from the Dutch approach by strengthening EPR laws, imposing landfill restrictions, promoting industrial symbiosis, and investing in chemical recycling technologies to maximize material recovery rates.

The waste management strategies employed by Germany, Sweden, and the Netherlands demonstrate how policy-driven initiatives can enhance recycling, material recovery, and landfill diversion rates. Greece can benefit from:

- Germany's EPR-based Dual System, focusing on producer responsibility for packaging waste.
- Sweden's Waste-to-Energy model, as an alternative to landfilling residual waste.
- The Netherlands' Circular Economy strategy, promoting material recovery, industrial symbiosis, and waste prevention.

By integrating these best practices, Greece can align with EU waste directives, improve waste treatment infrastructure, and move towards circular economy.

4 Waste Management Process, Economic Tools, Extended Producer Responsibility and Separate Collection at Source

Effective waste management is a critical component of sustainable development and environmental protection. The integration of systematic waste processing methods, economic instruments, producer responsibility policies, and efficient waste separation can significantly enhance recycling rates, resource recovery, and waste diversion from landfills. This chapter explores the waste management process, the role of economic tools, the effectiveness of Extended Producer Responsibility (EPR), and the importance of separate collection at source as fundamental strategies for improving municipal and industrial waste management.

4.1 Waste Management Process

The waste management process involves the systematic handling of waste from its generation to its final disposal or recovery. According to the Waste Hierarchy Framework, this process follows a priority order: prevention, reuse, recycling, recovery (including energy recovery), and disposal [72]. Proper waste management ensures the minimization of environmental impacts, the conservation of natural resources, and the reduction of greenhouse gas emissions associated with landfilling [73].

The key stages in the waste management process include:

- Waste generation and collection: Households, industries, and commercial activities generate different types of waste, requiring tailored collection systems [74]
- Transportation and sorting: Collected waste is transported to sorting facilities where recyclables are separated from residual waste [75]
- Recycling and recovery: Separated materials undergo processing to be reintegrated into production cycles, while non-recyclable waste may be used for energy recovery [76]
- Final disposal: Residual waste that cannot be recycled or recovered is sent to landfills or incineration plants with strict environmental controls [77]

Despite advancements in waste treatment technologies, challenges such as low source separation rates, infrastructure deficiencies, and illegal dumping remain significant obstacles in many countries, including Greece [78].

4.2 Key Economic Tools in Waste Management: A Pathway to Sustainability

Economic tools play a fundamental role in shaping waste management policies, influencing waste generation behaviors, and driving circular economy principles. By integrating pricing mechanisms, fiscal policies, and market-based incentives, governments can internalize the environmental costs of waste and encourage resource-efficient practices [79]. These instruments promote waste prevention, increase recycling rates, and reduce landfill dependency, ultimately leading to financially sustainable waste management systems [80].

4.2.1 Landfill Taxes and Bans

Landfill taxes are one of the most effective policy tools for reducing waste disposal **in landfills** and promoting **higher recycling and recovery rates**. The European Commission has emphasized the role of landfill taxation in shifting waste away from landfills towards more sustainable treatment options [81].

Sweden and the Netherlands have landfill bans on recyclable materials and impose taxes exceeding €100 per tonne of landfilled waste [82].

The United Kingdom introduced a landfill tax in 1996, increasing it progressively to £96.70 per tonne in 2021, leading to an 85% reduction in municipal waste sent to landfills between 1996 and 2020 [83].

Greece, with landfill taxes around €20 per tonne, still struggles with high landfill dependency (~80%), demonstrating that higher tax rates are necessary to achieve significant reductions [84].

4.2.2 Deposit-Refund Systems (DRS): A Legal and Policy Perspective on Circular Economy Implementation

Deposit-refund systems (DRS) represent a market-based environmental policy instrument designed to promote the circular economy and extended producer responsibility (EPR) by encouraging the return of beverage containers for recycling. These systems function by imposing an upfront deposit on packaging, which is refunded to consumers upon the return of the container to designated collection points [85].

The legal foundation of DRS in the European Union (EU) is embedded within the Waste Framework Directive (2008/98/EC) and the Single-Use Plastics Directive (2019/904), which mandate increased collection targets for plastic beverage containers and encourage EPR-based financial responsibility for producers [86]. The EU Circular Economy Action Plan (2020) further supports DRS as a proven mechanism for achieving high collection and recycling rates, thereby reducing littering, conserving resources, and improving waste separation at source [87].

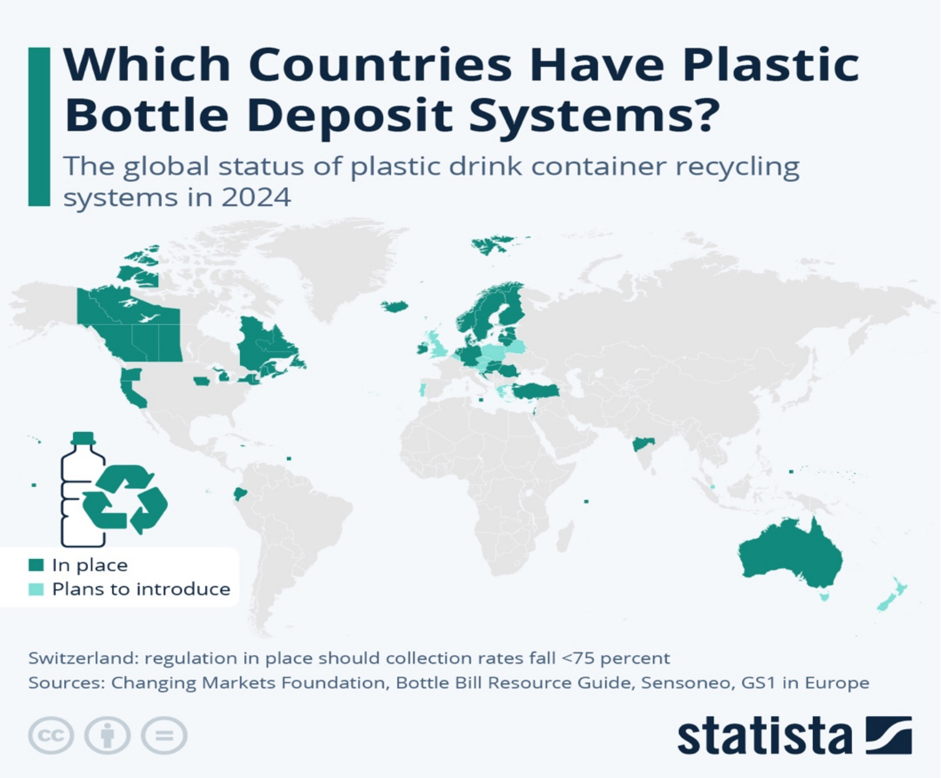


Fig.2. [88]

Despite EU-wide policy recommendations, DRS adoption remains uneven across member states, with significant variations in system design, financial responsibility, and collection infrastructure [89].

Germany operates one of the most legally structured and efficient DRS models in the EU, introduced under the Packaging Act (Verpackungsgesetz, 2019), which mandates a refundable deposit on single-use plastic and aluminum beverage containers [90]. Key legal provisions include:

- A mandatory deposit (€0.25 per container) for all PET bottles and aluminum cans
- A nationwide return infrastructure of reverse vending machines in supermarkets, ensuring accessibility for consumers
- Producer obligations under EPR laws, requiring beverage manufacturers to finance and operate collection systems [91]

The legal structure of Germany's DRS has resulted in a 98% return rate, effectively eliminating beverage container waste from public spaces and ensuring high-quality material recovery [92].

Lithuania introduced a nationwide DRS in 2016 under the Lithuanian Packaging Waste Management Regulations, aligning with the EU's EPR and circular economy requirements [93]. The system includes:

- A deposit of €0.10 per beverage container, covering PET, aluminum, and glass bottles
- The legal obligation for retailers to accept all returned containers, improving consumer participation
- Full financial responsibility on producers, ensuring the economic sustainability of the system

Following implementation, Lithuania's beverage container return rate surged from 34% to 92% within two years, demonstrating the effectiveness of legally enforced producer responsibility mechanisms [94].

Norway operates a unique, industry-led DRS system, regulated under the Pollution Control Act (1981) and the Waste Regulations (2004). Unlike other EU systems, Norway's DRS is voluntary but financially incentivized, where:

- Producers finance and operate the system, with state oversight ensuring compliance.
- A tiered taxation model provides tax exemptions for high collection rates, incentivizing producers to maximize returns [95].
- The system achieves return rates exceeding 95%, showcasing the efficiency of self-regulated industry-driven EPR frameworks [96].

Greece currently lacks a mandatory national DRS, relying primarily on municipal collection systems, which yield low beverage container recycling rates (~50%) [97]. The Waste Management National Plan (2020-2030) and Greece's alignment with EU Circular Economy goals necessitate the introduction of a comprehensive, legally binding DRS.

The key legal and policy considerations for Greece include:

- Amending national packaging legislation to mandate a deposit on all single-use beverage containers in compliance with Directive 2019/904/EU
- Establishing industry-funded collection systems, placing financial responsibility on producers and retailers under an EPR framework
- Introducing legal penalties for non-compliance to ensure retailers and producers participate in the system
- Creating a standardized return infrastructure to ensure consumer accessibility

Evidence from Germany, Lithuania, and Norway suggests that a well-structured legal framework with clear producer obligations, financial incentives, and enforcement mechanisms can significantly enhance beverage container recycling rates, reduce illegal waste disposal, and align Greece with EU waste reduction targets [98].

Deposit-refund systems have emerged as a legally effective tool for circular economy implementation, supported by EU waste regulations and national EPR frameworks. Case studies from Germany, Lithuania, and Norway demonstrate that clear legislative structures, strong producer responsibility mandates, and financial incentives are essential to the success of a high-performance DRS.

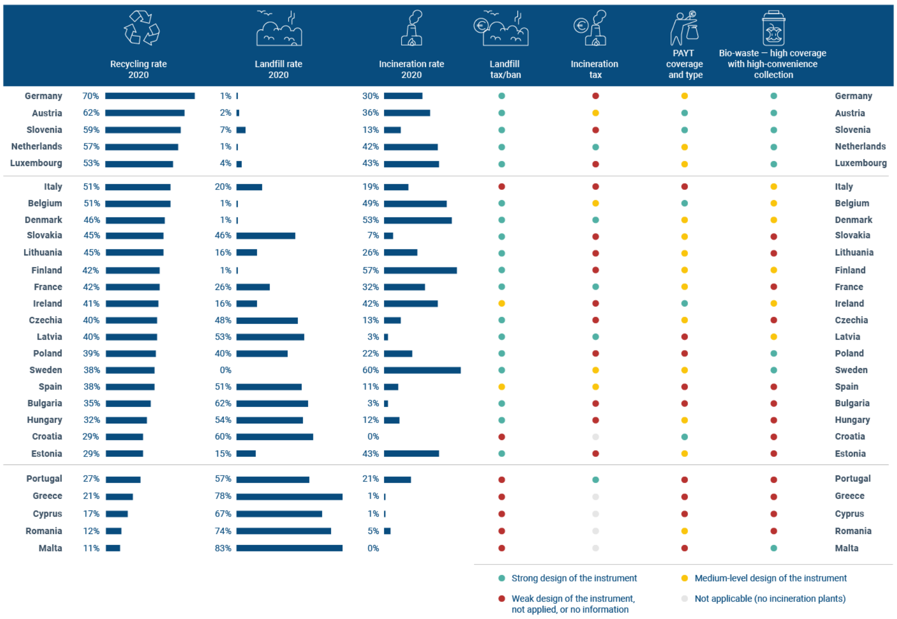
For Greece, establishing a nationally regulated, producer-funded DRS in line with EU waste directives would increase recycling rates, improve material recovery, and reduce littering, contributing to a more circular and sustainable waste management system.

4.2.3 Pay-As-You-Throw (PAYT): A Legal and Policy Analysis in Waste Management

Pay-As-You-Throw (PAYT), also referred to as variable-rate pricing or unit-based pricing, is a waste management policy that charges households and businesses based on the actual amount of waste they dispose of. This system operates under the "polluter pays principle" (PPP) outlined in the EU Waste Framework Directive (2008/98/EC), which mandates that waste generators bear the financial cost of waste disposal [99].

PAYT is recognized as a market-based environmental instrument that aligns with circular economy principles by internalizing the external costs of waste disposal, reducing waste generation, and incentivizing higher recycling rates [100].

At the EU level, the Circular Economy Action Plan (2020) promotes PAYT as an effective waste prevention tool, encouraging member states to adopt PAYT models to comply with landfill diversion targets under the Landfill Directive (1999/31/EC) [101]. PAYT systems are legally structured through municipal ordinances, national waste laws, and extended producer responsibility (EPR) policies, making them a critical regulatory tool for achieving waste reduction goals [102].



	Recycling rate 2020	Landfill rate 2020	Incineration rate 2020	Landfill tax/ban	Incineration tax	PAYT coverage and type	Bio-waste – high coverage with high-convenience collection	
Germany	70%	1%	30%	🟢	🔴	🟡	🟢	Germany
Austria	62%	2%	36%	🟢	🟡	🟢	🟢	Austria
Slovenia	59%	7%	13%	🟢	🔴	🟢	🟢	Slovenia
Netherlands	57%	1%	42%	🟢	🟢	🟡	🟢	Netherlands
Luxembourg	53%	4%	43%	🟢	🔴	🟡	🟢	Luxembourg
Italy	51%	20%	19%	🔴	🔴	🔴	🟡	Italy
Belgium	51%	1%	49%	🟢	🟡	🟢	🟡	Belgium
Denmark	46%	1%	53%	🟢	🟢	🟡	🟡	Denmark
Slovakia	45%	46%	7%	🟢	🔴	🟡	🔴	Slovakia
Lithuania	45%	16%	26%	🟢	🔴	🟡	🔴	Lithuania
Finland	42%	1%	57%	🟢	🔴	🟡	🟡	Finland
France	42%	26%	32%	🟢	🟢	🟡	🔴	France
Ireland	41%	16%	42%	🟡	🔴	🟢	🟡	Ireland
Czechia	40%	48%	13%	🟢	🔴	🟡	🔴	Czechia
Latvia	40%	53%	3%	🟢	🟢	🔴	🟡	Latvia
Poland	39%	40%	22%	🟢	🔴	🔴	🟢	Poland
Sweden	38%	0%	60%	🟢	🟡	🟡	🟢	Sweden
Spain	38%	51%	11%	🟡	🟡	🔴	🔴	Spain
Bulgaria	35%	62%	3%	🟢	🔴	🔴	🔴	Bulgaria
Hungary	32%	54%	12%	🟢	🔴	🟡	🔴	Hungary
Croatia	29%	60%	0%	🔴	⚪	🟢	🔴	Croatia
Estonia	29%	15%	43%	🟢	🔴	🟡	🔴	Estonia
Portugal	27%	57%	21%	🔴	🟢	🔴	🔴	Portugal
Greece	21%	78%	1%	🔴	⚪	🔴	🔴	Greece
Cyprus	17%	67%	1%	🔴	⚪	🔴	🔴	Cyprus
Romania	12%	74%	5%	🔴	⚪	🟡	🔴	Romania
Malta	11%	83%	0%	🔴	⚪	🔴	🟢	Malta

🟢 Strong design of the instrument
🟡 Medium-level design of the instrument
🔴 Weak design of the instrument, not applied, or no information
⚪ Not applicable (no incineration plants)

Fig.3. Recycling, landfill and incineration rates for municipal waste and key policy instruments used [103]

Among the EU States Belgium and Switzerland are developing success practices in PAYT implementation.

Belgium and Switzerland have implemented national PAYT frameworks, integrating the system within local waste management laws and municipal tax structures [104].

Belgium's Waste Decree (2012) legally mandates municipalities to implement PAYT schemes in compliance with EU waste hierarchy principles, resulting in a 40% reduction in municipal solid waste (MSW) generation and an increase in recycling rates [105].

Switzerland's Waste Management Act (2000) enforces PAYT at the municipal level, using prepaid waste bags and volume-based pricing. This policy has successfully reduced residual waste generation by nearly 50%, while ensuring high participation in source-separated recycling schemes [106].

Cyprus has undertaken several initiatives:

- Stakeholder Engagement: Regular meetings between the Ministry of Agriculture, Rural Development, and Environment, the Union of Municipalities, and the Union of Communities have been established to devise actionable plans for PAYT rollout [107]
- Pilot Programs: Municipalities such as Aglantzia have initiated pilot PAYT schemes to assess feasibility and gather data for broader application [108]
- Public Awareness Campaigns: Educational programs are being developed to inform citizens about the benefits of PAYT and encourage participation in waste sorting and reduction efforts.

The successful implementation of PAYT in Cyprus is expected to enhance Recycling Rates: Encourage citizens to sort waste effectively, thereby increasing recycling percentages, reduce Landfill Usage: Decrease the volume of waste directed to landfills, aligning with EU waste reduction targets and foster Environmental Responsibility: Promote a culture of sustainability and environmental stewardship among residents. By overcoming current challenges and leveraging legislative support, Cyprus aims to achieve a more sustainable and efficient waste management system through the PAYT initiative.

These cases demonstrate that mandatory legislative backing, coupled with strict enforcement and municipal oversight, is essential for PAYT effectiveness.

Greece generates approximately 500 kg of waste per capita annually, yet only 20% of waste is recycled, with the remaining 80% largely landfilled (13). Despite alignment with EU waste directives, Greece has not yet established a comprehensive national PAYT framework, relying primarily on fixed-rate municipal waste fees [109].

To effectively introduce PAYT, Greece must address several legal and policy challenges:

- Amending national waste legislation (e.g., Law 4042/2012, transposing the EU Waste Framework Directive) to mandate PAYT at the municipal level
- Incentivizing municipalities to adopt PAYT through financial grants and EU funding mechanisms
- Strengthening enforcement mechanisms to prevent illegal waste disposal resulting from PAYT cost avoidance

- Integrating PAYT with Extended Producer Responsibility (EPR) for packaging waste to offset implementation costs [110]

The success of PAYT in Belgium, Switzerland and Cyprus illustrates that clear legal frameworks, strong enforcement, and economic incentives are critical to ensuring the system's effectiveness. Greece's high waste generation and low recycling rates suggest that PAYT adoption could be a transformative policy, significantly improving waste separation at source, reducing landfill dependency, and lowering municipal waste management costs [111].

PAYT is a legally backed economic instrument that promotes waste reduction, recycling, and cost efficiency in municipal waste management. Case studies from Belgium, Switzerland and Cyprus show that legislative mandates, municipal enforcement, and technological innovations are key to successful PAYT implementation.

For Greece, introducing a PAYT-based national waste pricing policy could enhance compliance with EU waste directives, improve recycling rates, and reduce landfill dependency, contributing to a more sustainable waste management system.

4.2.4 Subsidies and Incentives for Sustainable Waste Management

Governments use subsidies and financial incentives to support circular economy initiatives, develop waste treatment infrastructure, and stimulate recycling industries [112].

France provides financial aid for recycling innovation, including tax incentives for companies adopting eco-design principles [113].

The EU's Horizon 2020 program allocates billions to waste management research and pilot projects, fostering circular economy solutions [114].

In Sweden, subsidies for biogas production from food waste have increased anaerobic digestion plant numbers, reducing organic waste landfilling by over 60% [115].

For Greece, increasing investment in waste-to-energy, biowaste treatment, and material recovery technologies through financial incentives is essential to modernizing its waste management system [116].

Economic tools such as landfill taxes, DRS, PAYT schemes, and targeted subsidies have proven to be effective policy instruments for improving waste management efficiency. Countries that implement these economic instruments achieve higher recycling rates, lower waste generation per capita, and reduced landfill dependency. For Greece, adopting a combination of PAYT, DRS, landfill taxation, and financial incentives will be crucial in transitioning towards a circular economy and sustainable waste management system.

5 Challenges and Opportunities in Greece's Circular Economy Transition

The circular economy aims to minimize waste generation, optimize resource efficiency, and close material loops through sustainable production and consumption patterns. While Greece has made legislative progress in aligning with EU circular economy policies, the country continues to face significant implementation barriers in transitioning from a linear to a circular waste management system. Despite these challenges, strategic policy adjustments, infrastructure investments, and enhanced stakeholder collaboration offer opportunities for advancing circular economy practices in Greece.

5.1 Challenges in Implementing Circular Waste Management in Greece

5.1.1 Regulatory Gaps: Weak Enforcement and Policy Inconsistencies

Although Greece has transposed key EU waste management directives such as the Waste Framework Directive (2008/98/EC) and the Circular Economy Action Plan (2020) into national law, weak enforcement and inconsistencies in policy application hinder effective implementation [117].

Lack of enforcement mechanisms results in high non-compliance rates among businesses and municipalities, particularly in waste separation and landfill diversion targets [118].

Greece continues to struggle with illegal dumping and poor landfill management, despite the EU Landfill Directive (1999/31/EC), which requires waste minimization and controlled disposal [119].

Regional disparities in regulatory oversight lead to inconsistent waste management standards across municipalities, affecting the efficiency of circular economy initiatives [120].

A stronger governance framework, including increased inspections, stricter penalties, and digital monitoring of waste streams, is crucial for ensuring compliance with EU circular economy goals.

5.1.2 Infrastructure Deficiencies: Limited Facilities for Advanced Waste Treatment

Greece’s waste management infrastructure remains underdeveloped, limiting the country’s ability to process, recycle, and recover materials efficiently [121].

Lack of material recovery facilities (MRFs) and modern waste treatment plants results in low recycling rates (~20%) compared to the EU average of 48% [122].

Limited anaerobic digestion and composting facilities restrict the potential for biowaste valorization, leading to high organic waste landfilling (~65% of municipal waste) [123].

Poor integration of digital tracking systems for waste collection and sorting contributes to inefficiencies in waste logistics and contamination of recyclables [124].

Expanding recycling and biowaste treatment infrastructure, along with integrating waste-to-energy (WtE) technologies, would enhance circular economy performance by diverting waste from landfills and promoting material recovery.

5.1.3 Public Engagement Issues: Low Awareness and Participation

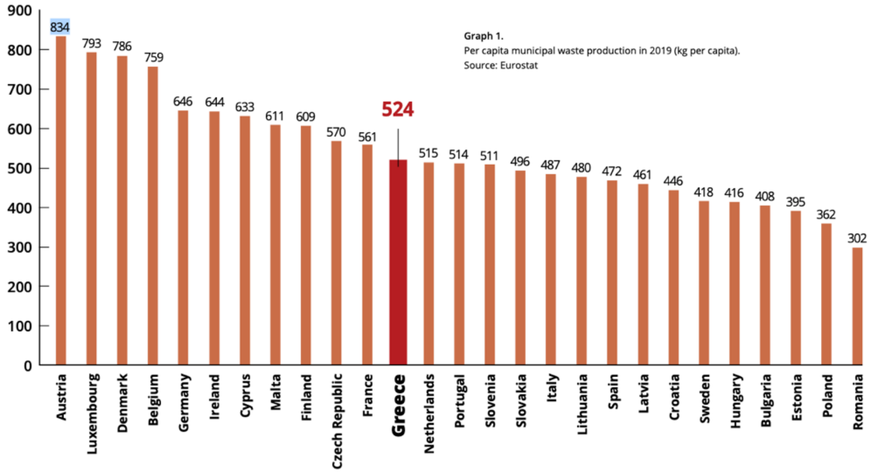
Public engagement is a critical enabler of circular economy success, yet low awareness and participation in Greece remain significant barriers [125].

Studies indicate that only 30% of Greek households regularly separate waste at source, compared to 70% in countries with mature recycling systems such as Germany and Sweden [126].

Limited environmental education programs and incentives for waste sorting reduce public motivation to participate in circular economy initiatives [127].

Consumer behavior trends favor single-use plastics, despite the EU Single-Use Plastics Directive (2019/904/EC) banning certain disposable items [128].

Increasing public awareness campaigns, deposit-return schemes (DRS), PAYT, and financial incentives could enhance participation in waste separation, recycling, and sustainable consumption behaviors.



Graph 1.
Per capita municipal waste production in 2019 (kg per capita).
Source: Eurostat

1. Data from Eurostat. Recovery from here.
2. There are serious doubts about the accuracy of the reported recycling rate in Greece, as the preparation for recycling does not necessarily translate into actual recycling. Moreover, the credibility of the data collected by the responsible authorities has been undermined. Recent report by the European Environment Agency shows that the actual recycling rate in Greece is not more than 16%.

Fig.4. Per capita municipal waste production in 2019 (kg per capita). Source: Eurostat [129].[103]

5.2 Opportunities for Advancing Circular Economy in Greece

5.2.1 Policy Refinement: Strengthening EPR Mechanisms and Market Incentives

The Extended Producer Responsibility (EPR) framework in Greece requires further strengthening to enhance market incentives for recycled materials and support circular product design [130].

Expanding EPR obligations to more product categories, such as textiles and electronics, could improve waste recovery rates [131].

Introducing tax incentives for circular businesses and eco-friendly packaging materials would drive investment in sustainable production models [132].

Harmonizing national recycling targets with EU directives, such as Directive 2018/851/EC, would ensure compliance with the EU Green Deal objectives [133].

5.2.2 Investment in Infrastructure: Expanding and upgrading Recycling and Waste Treatment Facilities

EU Cohesion and Recovery Funds offer an opportunity to invest in circular economy infrastructure, addressing long-standing deficiencies [134].

Allocating EU recovery funds (€5 billion by 2030) toward advanced waste treatment plants and recycling hubs can improve waste recovery efficiency [135].

Expanding biowaste treatment capacity through composting and anaerobic digestion plants would reduce organic waste landfilling [136].

Adopting AI-powered waste sorting technologies can increase the purity of recyclable materials and reduce contamination rates [137].

5.2.3 Stakeholder Collaboration: Encouraging Industry and Community Engagement

A multi-stakeholder approach involving government agencies, industries, and local communities is crucial for Greece's circular economy transition [138].

Industry partnerships with waste management firms and research institutions can drive eco-innovation [139].

Community-led circular economy initiatives can improve local recycling participation and waste prevention [140].

Cross-border cooperation with EU partners can facilitate knowledge transfer and investment in circular solutions [141].

While regulatory gaps, infrastructure deficiencies, and low public engagement present challenges, policy refinement, strategic investments, and stakeholder collaboration offer pathways to accelerate Greece's circular economy transition. Strengthening EPR frameworks, expanding waste treatment capacity, and enhancing public participation will be key to achieving sustainable waste management and resource efficiency goals.

6 Conclusion and Policy Recommendations

To achieve a fully functional circular economy, Greece must implement cohesive policy frameworks, enhance infrastructure investments, and encourage behavioral changes among consumers and businesses. Addressing existing challenges in waste management and resource efficiency is crucial for long-term sustainability. Based on the analysis, the following recommendations are proposed:

- Strengthen Extended Producer Responsibility (EPR) Implementation:
  Boost the implementation of the Greek National Plan on Circular economy through the implementation by joint ministerial decisions of all the 71 actions and initiatives it foresees.
  Enforce stricter accountability measures for producers to minimize waste generation, ensuring compliance with the EU Waste Framework Directive (2008/98/EC) and the Circular Economy Action Plan [142].

Encourage eco-design initiatives to ensure products are reusable and recyclable. Studies show that improved product design can reduce material waste by up to 30% [143].
Monitor and evaluate EPR compliance to enhance effectiveness, leveraging data from the European Environment Agency (EEA, 2023). Research indicates that countries with well-implemented EPR schemes have achieved packaging waste recycling rates above 60%, while Greece remains at 54.1% [144].

- Enhance Technological Adoption:
  Invest in digital tools such as AI-driven waste sorting systems and smart recycling bins, which can increase sorting efficiency by 40% [145].
  Upgrade waste treatment infrastructure, including modern material recovery facilities (MRFs) and anaerobic digestion plants, to address Greece's current low recycling rate of approximately 20%, compared to the EU average of 48% [146]. Countries with advanced waste treatment facilities, such as Germany and the Netherlands, have achieved over 65% recycling rates [147].
  Support research and innovation in circular economy technologies, allocating funds through EU programs such as Horizon Europe, which has earmarked €10 billion for green innovation [148]. Reports suggest that every €1 billion invested in circular economy initiatives generates approximately 50,000 new jobs [149].

- Promote Public Awareness Campaigns:
  Launch nationwide educational initiatives to inform citizens about waste reduction and recycling best practices. Surveys indicate that only 30% of Greek households consistently separate waste at the source, compared to 70% in countries like Germany and Sweden [150]. A study in Sweden found that strong public awareness programs contributed to their 99% municipal waste recovery rate [151].
  Develop incentive programs, such as deposit-return schemes (DRS), which have increased plastic bottle recycling rates to over 90% in countries where implemented, such as Germany [152]. In contrast, Greece's plastic bottle recycling rate stands at approximately 30% [153].
  Collaborate with schools, businesses, and local communities to increase engagement in sustainability efforts, using successful case studies from other EU member states. For example, Belgium's "Fost Plus" system has led to a 95% recycling rate for household packaging waste.

- Encourage Cross-Sector Collaboration:
  Establish partnerships between government, industry, and research institutions to develop sustainable waste management solutions, as seen in Finland's "Circular Economy Roadmap" [154]. Finland's collaboration model has helped achieve a 55% circular material use rate, compared to Greece's 3.1%.
  Facilitate knowledge sharing through circular economy networks and best practice exchanges, aligning with EU Circular Economy Stakeholder Platform initiatives. Studies show that knowledge-sharing platforms increase adoption rates of circular economy practices by up to 40%.

Promote circular business models, such as product-as-a-service (PaaS) and industrial symbiosis, which have been shown to increase resource efficiency by up to 50% in industrial sectors [155]. Reports suggest that transitioning to circular business models could add €1.8 trillion to the European economy by 2030.

By adopting these strategies, Greece can accelerate its transition towards circular economy. A concerted effort by policymakers, businesses, and the public will be essential in achieving long-term environmental and economic benefits. Implementation of these policies could result in a 25% reduction in landfill dependency and a 15% increase in material recovery rates by 2030 [160]. Additionally, a well-implemented circular economy framework could boost Greece's GDP by up to 2% and create over 50,000 green jobs by 2035 [156].

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A review of contemporary sewage sludge treatment and management methods in European countries with an emphasis on Greece

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Abstract. Municipal sewage sludge is an acute problem in both developed and developing countries. Researchers are conducting many experiments to solve this problem. There are many methods of disposal, neutralization, or reuse of sediments after neutralization. The review of contemporary sewage sludge treatment and management methods in European countries with an emphasis on Greece will provide more information about the most appropriate choice for the use of sewage sludge in Greece.

The challenges linked to aligning sewage sludge management with the principles of sustainable development are examined. The article references information sourced from the publication in Official Gazette 2692/B/21-04-2023, alongside ongoing projects in Greece concerning sludge treatment within Urban Wastewater Treatment Units. Furthermore, it delves into the projections and strategies for sewage sludge processing in Greece, by analyzing the obligations and projections outlined in the National Waste Management Plan 2015, juxtaposed with the revised National Waste Management Plan of 2020.

In Greece, following the initiation of the "Treatment and purification of urban wastewater in environmentally sensitive settlements and modernization of facilities" project under the Recovery and Resilience Fund from 17/01/2023, there is a noticeable shift towards thermal treatment of sludge utilizing drying methods (including solar, etc.). By 2025, this trend is expected to significantly alter the landscape of treated sludge disposal in Greece. However, addressing the management of sludge generated by municipal urban waste treatment units and selecting the most suitable strategy for urban sewage sludge management continues to pose a complex challenge.

Keywords: Wastewater treatment plants (WWTPs); Sewage Sludge; Management.

1. Introduction

Rapid population growth, climate change, urbanization and depletion of natural resources compel global society to prepare to be disadvantaged with respect to certain natural resources [1]. Other approaches to resource utilisation, such as the recycling of waste, particularly sewage sludge, offer potential solutions to mitigate this problem [2]. In line with this, the National Waste Management Plan [3] (ESDA, 2020) proposes that sewage sludge effluent should be recognised as a valuable resource rather than simply categorised as waste. Shaddel et al [2] state that wastewater contains nutrients, need research for food production, and that wastewater and sludge have been explored in the last decade for nutrient recovery. Shaddel et al [2] have however warned that the sludge may contain hazardous organic and inorganic contaminants. After its publication with the Official Gazette 2692/B/2023/21-04-2023 we notice that the environmental legislation in Greece, regarding the disposal of sludge, is being increasingly tightened. With the aforementioned ministerial decision (Ministry of Environment and Energy/ Official Gazette /41 828/630/21-04-2023) [4] strict restrictions and continuous controls are set for the correct use of treated sludge in agriculture, the calculation and other parameters such as conventional fertilization, and above all the control of the quality of the sludge and the care to avoid possible failure and non-compliance with the study of the sludge in each area. One of the primary objectives of municipal or industrial wastewater treatment plants is to attain the maximum possible removal of solids with the highest possible degree of solid concentration. To achieve this goal, a range of technological processes are employed, including sedimentation processes (commonly utilized in both water and wastewater treatment) [5], as well as mechanical thickening. The characteristics of sewage sludge largely hinge on the technology deployed at the sludge treatment facility [6], as well as the nature of the sewage itself (whether municipal or industrial).

According to Christodoulou and Stamatelatou [7], sewage sludge is considered as a source of renewable energy and material recovery, not as 'waste' but as a by-product to be processed for recycling.

The volume of sewage sludge has been increasing sharply in the past decate due to the unprecedented rate of industrialization and population growth [8]. Consequently, the management of sewage sludge in an economically and environmentally acceptable manner has become one of the most serious problems facing society today. Therefore, the operation of Wastewater Treatment Plants faces a new challenge regarding sustainable wastewater management, revealing a major new environmental issue in the management and long-term disposal of sewage sludge. The volume of wastewater and how it's treated varies according to a country's level of economic development. Managing sewage sludge from wastewater treatment plants (WWTPs), including processing and disposal in landfills, is a significant concern in wastewater management. Sewage sludge harbors a range of harmful pollutants that pose risks to both human health and the environment, emphasizing the importance of proper treatment and utilization [9,10,11].

The reuse of sewage sludge for the aforementioned purposes is economically viable and environmentally friendly compared to handling it as waste and disposing of it in local landfills, as was implemented for 98.50% of the produced sludge in 1998 and still at 38.5% in 2020 in Greece [12].

Therefore, it is understood that potential improvements in environmental protection are to be achieved through solutions already implemented in the European region and have been successfully applied, disposing of only 4.50% of the total produced sludge in landfills in 2020, as in the case of Finland (43.50% disposal in Agriculture, 47.30% composting, 3.7% thermal methods, and 0.70% other methods). Examining the current European reality forms the basis for a broader examination of the prevailing Greek legislation as shaped by recent laws which define the future of sludge management in Greece until 2030, essentially revealing to us the practical framework for implementing regulatory measures for sludge [3].

2 Legislative Overview of Sewage Sludge in Greece

The legal regulations in Greece regarding waste management are adapted to European legislation, specifically the Directives 86/278/EEC - Sludge Directive, concerning the limitation of composting and agricultural use of waste. Directive 99/31/EC for the limitation of disposal, Directive 2000/60/EC which establishes the rules for a common community action in the field of water policy, where sludge is defined not as waste, but as a product from the wastewater treatment process. Also, Directive 2000/76/EC which set the rules for the non-restriction of incineration and co-incineration as a method of managing wastewater treatment sludge. Additionally, Directive 91/271/EEC included guidelines for limiting the impacts from the increase of sludge mass, disposal processes, or treatment or decomposition of stored plant and animal residues.

Specifically, in Greece, in 2012, the Special Service for the Management of the Operational Program "Environment and Sustainable Development" (Ministry of Transport and Environment) 2007-2013 issued a call titled "Projects for the management and safe disposal of sludge" to the relevant bodies of the country ((MWSSC): Municipal Water Supply & Sewerage Company, Municipalities, etc.) for the submission of proposals to be financed by the NSRF. This call provided for the "implementation of sludge management and safe disposal projects aimed at the drastic reduction of sludge pathogens (sanitation) and/or the drastic increase in solid content, to make its subsequent disposal and overall utilization safer and with greater options." Although there was a response from the agencies, as evidenced by the submitted proposals, no relevant project was included for funding in the Program, and the process was interrupted, as the institutional definition of "sludge sanitation" could not be established, and the issuance of the relevant Joint Ministerial Decision was not finalized.

The Greek Government sought the support of the European Commission in specific areas (such as, among others, the improvement of urban waste management, regulatory issues in the waste sector, and the management of specific waste categories) with the aim of increasing the quality and quantity of recycling, improving the quality of data, and effectively using economic tools. To achieve the aforementioned goals, the Deutsche Gesellschaft für Internationale Zusammenarbeit GmbH (GIZ) provides "Technical support for the implementation of Greece's National Waste Management Plan (NWMP)" from 2018 to 2021. The project is funded by the European Union (EU) through the Structural Reform Support Program (SRSP), and the German Federal

Ministry for the Environment, Nature Conservation, and Nuclear Safety (BMU) and is implemented by GIZ and the Greek Ministry of Environment and Energy (YPE), in collaboration with the European Commission.

Furthermore, a technical report on the criteria for imposing a waste fee for biodegradable waste subject to biological treatment has categorized sewage sludge as a waste included in the positive list. Recently in Greece the interpretive circular was issued from 12-20-2021 pursuant to article 38 of Law 4819/2021 - Burial fee, in which it is stated that the competent bodies that have not included the burial fee in their pricing policy and budget, must promptly comply by revising their budget and pricing policy, while informing the General Secretariat of Waste Management Coordination. Greece, as a member state of the European Union, must attune its national legislation to the legislation of the European Union. The result of these actions is JMD (Joint Ministerial Decision) 80568/4225/1991 as replaced by the ministerial decision of 04-21-2023 (Government Gazette 2692/B/21-04-2023) [4] for the use of waste sludge in agriculture (in application of Directive 86/278/EEC, JMD 29407/3508/2002: Measures and conditions for the sanitary landfill of waste (Government Gazette 1572/02) which incorporated into our national law Directive 99/31/EC as was replaced by Official Gazette 2692/B/2023/21-04-2023, in which strict restrictions and continuous controls are set for the correct use of treated sludge in agriculture, JMD 22912/1117/2005: Measures and conditions for the prevention and limitation of environmental pollution from the incineration of waste, to incorporate Directive 2000/76/EC, Law N.4014/2011: Environmental licensing of projects and activities, regulation of arbitrary in connection with the creation of an environmental balance and others provisions of the competence of the Ministry of the Environment, as amended and in force (Article 12, Licensing for the operation of a landfill) (Government Gazette 209/A/21-9-2011), the law N.4042/2012: Criminal Protection of the Environment – Harmonization with the 2008 directive /99/EC – production and waste management framework – Harmonization with directive 2008/98/EC – Regulation of Ministry of Environment, Energy and Climate Change matters (Government Gazette 24/A/13-2-2012) and the JMD 51373/4684/2015 [13] which validates the National Waste Management Plan and the National Strategic Prevention Plan. With the latest joint ministerial decision, the following goals were set for sludge:

- Minimizing the disposal of the sludge in Sanitary Landfills
- Sludge recovery, 90% by weight of the produced quantity. The Disposal of the sludge must be less than 10% by weight of the produced quantity, by 2030
- Development of an infrastructure network for the recovery of sludge produced by the treatment of municipal wastewater
- Information regarding the possibilities of proper sludge management for sludge producers

In conclusion, studying the above legislation, the following alternatives can be distinguished through which, in general, the sludge from WWTPs can be utilized according to the Greek Legislation.

- By using the sludge in agriculture, either directly or after processing, always respecting the restrictions and specifications those have been set, in accordance with the respective legislation

- By using the sludge after drying, as a fuel, in industry and in thermal power plants
- By using the sludge after dehydration, in the biogas production units
- By using the sludge in landscape restoration after sanitation, stabilization and drying

The introduction of these legal regulations has differentiated the consideration of disposal in the management of sewage sludge before and after 12.31.2021, the date of application of the burial fee to the existing landfills of the Greek area and has troubled the municipal units for the treatment of urban waste regarding the ways of managing it.

Specifically, in Greece, in May 2022, the updated National Operational Plan for Wastewater was formulated, including the summary table of necessary funding for the proposed measures/actions (Table 8 of the Operational Plan) to ensure the country's compliance with Directive 91/271/EEC. The total cost of the necessary measures/actions (studies – expert opinions, construction of new WWTPs, improvement of operation and upgrading of WWTP infrastructure, sludge utilization projects, and effluent reuse projects) is estimated at €2,322,487,464 (excluding VAT).

Additionally, in August 2020, according to the Special Service for the Management of the Operational Program "Transport Infrastructure, Environment & Sustainable Development" 2014 – 2020 (Ministry of Transport and Environment), an inventory was made of the sludge management projects planned by 38 (MWSSC) Municipal Water Supply & Sewerage Company in the country, with a total indicative budget of €137 million. These proposed interventions include the construction of projects and the procurement of equipment for the implementation of mainly conventional methods of sludge treatment and management (drying, dewatering, composting, etc.), with few exceptions where alternative sludge management and utilization solutions are planned from WWTPs (e.g., Volos, Kalymnos, Zakynthos), as well as combined solutions for the management of sludge together with the organic fraction (biowaste) of municipal solid waste (e.g., Skiathos, Rethymno).

According to the studies of the projects included in the European program "Implementation of Sludge Management Infrastructure from Wastewater Treatment Plants" by Ministry of Environment and Energy, up to now (May 2024), a total of 19 projects have been included in the sector "Implementation of sludge management infrastructure from wastewater treatment plants," amounting to €140,761,787.00.

3 Sewage Sludge Treatment Methods

During the wastewater treatment process, sewage sludge is generated through primary, secondary, and sometimes tertiary treatment. These sludges are often combined into "raw" sewage sludge, containing approximately 1-4% solids. Treatment of sludge is necessary before disposal or further use. The primary objectives of sludge treatment are:

- Reducing the volume of sludge to lower treatment and transportation costs
- Decreasing the presence of pathogens and minimizing foul odors [14]

4 Sludge Disposal

Historically, sewage sludge has been viewed as waste due to its potential high pollutant levels, including pathogens and other contaminants, resulting in its disposal [1]. With increasing population and urbanization, sludge production is rising, making traditional disposal methods unsustainable. Sustainable waste management prioritizes alternatives to landfilling, placing it as the least favorable option in the waste management hierarchy.

4.1 Sanitary Landfilling

The advantage of sanitary landfilling of sludge is that it prevents the release of pollutants and pathogens into the environment by concentrating the sludge in a single location [15]. As a disposal method, it is low-cost, and with the application of appropriate technology, methane (CH_4) recovery can be achieved. However, this only applies to cases where the landfill is properly constructed and maintained to reduce environmental risks [15]. Disadvantages include air emissions, water runoff – heavy metals, a burdened past due to previous use, the loss of useful components, space occupation, and the unutilized organic fraction [16].

4.2 Land Application

Treated sewage sludge can be repurposed for agricultural use due to its organic matter and nutrient richness, serving as a fertilizer or soil conditioner for various crops [1]. The application of sewage sludge provides nutrients and organic matter that offer positive agricultural benefits [17] and is of particular interest for the Mediterranean region due to the widespread lack of organic matter in the soil [18, 19]. However, there are contamination risks associated with soil application, such as heavy metals, organic pollutants, and pathogens. In addition to nutrients, sewage sludge also contains toxic heavy metals and organic pollutants [20, 21].

4.3 Green Energy

Energy recovery from sludge, primarily through anaerobic digestion, has become a prominent feature of sludge management strategies globally [22]. Biogas produced can be utilized for heat and electricity generation, with alternative methods including incineration, pyrolysis, and gasification [23]. Thermal methods of sludge disposal aim to reduce the pollutant load, achieve the maximum possible reduction of its volume, convert it into materials that are harmless to the environment and easily disposable, while simultaneously utilizing its calorific content. Generally, there is increasing interest in the use of thermal conversion in waste management technologies [24]. These methods generally aim to utilize waste streams while simultaneously reducing the risks associated with waste reuse [25]. Although the high cost of machinery is usually a significant obstacle to the implementation of thermal routes, investments in sludge treatment can become attractive if a 20% increase in energy prices in the international market is taken into account [26].

4.4 Use in the Construction Industry

Sewage sludge finds applications in construction, including its use in concrete mixes and the production of ceramics and glass [27]. The main metallic elements of sludge, including calcium, iron, and aluminum compounds, are included in cement mortars and other commercially used construction materials [28]. The construction industry is the most suitable sector of technological activity for the absorption of solid waste, due to the large quantity of raw materials and final products used [29].

4.5 Other Applications

The National Waste Management Plan (ESDA) outlines various alternative uses for sludge, such as mine deposit remediation, enhancing soil remediation, acting as an adsorbent material, aiding nursery development, and improving degraded soils [3].

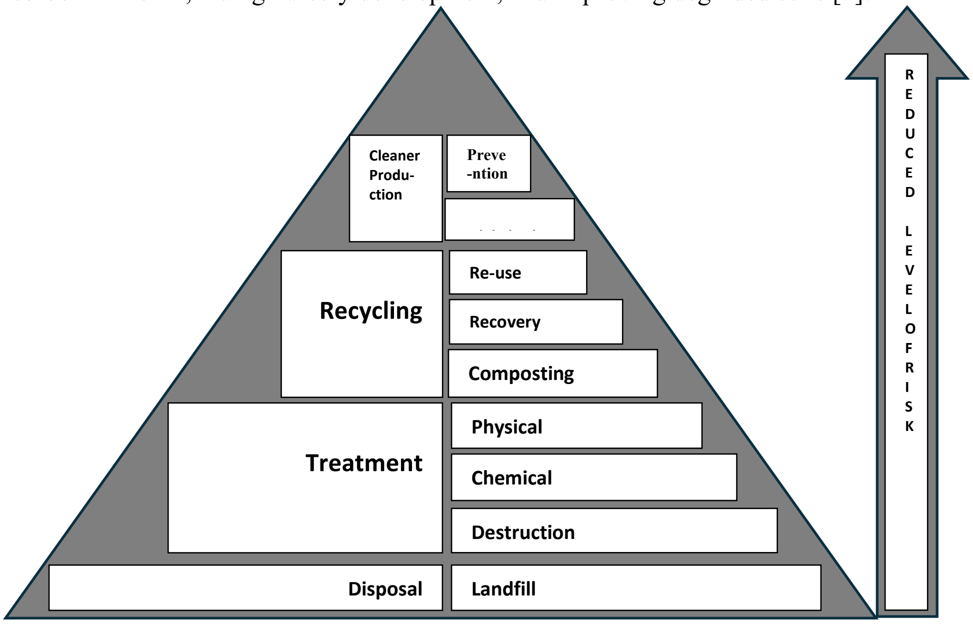

Fig. 1. Waste Management Hierarchy, *Source WRC, 2009*

In Spain, over one million tons are applied to the land annually (approximately 83% of the produced sludge) [19]. The application of sewage sludge provides nutrients and organic matter that offer positive agricultural benefits [17] and is of particular interest for the Mediterranean region due to the widespread lack of organic matter in the soil [18, 17]. Some authors have investigated the direct application of dried sewage sludge as an adsorbent [30]. Due to its high organic content, sludge has been proposed as a suitable and low-cost raw material for the production of activated carbon through pyrolysis [31, 32].

5 Production of sewage sludge

As it can be seen in the following Table 1, sludge production appears to vary significantly between the various EU countries. When searching for recent data on both the production and management of sludge from Wastewater Treatment Plants (WTPs) in the EU, it was found that there is a lack of continuous and reliable information as various member states do not submit regular data to the European Commission or do not submit data as required according to the European Directives. The "safest" data for sludge management essentially come from the first 15 member states (EU-15).

Germany is the largest producer of sludge followed by the UK and France and together with Spain and Italy, it is estimated that these countries (the UK is no longer part of the EU) produced over 76% of the sludge produced in the EU-15 [33]. Eurostat figures for 2019 confirm this claim with Germany's annual sludge production rate amounting to 46% of the total sludge production in the 28-nation European Union.

As far as the EU-13 countries (countries that joined the EU after 2004) are concerned, Poland produces the largest amount of sludge with a percentage of 42% of the total amount of sludge produced by these member states, while at the opposite end is Malta with the smallest percentage of production. It should be noted that Poland, Hungary, and the Czech Republic account for more than 70% of the produced sludge in this group of member states (www.ec.europa.eu, last updated 11/28/2018) [34].

Table 1. Sludge production in the EU countries 2014-2020 (10^3tn in dry substance (ds)) (Eurostat, 2023) [34]

COUNTRIES	2014	2015	2016	2017	2018	2019	2020
AUSTRIA	239.04	n/a	237.94	n/a	234.48	233.56	228,81
BELGIUM	177.96(p)	172.20(p)	177.67(p)	170.80(p)	166.98(p)	164.00(p)	165.96(p)
BULGARIA	54.9	57.4	65.00	68.60	53.10	44.43	n/a
FRANCE	1,059.00	1238,00	1,006.00	1,174.00	n/a	n/a	n/a
GERMANY	1,830.82	1,820.57	1,794.36	1,785.55	1,761.62	1,749.86	n/a
DENMARK	n/a	n/a	n/a	n/a	n/a	n/a	n/a
GREECE	16.1	119.77	119.77	103.28	103.28	103.28	n/a
ESTONIA	19.91	19.11	18.65	20.94	25.54	19.48	18.99
UNITED KINGDOM	n/a	n/a	n/a	n/a	n/a	n/a	n/a
SPAIN	1,131.60	1,252.60	1,174.40	1,192.00	1,210.40	n/a	n/a
ITALY	n/a	n/a	n/a	n/a	n/a	n/a	n/a
NETHERLANDS	345.00	354.60	347.60	n/a	341.77	n/a	353.85
CROATIAN	16.31(p)	17.94	19.72	17.60	19.23	19.23	22.51
CYPRUS	6.16	6.70	7.41	7.17	8.41	n/a	n/a
LATVIA	22.00	21.92	25.92	24.94	24.59	24.18	23.15
LITHUANIA	40.71	44.45	44.42	42.49	44.19	39.94	41.05
LUXEMBOURG	n/a	9.16	8.92(p)	9.32(p)	9.08(p)	8.89(p)	9.47(p)
MALTA	8.50	8.44	10.77	10.30	8.28	9.69	10.36
HUNGARY	163.12	177.78	217.96	266.84	233.66	227.89	n/a
POLAND	556.00	568.00	568.33	584.45	583.07	574.64	568.86
PORTUGAL	85,89	n/a	119,17	n/a	n/a	n/a	n/a
ROMANIA	192.33	210.45	240.41	283.34	247.76	230.59	254.22
SLOVAKIA	56.88	56.24	53.05	54.52	55.93	54.83	55.52
SLOVENIA	28.30	29.10	32.80	36.70	38.10	34.80	31.00
SWEDEN	200.50	197.50	204.30	205.30	211.60	n/a	n/a
CZECH REPUBLIC	238.59	210.24	206.71	223.27	228.22	221.09	219.11
FINLAND	115.70	146.00	146.99	161.19	146.62	160.17	n/a
TOTAL	6,564.59	6,624.36	6,717.70	6,321.25	5,635.08	3,806.29	2,038.33

(p): Data provisional **n/a: not available**

6 Sludge management data in European countries

The solid residue of wastewater treatment is sewage sludge whose nature is rich in nutrients, but also often filled with high concentrations of pollutants such as heavy metals, a fact that prompts countries to look for different ways to discard it.

Below are presented the methods of disposal of sludge from sewage treatment plants in European countries with data on treatment and disposal of sludge in the countries of the European Union.

In particular, the sludge treatment methods from E.E.L. in various European states are as follows [34-35-36]:

Austria uses aerobic and anaerobic digestion, mechanical dewatering, drying and composting, for sludge stabilization. Also, while initially disposal in agriculture was the most basic use of sludge, it has now been almost abandoned with 86% of the sludge being used for combustion and only 5% for agriculture.

Belgium applies aerobic or anaerobic stabilization, addition of improvers (lime or polymers), mechanical dehydration, thermal drying and in a few Sewage treatment plants (WWTPs) composting. Also in Belgium, the usual landfill method that was initially followed has been almost abandoned, with 80% of the sludge being disposed of in other methods such as incineration and 10% in burning and agriculture.

Aerobic digestion, mesophilic anaerobic digestion, calcification, dewatering with filter presses and long-term storage are used in Bulgaria. Composting is barely used at 7%, while 71% is allocated to agriculture.

In France, aerobic and anaerobic stabilization, calcification, composting, improvement by adding lime, dewatering with filter presses or centrifuges and drying are applied. Sludge from 1992 until today continues to be allocated mainly to agriculture at a rate of 65%.

In Germany, the most common sludge treatment method is thermal drying. Other methods also used are anaerobic stabilization, calcification, thermal stabilization and thermal anaerobic digestion (TPAD). The main method of sludge disposal was initially agriculture at a rate of 46% in 1992, while recently in 2021 combustion has taken its place at a rate of 55% with agriculture accepting only 30% of the produced sludge.

Mesophilic or thermophilic anaerobic digestion, aerobic digestion, liming, composting, thermal drying and pasteurization are practiced in Denmark. Only three values are available from Eurostat for the years 2007, 2008 and 2010, equal to 140.00 – 108.00 and 141.00 $*10^3$tn in dry substance (ds), respectively. Agriculture was initially the main method of disposal of sludge at a percentage of 65%, while recently, the disposal in agriculture and in combustion maintain almost equal percentages, 50% and 45% respectively.

In Greece, the stabilization methods applied are mesophilic anaerobic digestion, aerobic digestion, calcification, improvement with polymers, dehydration in drying beds, centrifuges or belt filter presses and solar drying. Composting is little applied (8% in 2014 and 0% in 2020). Regarding the sludge disposal methods, an analysis is carried out in the next thematic section.

The main method used in Estonia for sludge treatment is composting and mesophilic anaerobic digestion. Agriculture at 79% and composting at 15% are the main methods of sludge disposal.

In Ireland, thermophilic aerobic digestion, anaerobic stabilization, calcification, dewatering with centrifuges or belt filter presses, thermal drying and long-term storage are used. Ireland in 1992 had 43% of its sludge in landfill or 38% in surface water. Now, 70% of sludge is used in agriculture.

The most common treatment method in Spain is anaerobic stabilization. Other methods applied are aerobic digestion, calcification, thermal drying and long-term storage. Spain, from 1992 until today, disposes of sludge in agriculture at a rate of 83%.

Anaerobic digestion is mainly used in Italy, followed by aerobic digestion, calcification, composting, improvement with lime or ammonia, mechanical dehydration and where few Sewage treatment plants (WWTPs), thermal drying and pasteurization. From Eurostat, only one value is available for the year 2010, equal to 1,102.70 *103tn in dry substance (ds). For this reason, the country does not appear in the following Figure 2 with 2020 Eurostat data.

In the UK the most common technology is mesophilic anaerobic digestion and thermophilic aerobic digestion, calcification, composting, dewatering with filter presses or belt filter presses, thermal drying and long-term storage. From Eurostat, only one value is available for the year 2012, equal to 1,136.70 *103tn in dry substance (ds). The main mode of sludge disposal since 1992 remains agriculture at 78% for 2012. It should be emphasized that as of 2019 the United Kingdom is not a member of the European Union anymore (MS), and does not participate in Figure 2.

More generally, there is a wide variety of sludge treatment technologies used in the European Union of 27, which are related to the final disposal practices and the size of the waste treatment plants. Significant differences can be observed between EU member states, as well as between different regions of the same country (e.g. Belgium).

In particular, the Figure 2 lists the sludge disposal methods of European countries, for 2020.

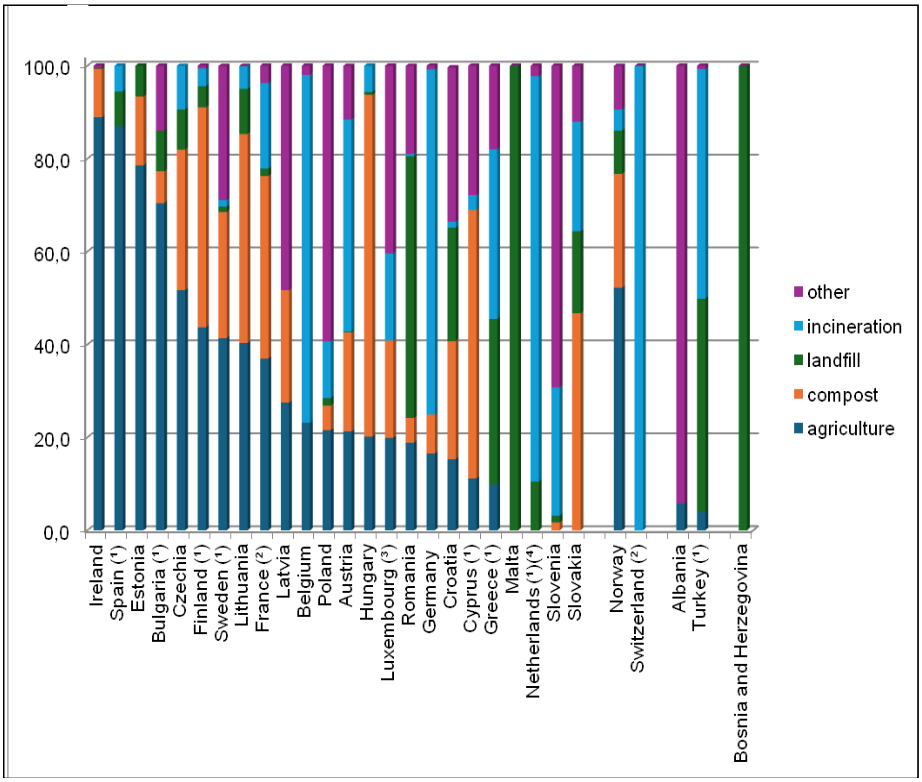

Fig. 2: Disposal of sewage sludge from municipal wastewater treatment by disposal method, 2020 (% of total) [39]

As there are more and more environmental concerns about reducing or eliminating the spread of pollutants to land, incineration is increasingly the method of choice: while the Netherlands (96%), Belgium (75%, provisional data), Germany (74%, 2019 data), Austria (52%), Greece (37%, 2019) and Luxembourg (34%, estimated) reported incineration as the main form of treatment for their disposal, disposal in controlled landfills was carried out as the main type of treatment only in Malta, Serbia, Bosnia and Herzegovina (in these countries it is the only form of treatment), Romania (55%), and Turkey (45 %).

7 Sludge management in Greece

Regarding the management of sludge from waste treatment plants in Greece, the reduction in the percentage of landfills, following the effort to harmonize the member states with the relevant Directive, is noticeable, from 98.5% in 1992 to 33% in 2014 [37-38]. The updated data for 2020 (2020 forecast with 2019 data) according to the data submitted to Eurostat which can be seen in Figure 3 above, 10% is allocated to agriculture, 35% to land restoration, 37.5% to incineration and the remaining 17.5% in other uses with the predominant disposal in landfill [39].

The quantitative targets of recovery (95% by weight) and disposal (5% by weight) of the produced sludge set by the 2015 National Waste Management Plan (ESDA) for 2020 were not achieved, according to the data also highlighted in the Early Warning Report of European Commission (SWD (2018) 418 final / 24.09.2018) more realistic targets were set for 2030 (five years earlier than the implementation schedule set by the European Union), in the National Waste Management Plan (ESDA) 2020 that mention 90% and .b. and disposal of up to 10% by weight of the produced sludge.

The recycling of sludge for agricultural purposes is an alternative solution to handle the continuous increase in the quantities produced in recent years [40]. The utilization of sludge in today's agriculture represents a widespread practice in developed countries, as an alternative that is more efficient than incineration or storage [41]. But in addition to nutrients, sewage sludge also contains toxic heavy metals and organic pollutants [39]. On 04-21-2023, Official Gazette 2692/B/2023 was published, which aims to harmonize the National legislation with the provisions of the Directives of the European Parliament regarding the territorial utilization of this sludge in agriculture and soil restoration. With the above decision, the use of treated sludge is prohibited in: **a**. Grounds frozen or covered with snow, **b.** Soils flooded or saturated with water, **c.** Soils with a pH lower than 5, **d.** Parks and groves with recreation areas and playgrounds and in outdoor forest recreation areas, **e.** Sports fields, **f.** Natural forests and in forested and reforested areas, **g.** Soils that are less than 50 meters from lakes, rivers and streams, **i.** Wetlands and marshy areas **j.** Very light soils (sandy - sandy loam). In addition, the requirement for a license to use sludge for disposal in agriculture and soil restoration is established from 04-21-2023.

In Greece, since 2008, Municipal Water Supply & Sewerage Company (MWSSC) of Larisa implements a plan for the disposal of sludge in agriculture, in collaboration with the agricultural producers of the Thessalian plain [42]. Additionally, the most important project is the disposal of sludge for agricultural crops on behalf of Municipal Water Supply & Sewerage Company (MWSSC) of Thessalloniki approximately 45,000 tons of calcified sludge from the facilities of MWSSC of Thessaloniki in Sindo which were transported and distributed to plots of land in the Prefecture of Thessaloniki from the Spring of 2012 to the Spring of 2015 in a total of seven growing seasons. In April 2016, MWSSC of Katerini implemented, on a pilot basis, the application of 390.6 tn of sludge from the Municipal Water and Wastewater Treatment Plant (MWWTP) of Korinos and Katerini to crops in the area. In 2016, the MWSSC of Ioannina built an open composting unit for the management of biological cleaning sludge. In addition, it should be considered that in the existing Mud Treatment Facility, which operates on the grounds of the Ioannina Municipal Water and Wastewater Treatment Plant, the sewage sludge of the Ioannina MWWTP is already processed. With the December 2013 decision to approve environmental conditions, the permission has been given for the treatment of sewage sludge originating from the MWWTP of Igoumenitsa.

Following the Publication of Official Gazette 2692/B/21-04-2023 and the establishment of strict restrictions and continuous controls for the proper use of treated sludge in agriculture, the inclusion of other parameters such as conventional fertilization, and above all, the control of the quality of sludge and the care to avoid possible failure and non-observance of the sludge application study in each territorial area, most producers of treated sludge, where are the MWSSC, have turned to other methods of its disposal.

Based on the data from the Union of Municipal Water Supply and Sewerage Companies, the tendency is to increase, as much as possible, the share of thermal methods and drying. At the Urban Wastewater Treatment Unit (UWTU) of Psittaleia, the sludge produced is dewatered, dried, turned into powder and used as an alternative fuel in the cement industry. At MWWTP of Thessaloniki, a thermal sludge drying unit with two (2) parallel drying lines is used for sludge management. A small solar drying greenhouse has been installed on a pilot basis at MWWTP of Kavala premises since 2010, in which quantities of dewatered sludge are transported and subjected to natural drying. Samples of these sludges have been tested experimentally and found to yield a sufficient calorific value equal to 17 MJ/kg liquid to achieve self-sustaining combustion of the sludge [6]. Fo.S.D.A. (Solid Waste Management Authority) of the Northern Plains in Heraklion, Crete, also applies contact-based aging drying under a greenhouse.

In particular, in Greece after 01/17/2023 and the inclusion of the project "Treatment and purification of urban wastewater in environmentally sensitive settlements and modernization of facilities" of the Recovery and Resilience Fund (OPS Code TA 5164462), many projects have been financed and are in the implementation stage, concerning **a.** Sewer network infrastructure and sewage treatment facilities, **b.** Upgrading, expanding and modernizing sewage treatment facilities and reuse of treated water and **c.** Implementation of sludge management infrastructure from sewage plants [3].

According to the studies of the projects that are included in the European program "Implementation of sludge management infrastructure from sewage treatment plants" of the Ministry of the Interior, there is no composting plant construction project among the 19 included projects, except those for the use of sludge in co-composting after the sludge has drying. By the submitted studies, 122,113 tons of sludge can be treated annually with the aim of reducing the volume of landfill disposal to 5%. Amount exceeding the annual sludge produced nationally. In 2019 the amount of produced sludge was 103,280 tons approximately.

A total of 19 projects, shown in Table 2, for a total amt. of 140,761,787.00 € have been included in the above European program in the field of Implementation of sludge management infrastructure from sewage plants. The obligation date for the completion of the above projects as well as all the others that will be included until 12/31/2023 in the above European program is 12/31/2025 [42].

Table 2. SUB-PROJECTS C- Implementation of sludge management infrastructure from sewage treatment plants

A/A	BUDGET (€)	CAPACITY (tn/y)	BENEFICIARY	INTEGRATED PROJECT
1	8,800,000	8,000	MWSSC Ioannina	Construction of a solar drying unit Ilyos EEL Ioannina
2	7,658,731	8,001	MWSSC Larisa	Solar sludge drying unit EEL Larisa with operation and maintenance
3	8,350,147	2,053	MWSSC Chania	EEL Chania sludge management infrastructure and photovoltaic plant installation
4	2,285,000	3,350	MWSSC Arta	EEL Arta Dewatered Sludge Treatment Unit
5	5,655,000	7,395	MWSSC Xanthi	Implementation of a sludge drying unit EEL Xanthi
6	4,792,587	2,711	Solid Waste Management Agency of Northern Plains SA OSA	Center for the treatment of sludge from wastewater treatment facilities of OSA-members FOSDA of the Northern Plains
7	5,950,000	6,240	MWSSC Lamia	Solar sludge drying unit EEL Lamia
8	6,400,000	8,400	MWSSC Drama	Construction of a Solar Sludge Drying Unit EEL Drama
9	3,782,650^c	2,683	MWSSC Livadia	Implementation of a sludge management unit from the Livadia and Kyriaki wastewater treatment facilities
10	19,717,611	15,125	Union for Waste Management of Crete	Sludge treatment center of Heraklion PE sewage treatment facilities Crete
11	2,441,674	1,800	MWSSC Agios Nikolaos	Dewatered sludge treatment unit from the EEL of the Municipality of Agios Nikolaos Ctete
12	6,900,000	11,000	MWSSC Aegialia	Supply, installation, and operation of equipment for thermal drying of EEL Aigio sludge
13	3,750,000	2,000	MWSSC Orestiada	Construction of a solar sludge drying unit of EEL Orestiada
14	6,428,500	11,012	MWSSC Kalamata	EEL Kalamata Sludge Solar Drying Unit
15	9,936,000	1,987	MWSSC Serres	Construction of a solar drying unit for the sludge of the EEL Municipality of Serres
16	7,797,571	4,000	MWSSC Alexandroupolis	Solar drying of sludge EEL Alexandroupolis.
17	7,916,316	3,650	MWSSC Kilkis	Sewage sludge treatment PE Kilkis
18	12,200,000	9,125	MWSSC Volos	Integrated management and utilization of sludge from EEL Volos
19	10,000,000	13,581	MWSSC Kavalas	Construction of an advanced sludge treatment unit by the EEL of the Municipalities of Kavala and Pangaio

(MWSSC): Municipal Water Supply & Sewerage Company **(C): contracted**

Therefore, according to the above data, the growing trend towards thermal treatment of sludge with drying methods (solar, etc.) is confirmed, and by 2025 will have changed the data on the disposal of treated sludge in Greece.

Following the Early Warning Report of the European Commission (SWD (2018) 418 final / 24.09.2018), it was realized that the quantitative goals of recovery (95% by weight) and disposal (5% by weight) of the produced sludge in WWTP that had been set by the ECHR 2015 for 2020 were unattainable. The new ESDA2020 set more realistic goals which, after the implementation of the European program "Treatment and purification of urban wastewater of environmentally sensitive settlements and modernization of facilities" on 31-12-2025, can be implemented by 2030.

The largest percentage of the total sludge produced in Greece comes from Attica (50.2%), followed by Central Macedonia (14.7%), the South Aegean with 5.1%, Thessaly (5%), Western Greece (4.0%), Epirus (3.9%), Eastern Macedonia and Thrace and Crete with 3.8% respectively, Central Greece (3.7%), Peloponnese (2.5%), the Ionian Islands (1.4%), the North Aegean with 1 ,0%, and Western Macedonia (0.9%) [21]. Attica and Thessaloniki are already successfully managing the produced sludge with the Psittaleia and Sindos plants, according to the data published with the ESDA 2020.

According to the submitted data of the country's Wastewater Treatment Facilities, in the Registry, Licensing and Statistical Waste Department of the Waste Management Directorate of the Ministry of the Interior, for the reference year 2019 until January 2021, the recovery rates in the Regions of the country are for Attica 98.2% followed by Western Macedonia 90.3%, Central Macedonia 67.3%, Peloponnese 51.9%, Central Greece 46.9%, Eastern Macedonia and Thrace 38.2 %, Epirus 31.8%, Thessaly 26.9%, Western Greece 10.2%, Crete 4.6%, North Aegean, South Aegean and Ionian Islands 0.0%. That is, only the Region of Attica (98.2%) and the Region of Western Macedonia (90.3%) achieve the recovery targets set with the ESDA 2020. Consequently, 51.1% of the produced sludge in Greece can so far be recovered according to the National plan.

Observing the beneficiaries of Table 2 and the regions to which they belong, we conclude that 6 of the 19 projects are implemented in the Region of Eastern Macedonia and Thrace, 4 of the 19 projects are implemented in the Region of Crete, 2 of the 19 projects respectively are implemented in the Regions of Epirus, Central Greece and Thessaly, while 1 of the 19 projects are respectively implemented in the Regions of Western Greece, Peloponnese and Central Macedonia. While the Regions of Attica, North Aegean, Ionian Islands, Western Macedonia, and South Aegean are not beneficiaries. Consequently, since the Region of Attica and the Region of Western Macedonia already comply with the National plan for sludge recovery, only 7.5% of the produced sludge will not be recovered.

The National plan for the recovery of sludge until 2030 stipulates that up to 10% of the produced sludge may be available for landfill. Consequently, we conclude the necessity of implementing the projects in Table 2, which will achieve the national goals for sludge management.

8 Discussion

Sludge, when processed into various materials such as granules, fertilizers, or compost, proves to be highly beneficial for agricultural purposes and natural applications, provided heavy metals and other contaminants are adequately removed. Compost derived from sludge treatment can serve purposes like soil conservation or the restoration of degraded areas through re-cultivation. Following the Publication of Official Gazette 2692/B/21-04-2023 entitled: "Measures, conditions and procedures for the use of treated sludge in agriculture and soil restoration", within which strict restrictions and continuous controls are set for the correct use of treated sludge in agriculture, most treated sludge producers, as MWSSC for example, have turned to other methods of treated sludge disposal.

In today's era, Goswami & Thakur [43] state that globally, challenges arise primarily due to the increasing population and the ensuing issues related to water, energy, and food security. Additionally, greenhouse gas emissions and climate change pose global threats that widen the gap between economic development and environmental sustainability. Therefore, the need for implementing sustainable practices and circular economy technologies to prevent climate change and meet the growing energy demands is imperative, especially in developing countries.

Reducing the production of sewage sludge from wastewater treatment is a primary factor for its successful management. According to Collivignarelli et al. [44], the quantity of sewage sludge must be minimized to comply with the European Directive 2018/851, and due to its high management cost, which represents approximately 50% of the total operational cost of a WWTP. The concept of the circular economy serves as an economic model aimed at enhancing environmental sustainability, fostering economic growth, and promoting social equity. By prioritizing the efficient use and reuse of resources, it seeks to benefit not only the present generation but also future ones [45, 46, 47]. At the microeconomic level, implementing the circular economy leads to enhancements in production models and fosters greater collaboration with other firms within the supply chain. This collaboration aims to achieve a more economically efficient closed-loop cycle, wherein resources are utilized and reused optimally [48, 49]. According to circular economy principles, the reuse, treatment, and renovation of products lead to a reduced demand for resources and energy. This approach promotes sustainability by maximizing the lifespan and value of materials and products [46, 48]. A key assumption of the circular economy is that incineration for energy recovery is a preferable option, while waste landfilling is considered the last resort. This approach ensures that the production value chain and product life cycle maintain optimal effectiveness and quality whenever possible, and maximize energy efficiency [50, 45, 46].

If sludge fails to meet legislative requirements, the most cost-effective method of utilization is through thermal methods such as incineration or co-incineration. Current plans for Greece propose primarily incineration, with an alternative option being the use of sludge as a fuel in cement industries.

Energy production processes from renewable sources such as, for example, solar energy, tidal energy, biomass, or biofuels, cause many adverse economic and social effects, because it also causes a reduction in the areas covered by forests and permanent pastures [51].

In Greece after the inclusion of the project "Treatment and purification of urban wastewater in environmentally sensitive settlements and modernization of facilities" of the Recovery and Resilience Fund from 01/17/2023, there is a growing trend towards thermal treatment of sludge with drying methods (solar etc.) which by 2025 will have changed the facts of the disposal of treated sludge in Greece. Due to the satisfactory calorific value of sewage sludge, there has been significant interest in its potential use as a renewable fuel. Analysis of sewage sludge from the Eastern Macedonia and Thrace region has revealed its suitability as an energy and heat source in both conventional and emerging technologies. Additionally, it can serve as a substrate for fertilization and soil remediation, provided that the technology utilized yields a high-quality product [6].

Aligned with the principles of a closed circular economy, sustainable sewage sludge management should prioritize recovery over disposal. Implementing solutions already established in the European region, which promote circular economy principles and sustainable development, can lead to environmental benefits such as reduced greenhouse gas emissions, enhanced soil conditions, and decreased reliance on fossil fuels. The economic potential of these initiatives lies in several factors:

- Decreasing compensation costs associated with traditional waste treatment methods, particularly landfill disposal
- Lowering the expenses related to waste treatment, sanitation, and remediation
- Reducing energy costs by utilizing biogas and biofuels as alternatives to traditional fuels, thus partially replacing them

The recovery of value-added products, such as biogas, biofuels, building materials, soot, and nutrients (nitrogen and phosphorus) from sewage sludge, represents an option for sustainable management. This approach reduces dependence on non-renewable resources, contributing to the conservation of natural resources and the reduction of environmental pollution and human health risks. However, despite the advancement of resource recovery technologies, most technologies are still in their early stages (Gurjar & Tyagi, 2017) [52]. Currently, biofuel is a fundamental renewable energy source. Utilizing biofuels offers the potential to reduce greenhouse gas emissions compared to crude oil fuels and aids in storing CO_2 in the soil. This benefit arises from the methods employed in producing biofuels and their byproducts. Maintaining soil organic carbon during the initial stages of biofuel development mitigates climate change [53, 54].

Biological sludge is a renewable natural resource, and its rational utilization is vital for the development of the circular economy and the sustainable management of natural resources, one of the main priorities of modern society.

In this direction, the plan for sustainable sludge management in Greece must:

i. Meet the country’s needs for compliance with Directive 91/271/EEC, which includes studies, construction of new infrastructure for urban wastewater and sludge treatment, improvement of the operation and upgrade of existing wastewater treatment plants (WWTPs), sludge utilization projects, and effluent reuse projects, as presented in the updated (May 2022) "National Operational Plan for Wastewater"

ii. Adopt national criteria for the design of urban wastewater treatment infrastructure, as mentioned above, aiming to reduce the produced sludge and implement the circular economy
iii. Establish the use of sewage sludge as a renewable resource for the recovery of value-added products

However, the current reality in Greece is not so ideal. With the decision of 15.10.2015, the Court of Justice of the European Union (CJEU) imposed a financial penalty on Greece for failing to comply with an earlier judgment concerning the treatment of urban wastewater. Specifically, the Hellenic Republic was required to pay the European Commission "a penalty payment of €3,640,000 per six months of delay in taking the measures necessary to comply with the judgment Commission v. Greece (C-440/06, EU:C:2007:642), from the date of publication of the present judgment until the full implementation of the judgment Commission v. Greece (C-440/06, EU:C:2007:642)." (Court of Justice of the European Union. Judgment of the Court (Fourth Chamber) of 15 October 2015, European Commission v. Hellenic Republic, C-167/14.)

In November 2015, Greece was referred again for non-compliance (for 11 years) with an earlier judgment from June 24, 2004, concerning the lack of a sewer system in the Thriassio Plain and the discharge of untreated urban wastewater into the sensitive area of Elefsina Bay (European Commission - Press release. (14.11.2015). Commission proposed fines and referred GREECE back to the Court of Justice of the EU over persistent poor wastewater treatment. [55]

According to the eighth implementation report (2016) of the Urban Wastewater Directive, in 2012, there were 33 settlements in Greece where urban wastewater management was not compliant with the legislation (reporting date 31.12.2012). (European Commission. (2016). Urban wastewater. Implementation Reports. 8th Technical assessment of information on the Implementation of Council Directive 91/271/EEC. Annex V. Table 9-4-1. Retrieved on 16.7.2016 [56].

Certainly, Greece is not the only country that has violated the related directive or has been fined for non-compliance with a court ruling on the same issue. However, considering the overall economic and environmental challenges the country faces, these decisions are a particularly unpleasant development.

Greece also faces many similar issues in national courts. In another significant decision regarding the Asopos ecosystem (Council of State (5th Chamber) 3943/2015 and Council of State (5th Chamber) 4368/2015), the administration was obliged to take appropriate preventive and remedial measures as defined by the provisions of the Environmental Liability Directive.

Furthermore, according to the relevant database of the Special Secretariat for Water, a significant number of wastewater treatment plants either did not report data or did not achieve the required limit values (data from 2015). (Special Secretariat for Water. (2016). Wastewater Treatment Plants. Monitoring Operation Database [57]).

Therefore, the available data indicate that the country continues to face significant challenges and major problems in implementing the legislative framework concerning broader environmental issues and specifically the management of wastewater and sludge, both internationally and nationally.

Consequently, it is imperative to implement the aforementioned measures, which will contribute to reducing the environmental impacts of sludge disposal, resolve the growing problem of managing this waste, and support the new economic model of sustainable development of the circular economy.

9 Conclusions

In recent years, significant advancements in water and wastewater management have resulted in substantial improvements in sludge management in Greece. These improvements indicate promising prospects for further enhancement, as evidenced by proposed national planning initiatives. The deliberation of the complex issue of managing sludge, produced by municipal sewage treatment plants, and chooses of the appropriate strategy for municipal sewage sludge management, is a complex problem. The resolution of this issue should comprehensively consider environmental and economic factors, alongside numerous zoning constraints related to both new and existing facilities. It should involve a thorough analysis of the market for the final product, assessing the size of the target market, and determining the implementation timeline for each proposed solution. This holistic approach will ensure that the chosen strategy not only addresses sludge management effectively but also aligns with broader environmental goals and economic considerations.

Taking into account the social acceptance factor, which was not reflected in the research of the current national planning for Greece, and which should focus on the diversity of the various regional departments of the Greek space, with the aim of sludge recovery, for the benefit of agriculture or energy utilization as a priority, in accordance with the ESDA, this may be a future research topic.

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Food industry biowaste as substrate for biosolvents production focusing on lactic acid and ethyl lactate

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Abstract. Solvents represent a major category of chemicals due to their necessity in a variety of industries. The majority of solvents derived from fossil carbon are hazardous to both human health and the environment. In this context, it seems imperative to convert biomass into new alternative greener solvents. The present study concentrates on the production of two biosolvents; namely lactic acid and ethyl lactate, from biowaste of baby food industry. For the production of lactic acid parameters as the dosages of enzymes (5 $mg/g_{Lactose}$ and 20 $mg/g_{Lactose}$) and inoculum size (5% v/v and 10% v/v) were examined. The lactic acid concentration reached almost 17.3g/L after 144 hours with $5mg_{LactozymePure}/g_{lactose}$ and 10%v/v inoculum size. Repeated fermentation was also applied yielding a lactic acid productivity of 0.97 g/L h, which is 8 times higher than the conventional batch fermentation. Moreover, the production of ethyl lactate from bioethanol and lactic acid from the fermentation broth was examined. Lactic acid conversion yields as high as 59.9% at 255min were observed. Overall, the results of this work are very promising but further research is needed to optimize conditions and evaluate scalability of the production of these biosolvents from biowaste, since the production of lactic acid and ethyl-lactate from biowaste provides a sustainable approach to the circular economy, limiting waste and minimizing the environmental effect of industrial processes.

Keywords: Biosolvents, Biowaste, Ethyl Lactate, Fermentation, Lactic Acid

1 Introduction

Solvents are mainly applied in the chemical, food, pharmaceutical, wood and furniture, textile, oil and gas industries, including cleaning processes and chemical formulations. The environmental movement that took place in the 1970s at the United Nations Conference on the Human Environment in Stockholm in 1972 was the landmark of the development of new technologies in the production of solvents. Ever since, environmental, health and safety issues have raised serious concerns about the continuous processing of mineral-based raw materials for the production of chemicals such as fuels and solvents since most solvents are flammable and toxic. Therefore, much effort has been put on reducing the use of hazardous substances (particularly volatile organics) and on eliminating or minimizing the production of by-products in chemical processes [1]. Green solvents are an emerging renewable alternative to fossil chemicals and have attracted recent research interest [2].

Regarding waste, in the European Union every year, around 7.3 billion tonnes of natural resources are consumed and around 2.7 billion tonnes of waste are produced, of which only 40% is reused or recycled, with the rest going to landfill or incineration. For this reason, in recent years there has been a clear effort to valorize waste, which has increased in quantity, in order to reuse it for energy recovery or for the production of new green products. This effort is very complex and involves several stages. The 2008 revised Waste Directive has established a 5-step hierarchy pyramid, in which prevention is the best option, followed by reuse, recycling, other forms of recovery and finally landfill. According to the new European Circular Economy Strategy, all EU member countries must move to a resource-saving and waste-reusing economy.

The two most common ways of treating organic waste are composting and anaerobic digestion. Composting is the simplest and cheapest process, while anaerobic digestion is best suited to large-scale facilities because of the higher initial cost, but both can be used at any scale [3].

In this paper, the production of lactic acid ($C_3H_6O_3$), which is an organic chemical compound was studied. It finds many applications mainly in the food industry (about 70%) while it is also used in the fields of medicine, cosmetics, animal husbandry, textiles, pharmaceuticals, etc. Lactic acid, classified as a harmless substance by the United States Food and Drug Administration, has a relatively high added value. In addition, many inexpensive materials such as molasses and other residues from agriculture and industry in general have been used as substrates for the fermentation of lactic acid and studies have been conducted to improve the efficiency of microorganisms for the production of lactic acid through gene modification. All of the above makes this solvent ideal for use in industry and particularly capable of becoming one of the key green solvents in the future [4].

The production of lactic acid can be carried out by either chemical or biological processes. The chemical routes are not economically or environmentally viable processes. On the other hand, biotechnological processes (fermentation) have an advantage as they use alternative raw materials as substrates which can be starchy, cellulosic sources or simply organic municipal or industrial waste [5]. Some of the sugars that have been used in the fermentation of lactic acid are glucose, xylose, sucrose, lactose and cellobiose. However, glucose is the most favourable sugar for assimilation by microbial strains for the production of lactic acid. Lactic acid bacteria follow a hierarchical pattern of sugar utilisation, starting with glucose, leading to the suppression of carbon catabolite, which occurs when sugars are not fully utilised, resulting in reduced fermentation efficiency and increased production costs. In order for the fermentation process to take place and produce lactic acid, the presence of microbial strains called lactobacilli (lactic acid bacteria) is required. Lactic acid bacteria (LAB) are a broad, heterogeneous group of common food-grade microorganisms [6]. The nutrient medium is a general-purpose medium used to culture a wide variety of easy-to-use and non-microorganisms, with one of the most effective media being Man, Rogosa, and Sharpe medium (MRS) [7].

In addition to lactic acid, the production of ethyl lactate (EL) was also examined, which is an environmentally friendly and safe chemical substance, mainly produced from biological resources. EL is produced from the esterification reaction of lactic acid and ethanol, particularly from the fermentation of agro-food based materials.

Lactic acid + Ethanol ⇆ Ethyl lactate + Water

It is capable of replacing conventional gasoline-based solvents in many applications, such as paints and cleaners, improving air quality by reducing the amount of carbon dioxide in the atmosphere. Organic esters in general are a very important class of chemicals that have applications in various areas of the chemical industry, such as in perfumes, pharmaceuticals, as plasticisers, as solvents, etc. Almost all manufacturing and processing industries depend heavily on the use of solvents. Some industry experts claim that ethyl lactate could replace traditional solvents in more than 80% of their applications [8]. However, the cost of producing the ester is quite high and as a result it is not yet widely applicable [9].

2 Materials & Methods

2.1 Materials

The substrate used in this study was biowaste generated from the food industry, and more specifically from a single production line, of the baby food sector. This substrate exhibits a substantial content of starch and sugars. It also presents a homogeneous nature and stable composition as a waste material. Analytical methods were employed to scrutinize its initial composition. Moreover, for the production of lactic acid, the amylolytic enzyme Spirizyme EXCEL (40μL/g starch) and the lactase Lactozyme Pure (5 and 20mg/g lactose) were used.

2.2 Analytical Methods

For the estimation of total and water-soluble solids, hemicellulose, cellulose, and lignin in food waste (raw and pretreated), the National Renewable Energy Laboratory (NREL) procedure was applied [10, 11]. For total starch determination, the Total Starch (AA/AMG) test kit (e.g., Megazyme, Wicklow, Ireland) was used (AACC Method 76-13.01). The Soxhlet standard method (5520E) was utilized for the quantification of fats and lipids [[12, 13]. Marketable kits (Glucose oxidase-peroxidase method (GOD/PAP), Biosis SA, Athens, Greece; Spectro-quant Volatile Organic Acids Test 1018909 by Merck KGaA Mellipore, Darmstadt, Germany; Ethanol Assay Kit, K-EtOHLQR, Megazymes) were used for the photometric determination of glucose, volatile fatty acids, and ethanol in the liquid fraction, respectively. Analysis of ethanol, glucose and volatile fatty acids was performed by a high-performance liquid chromatography (HPLC) system equipped with a HyperREZ XP Carbohydrate H+ Counter-ion (8 μm) column. The analysis was carried out at a flow rate of 0.6 mL/min and at 70°C in acidified (0.005M sulphuric acid) ultrapure water as the mobile phase. All analyses took place in triplicate.

2.3 Experimental Methods

Preparation of the fermentation broth for Lactic Acid (nutrient medium MRS and inoculum). The MRS, used as a nutrient medium, after appropriate pretreatment, stood as the substrate for the culture of microorganisms [9]. During its pretreatment, the MRS medium underwent autoclaving at 100°C for 15 minutes. Subsequently, the medium was allowed to cool to a temperature below 40°C to mitigate the risk of microbial degradation. A measured quantity of microorganisms, derived from a pharmaceutical probiotic preparation in powdered form (concentration: 10 mg/mL MRS), was introduced into the culture medium. The resulting solution was then subjected to agitation within a shaking air bath at 37°C and 150 rpm for the required duration stipulated by each distinct experimental procedure.

Production of Lactic Acid. For the purpose of lactic acid production, systematic experimentation was conducted to optimize the process with a focus on enhancing both the concentration of lactic acid generated and the duration of its production (Tables 1-3). Varied parameters were methodically assessed in these experiments to determine the optimal process conditions, while the parameters of load, temperature, volume, and stirring rate remained consistently controlled. All experiments were performed thrice and the results reported are the mean values.

The controlled conditions included a 10% w/w dry solids loading at 37°C, with a reaction volume of 200 mL, and a stirring rate set at 140 rpm. Furthermore, inoculum was introduced in an amount proportional to the load required for each experiment, typically at 5% v/v or 10% v/v, based on the experimental design. At the end of the experiment, a 7.5 mL aliquot was extracted and subjected to a sequential process involving centrifugation, filtration, dilution (D=10), and quantitative analysis.

Table 1. Experimental conditions for testing the effect of lactase

Experiment	Solid Load (% w/w)	Amylase (μL/g starch)	Lactase (mg/g lactose)	Lactic Acid Bacteria & MRS 24h (% v/v)	T (°C)
1	10	40	5	5	37
2	10	40	20	5	37

Table 2. Experimental conditions for testing the effect of the time of microorganism cultivation

Experiment	Solid Load (% w/w)	Amylase (μL/g starch)	Lactase (mg/g lactose)	Lactic Acid Bacteria & MRS 24h (% v/v)	T (°C)
3	10	40	5	5	24
4	10	40	5	5	48

Table 3. Experimental conditions for testing the effect of inoculum size

Experiment	Solid Load (% w/w)	Amylase (μL/g starch)	Lactase (mg/g lactose)	Lactic Acid Bacteria & MRS 24h (% v/v)	T (°C)
5	10	40	5	5	37
6	10	40	5	10	37

In an effort to increase the productivity of lactic acid, repeated fermentation was also applied examining the addition of enzymes (see Fig. 1). Repeated batch culture usually offers several advantages, including good depletion of medium in the reactor at the end of cultivation, the reuse of microbial cells for subsequent fermentation runs, high cell concentration in the culture, low time required for process operation, and process productivity. Moreover, repeated fermentation achieves greater degradation yields of waste in less time.

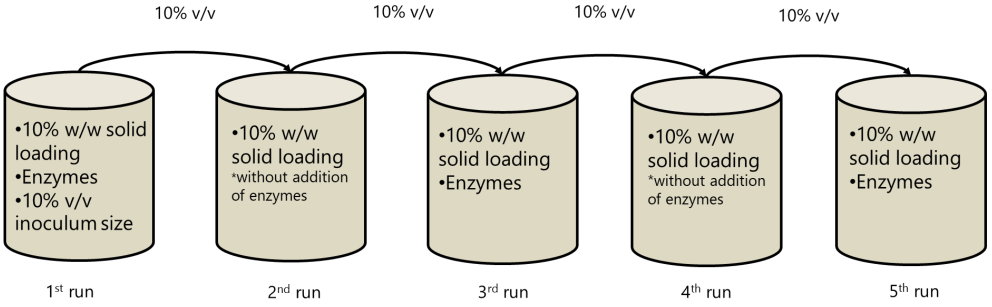

Fig. 1. Experimental protocol for one of the tests conducted during repeated fermentation

Production of Ethyl Lactate. The synthesis of ethyl lactate, as previously outlined, entails the utilization of lactic acid and ethanol as primary substrates, catalyzing a biphasic esterification reaction. This process generates water as a byproduct. The optimal ethanol-to-lactic acid molar ratio, according to Stipsitz et al. [14], is nEtOH/nLA = 3/1. This ratio was selected due to its ability to curtail the formation of lactic acid oligomers, specifically intramolecular autoesterification, to a minimal extent of approximately 0.4%, contrasting sharply with the 2.4% observed at a 1/1 ratio [14].

An effort to produce ethyl lactate employing bioethanol (98 v/v %) and lactic acid from the fermentation broth as raw materials was also made. The fermentation broth had the necessary concentration of lactic acid, derived from the aforementioned process (0). However, it also included a considerable volume of water, ethanol, and other constituents, thereby exerting notable interference on the esterification reaction. Consequently, pretreatment of the fermentation broth was imperative to mitigate these inhibitory effects.

Upon determination of the lactic acid concentration, the required amount of lactic acid was mixed with an appropriate volume of bioethanol in a flask. The reaction was initiated as soon as Amberlyst 15 catalyst was introduced.

Periodically, samples were extracted from the reaction mixture to monitor the reaction progress. Ethanol was supplemented to the reaction vessel at predefined intervals to counteract ethanol depletion and uphold the initial ethanol-to-lactic acid molar ratio of 3:1.

The trials of ethyl lactate synthesis were performed in a conventional rotary evaporator.

3 Results and Discussion

3.1 Substrate Characterization

By applying analytical methods, the results of the following table (Table 4) for the composition of the waste were obtained.

Table 4. Substrate characterization.

Components	Percentage (%)
Total Solids	99.87±0.16
Moisture	0.13±0.01
Volatile Solids	96.5±0.12
Ash	3.5±0.12
Water Soluble Solids	41.81±0.35
Free Sugars	1.66±0.1
Starch	37±2.26
Oils	2.5±0.43
Total Nitrogen	2.83±0.1
Acid-insoluble residue	5.68±0.45

3.2 Lactic Acid Production

Effect of lactase. Table 5 presents the maximum yields obtained for each experimental condition and the corresponding time intervals. As can be observed from Fig. 2, variations in the lactase enzyme load exhibited negligible influence on lactic acid production over time. However, an observable deceleration in production rate accompanied elevated enzyme loading. Notably, the utilization of 5 mg/g lactose yielded slightly superior production efficiency within a reduced timeframe. Consequently, the use of a lower lactase enzyme load is deemed optimal for lactic acid production, yielding the highest productivity (15± 0.5 g/L within a 168-hour duration).

Table 5. Maximum yields obtained while testing the effect of lactase

Experiment	Examined parameter	Duration (h)	Yield (%)
1	5mg lactase/g lactose	168	48±1
2	20mg lactase /g lactose	288	51±3

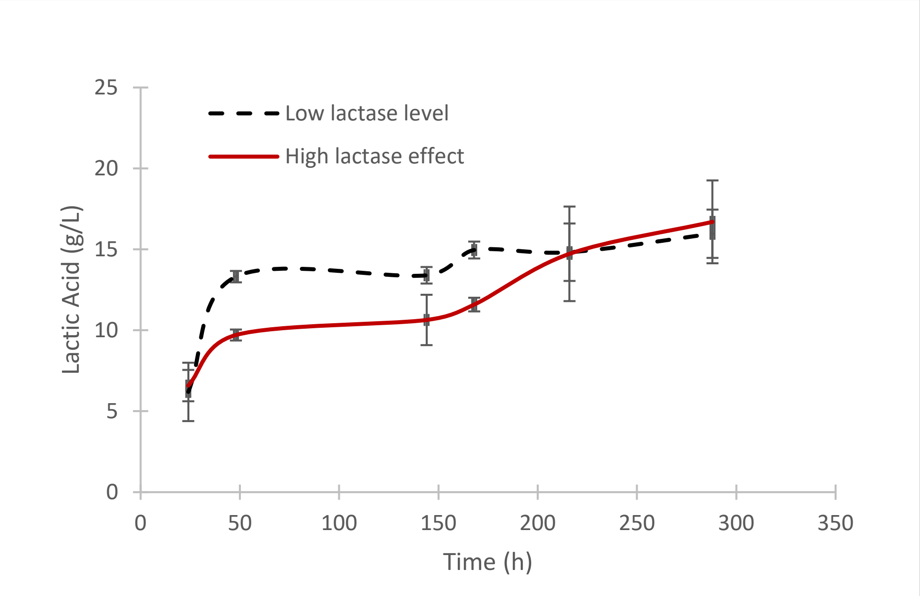

Fig. 2. Effect of lactase dosage on lactic acid production

Effect of microorganism time cultivation. Regarding the effect of microorganism time cultivation, the maximum yields of each experiment and the times at which they are achieved are shown in Table 6. The different cultivation time of the microorganisms, over time, brought about the same result in the production of lactic acid, i.e. the same concentration was ultimately observed (see Fig. 3). However, a lower production rate was observed in the 48-hour culture, as it took longer to reach maximum concentration 23.85±0.17 g/L than in the 24-hour culture. Therefore, the 24-hour culture of micro-organisms is considered more suitable for optimal production of lactic acid, which also benefits the whole process as it is carried out in a shorter overall time.

Table 6. Maximum yields attained while testing effect of microorganisms time cultivation

Experiment	Examined parameter	Duration (h)	Yield (%)
3	24h of microorganism cultivation	122	88±1
4	48h of microorganism cultivation	263	74±4

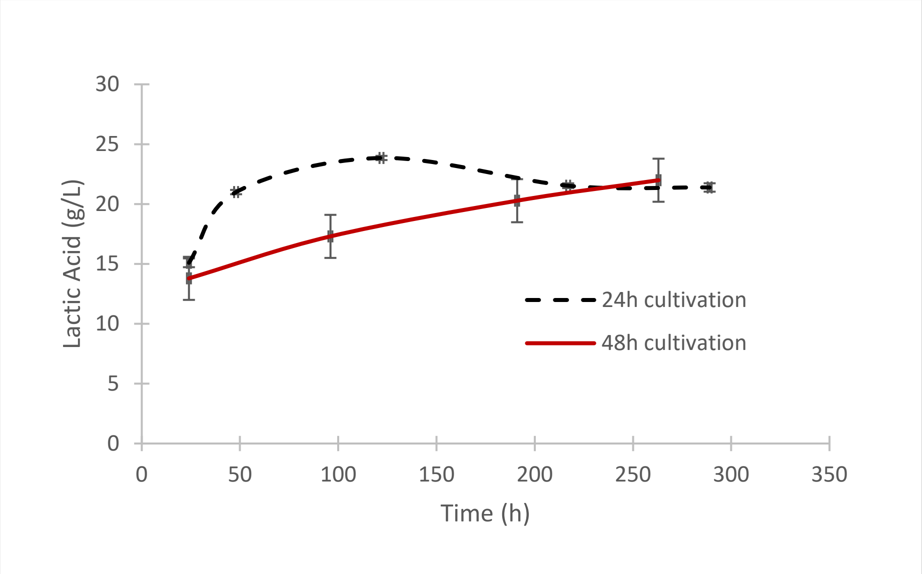

Fig. 3. Effect of microorganism time cultivation

Effect of inoculum size. As for the effect of inoculum size, the maximum yields of each experiment and the time, in which they were achieved are presented in Table 7. The load of microorganisms significantly affected the production of lactic acid. With the increase of the load, as can be seen in Fig. 4, the concentration of lactic acid increased, with a maximum value of 17.8 ± 0.9 g/L over 288h.

Table 7. Maximum yields attained while testing effect of inoculum size

Experiment	Examined parameter	Duration (h)	Yield (%)
5	5% v/v Lactic Acid Bacteria & MRS 24h	168	47 ± 4
6	10% v/v Lactic Acid Bacteria & MRS 24h	144	56 ± 3

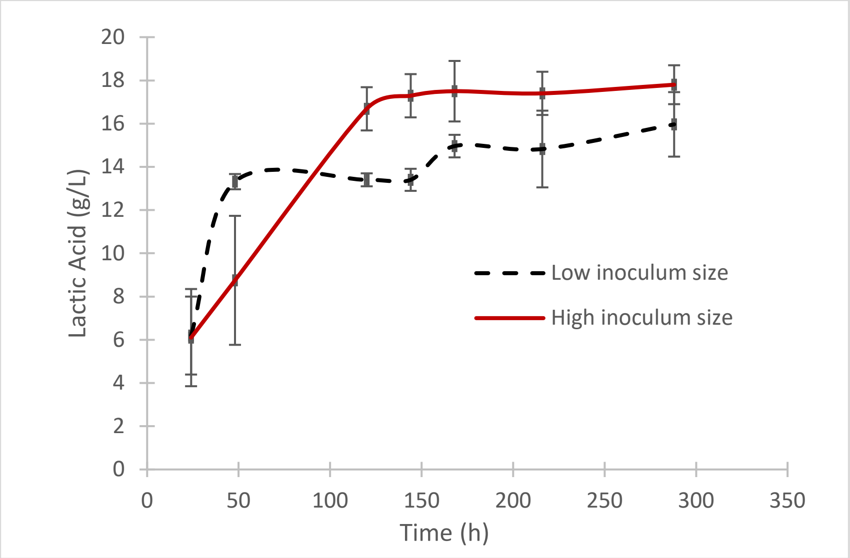

Fig. 4. Effect of inoculum size on lactic acid production

Repeated Fermentation. Two experimental runs were performed with a microorganism load, 10% v/v but different frequencies of enzyme addition.

In the experiment with alternate enzyme addition, a maximum lactic acid concentration of 24.82 g/L and yield of 87% was obtained in the 4th run as showed in Table 8, compared to the maximum lactic acid concentration in the experiment with continuous enzyme addition, which reaches 20.64 g/L and yield 73% in the 3rd run at 48h as showed in Table 9. Thus, adding enzymes alternately in each cycle contributed greatly to the production of lactic acid, increasing the yield. In contrast, the continuous addition of enzymes seems to hamper the process, reducing productivity accordingly.

Table 8. Yields of repeated fermentation adding enzymes alternately

Run	Duration (h)	Yield (%)
1	72	60
2	72	74
3	48	70
4	24	65
	48	87
5	24	75

Table 9. Yields of repeated fermentation adding enzymes in every run.

Run	Duration (h)	Yield (%)
1	72	72
2	72	70
3	48	73
4	24	43
5	24	56

3.3 Ethyl Lactate Production

Ethyl lactate production by bioethanol and lactic acid from the fermentation broth was achieved, with the maximum lactic acid conversion being 59.9% at 255 min (see Fig. 5). Comparable values of 57.5% were achieved at 180 min. The mean lactic acid conversion was 56.2 ±3.2% at 225 ±35min. The water content in the reaction mixture strongly influenced the esterification reaction. Thus, the higher the grade of reactants, the higher the lactic acid conversion.

In general, the production of ethyl lactate using biodegradable solvents poses several challenges primarily due to the nature of lactic acid. The substrate of the present study constitutes a raw material rich in polysaccharides, which, upon water and ethanol removal in the rotary evaporator (lactic acid pretreatment), forms a viscous solution. This solution, detrimental for the reaction with ethanol in the presence of catalyst for ethyl lactate production, becomes even more viscous and dysfunctional over time, rendering it unsuitable for further processing. However, the results are promising although further research is necessary in order to achieve greater conversion of lactic acid and hence production of ethyl lactate.

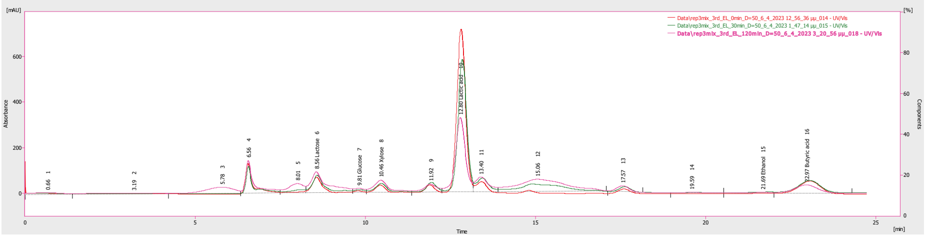

Fig. 5. HPLC chromatogram for the ethyl lactate production reaction with a catalyst at a weight fraction w_{cat}=0.3 and initial lactic acid concentration of 224.9 g/L

4 Conclusions

This study delved deeply into the production of lactic acid and ethyl lactate from biowaste generated in a baby food industry, yielding highly significant findings. Specifically, it was demonstrated that lactic acid production from organic waste is technically feasible and offers high yields; therefore, the crucial aspect is its recovery. Additionally, it is noteworthy to mention that the cultivation of microorganisms is an essential process for lactic acid production, as well as the medium in which they thrive, MRS. The selection of this medium proved successful, as it yielded good results.

Furthermore, the production of lactic acid was deemed feasible, albeit requiring further research. Experiments were conducted to explore various parameters aiming to identify the optimal process, while maintaining constant load quantity, temperature, volume, and stirring rate. It was revealed that experiments with 5 μg/g lactose exhibited maximum production (15g/L) within a shorter timeframe (168h) with a 48% yield. Therefore, employing a reduced lactase loading is considered optimal for lactic acid production, resulting in the highest productivity. Additionally, the influence of pre-cultivation time of microorganisms before their addition to the solution resulted in similar lactic acid concentration outcomes. However, experiments with a 48h cultivation period showed maximum production (23g/L) within a shorter timeframe (122h) with an 88% yield. Furthermore, it was observed that the lactic acid concentration is highly influenced by microorganism loading. Experiments were conducted with loads of 5% and 10%, showing noticeable differences in experiments with higher loads. Last but not least, during repeated fermentation, the alternate addition of enzymes in each cycle significantly contributed to lactic acid production, notably increasing both the yield and productivity (24.82 g/L is obtained in the 4th run at 48 h). Conversely, continuous enzyme addition, appears to impede the process, correspondingly reducing productivity (20.64 g/L in the 3rd run at 48 h).

On the other hand, the bioethanol and lactic acid fermentation broth successfully yielded ethyl lactate production, reaching a maximum lactic acid conversion of 59.9% at 255 minutes. The average lactic acid conversion stood at 56.2 ± 3.2% within a time frame of 225 ± 35 minutes. The esterification reaction was significantly impacted by the water content in the reaction mixture. Consequently, the lactic acid conversion increased with a higher grade of reactants, highlighting a positive correlation.

Generally, the development of biodegradable solvents is poised to revolutionize industry, hence bolstering research in this realm is imperative. A comprehensive study was conducted on lactic acid production from infant food waste, yet the production of ethyl lactate certainly requires further investigation. It is essential to continue research in this direction aiming to optimize processes and possibly formulate an experimental protocol for biodegradable solvent production to be tested and implemented on a larger scale. Furthermore, at this stage of research, conducting a Life Cycle Assessment (LCA) of one of the biodegradable solvents would be particularly intriguing, allowing for examination of both technical and economic factors. Thus, the production of green solvents from organic waste would be even closer to industrial implementation.

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Design of an innovative system for the detoxification of pharmaceutical wastewater

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Abstract. The concentration of Active Pharmaceutical Ingredients (APIs) in wastewater is directly affected by the increasing worldwide use of pharmaceuticals. The release of the wastewater may contaminate the surface water and marine life. Conventional wastewater treatment plants (WWTPs) are unable to remove completely all APIs. The most frequently used methods are conventional activated sludge system (CAS) and membrane biological reactors (MBR); based on studies the removal percentage of APIs in these methods was lower than 10% in some compounds. Catalytic hydrogenation is a highly effective water treatment process that offers superior selectivity and reactivity compared to traditional methods, without the use of any chemicals. There is no need for additional wastewater treatment to remove any toxic byproducts that may be produced, making the process cost-effective and efficient. The catalytic reactions of hydrogenation are also rapid reactions with short residence times and smaller reactors, reducing both the operations and installation costs. The main components of the proposed pilot system are a mixing tank, a filtration system, a water electrolysis unit operating with Renewable Energy Sources (RES), and a catalytic reactor where the concentrated stream from the filtration system will be treated. In this reactor, the pharmaceutical compounds in the presence of a catalyst will be hydrogenated and converted to non-critical organic matter. The designed system fully operates with renewable energy-solar energy, under room temperature and pressure conditions.

Keywords: APIs, wastewater, pharmaceutical industries

1 Introduction

1.1 Environmental Problem

In recent decades, there has been a significant surge in the use of pharmaceuticals, placing an increasing burden on the environment due to their widespread release [1,2]. Human and veterinary drugs enter the environment primarily through manufacturing processes, improper disposal, and metabolic excretion. Numerous studies confirm the presence of pharmaceuticals in aquatic ecosystems, particularly antibiotics, which comprise a substantial portion of global pharmaceutical consumption. Antibiotic residues have been identified in various water sources, including surface waters [4], groundwater [3], seawater, drinking water [5], municipal wastewater treatment plant effluents [6], and hospital wastewater.

Based on the literature [7-9], the number of residues (ng/L to low µg/L) that remain even after wastewater treatment can still induce toxic effects. The persistence of these residues is attributed to the extensive use of pharmaceuticals worldwide, both in human and animal contexts. This continuous usage results in the continuous introduction of pharmaceuticals into the environment, leading to their bioaccumulation. Despite the relatively short environmental half-lives of pharmaceuticals, their continuous presence and impact on the environment are described as pseudopersistent. This term reflects the ongoing introduction of pharmaceuticals into ecosystems, contributing to their sustained presence and potential ecological consequences. Some pharmaceuticals remain in the aquatic matrix because they are highly polar and non-volatile.[8]

Many of these pollutants possess endocrine-disrupting qualities, and are non-biodegradable, toxic, or persistent, emphasizing the need for their degradation and removal before being released into the environment. This becomes particularly crucial when considering the reuse of treated water for irrigation, a process known as wastewater reclamation. In this context, there is a heightened concern as these contaminants may accumulate in soil and crops.[10] The significance of wastewater reclamation lies in its contribution to better water resource management, as it generates water of adequate quality for non-potable uses. These non-potable uses do not necessitate water that meets drinking water standards. By reclaiming water, we can substitute it for freshwater, resulting in substantial freshwater conservation that would otherwise be wasted. However, the reclaimed water must be devoid of persistent, toxic, endocrine-disrupting, or non-biodegradable contaminants to ensure its suitability for reuse without posing risks to the environment and agriculture.

Conventional WWTPs are capable of removing only some contaminants. Non-biodegradable contaminants may not be treated adequately and be released into the environment, as is documented by several studies.[11]

In a study conducted by Verlicchi et al. in 2012 [6], they collected and analyzed data from 264 WWTPs located across various global regions. Out of the 264 WWTPs investigated in this study, 244 were CAS systems and 20 were MBR. The study identified five compounds—diclofenac, ibuprofen, indomethacine, ketoprofen, mefenamic acid, and tramadol—with removal percentages lower than 10%. The researchers noted that the presence of certain pharmaceutical compounds in the effluent released from WWTPs into surface water bodies could pose a medium to high-acute risk to aquatic life.

This study highlighted that some pharmaceutical compounds, individually non-toxic, were being released into the environment at high daily mass loads. This raised concerns about potential negative effects on aquatic life over the long term, considering chronic exposure and a mixture of toxicities. Additionally, they found the presence of several pharmaceuticals, including ibuprofen, ketoprofen, diclofenac, ofloxacin, and azithromycin, in sewage sludge.

Several independent studies have suggested that the repetitive application of biosolids, sludge, or even the irrigation of wastewater rich in pharmaceutical residuals to agricultural soils may lead to an increase in the concentration of these compounds in the soil over time. This could have implications for key ecological functions, such as the carbon cycle, and may impact the environment significantly.[12] Five hundred fifty-nine different pharmaceuticals have been detected globally in the wastewater matrices of sewage, WWTP effluent, effluent, and sludge. A close relationship between occurrences in treatment plants effluent and surface waters can be assumed since most treatment plants discharge directly into surface waters, such as rivers and lakes.[13]

More than a hundred different pharmaceutical substances were found in several European countries and the United States of America in the aquatic environment (surface water, groundwater, and /or drinking water).[13]

In 2016, the United Nations recognized the urgent need for immediate action to address the global threat of antimicrobial resistance (AMR). While the contribution of antibiotic release from manufacturing sites constitutes a relatively small portion of overall antibiotic emissions into the environment, poorly controlled discharges in certain manufacturing sites can lead to elevated levels of active residues in water, soil, and sediments surrounding these areas, creating hotspots of AMR. Acknowledging this concern, the pharmaceutical industry has undertaken commitments to mitigate the release of antibiotics into the environment resulting from its operations.

To achieve this goal, a coalition of companies collaborated to specifically tackle issues related to antibiotic residues discharged from manufacturing sites. Beyond establishing a framework outlining minimum environmental expectations for antibiotic manufacturers, this alliance, dedicated to combating antimicrobial resistance, also sets science-based targets for receiving waters. These targets, expressed as predicted no-effect concentrations (PNECs) for antibiotics discharged during manufacturing operations, mark a significant step forward in establishing a quantitative basis for implementing effective methods to reduce the environmental impact of manufacturing emissions.

In March 2019, the Commission adopted the European Union Strategic Approach to Pharmaceuticals in the Environment (PiE) which focuses on addressing the environmental impacts of all stages of the lifecycle of pharmaceuticals (both human and veterinary), from design and production through use to disposal.

The proposed system is expected to align with and contribute to several important European environmental policies and objectives. These include the Circular Economy package of 2018, Water Framework Directive 2000/60/EC, a strategy against the pollution of water that sets environmental quality standards, Directive 2008/105/EC which sets environmental quality standards (EQS) for priority substances and certain other pollutants, Directive 2000/60/EC which aims to achieve good surface water chemical status, Commission Implementing Decision C(2020)5205 and the selection of substances for the 4th Watch List under the Water Framework Directive, as well as the reference Document for the Production of Large Volume Organic Chemicals. The key targets of the 2030 Climate & Energy Framework are to reduce greenhouse gas emissions from 40% to at least 55%, increase the share of renewable energy from 32% to 42.5%, decrease energy consumption from 32.5% to 36%, and achieve a 39% improvement in energy efficiency by 2030.

The overall aim of this study is to design a system for the detoxification of wastewater from the pharmaceutical industry. This will be achieved by developing and implementing an innovative, economically viable, and cost-efficient system for transforming pharmaceutical compounds into non-toxic substances (a novel detoxification process). The system will be able to treat the wastewater generated from production activities, ensuring the safe reuse of treated water for irrigation, cleaning, and cooling purposes. Ensuring in this way that no APIs would end up in the wastewater sewage system without being processed and detoxified by the system.

2 Applied techniques for the detoxification of pharmaceutical substances in wastewater

2.1 Conventional Methods

Pharmaceuticals are now recognized by the scientific community as chemicals of emerging concern (CEC) that were found to be harmful to aquatic life, the ecosystem, and potentially human health.[14] Conventional WWTPs are not designed to remove pharmaceutical compounds from wastewater and as a result, pharmaceuticals are released into surface waters.[13-16]

Conventional wastewater treatment facilities typically use biological degradation using an activated sludge process, whereas advanced facilities have treatment processes, such as membrane filtration (reverse osmosis), ozonation, and advanced oxidation technologies. Pharmaceuticals are a diverse group of chemicals, with varying physical and chemical properties. Treatment efficacy depends on these physical and chemical characteristics (e.g. hydrophobicity), their reactivity towards different treatment processes, and process control, such as solids retention time, temperature, and hydraulic retention time. Many pharmaceuticals are hydrophobic, which makes them less effectively removed by sorption into sludge. This means that treatment removal efficiency can vary significantly between different treatment facilities or at different times within the same facility.[17]

Membrane filtration has been used more extensively recently as a tertiary treatment step, but this method can not remove pharmaceutical pollutants effectively. Moreover, in membrane filtration, the membranes get clogged and need regeneration which increases the cost of the method. This method needs a high initial investment and has a high operating cost.

Ultraviolet radiation needs a very high initial investment and high operating costs due to high energy demand. Electro-oxidation also has high operating costs and is only efficient when the effluent is conductive. Another drawback of this method is that electron fouling occurs as a result of the deposition of material on the electrode. Disinfection of wastewater using chlorine may produce harmful by-products.

Advanced Oxidation Processes (AOPs) are studied extensively by the scientific community, but very few WWTPs have applied AOPs. Advanced oxidation processes usually require high treatment time and high energy costs, and methods like Fenton oxidation or Fenton-Zeolite catalysis need additional process steps for the separation of the catalyst or the removal of toxic products and additional reagents like ozone, hydrogen peroxide, or ultraviolet light. These additional requirements increase the installation and operating costs further. Table 1 shows the results of several studies that illustrate the removal rates that different wastewater treatment processes can expect. These are based on observations of treatment processes ranging from single-unit processes to full-scale wastewater treatment facilities found in the various studies.[18]

Table 1. Results of several studies illustrate the removal rates that can be expected by different wastewater treatment processes.

Treatment Process	Removal Range (%)	Water Source	Studied Area	Reference
Conventional wastewater treatment processes				
Activated Sludge	11-99	Raw Sewage	Australia	Watkinson, Murby & Costanzo (2007)
	7-100	Primary settled sewage	Europe, Japan	DWI (2007)
	<20-80	Primary settled sewage	France	Gabet-Giraud et al. (2010)
	-193-86	Primary settled sewage	Europe	Vieno, Tuhkanen & Kronberg (2007)
	8-98	Not specified	Brazil, Europe, Japan	Ziylan & Ince (2011)
Biological filtration	6–71	Primary settled sewage		DWI (2007)
Primary settling	3–45	Not specified	Brazil, Europe, Japan	Ziylan & Ince (2011)
Coagulation, filtration, and settling	5–36	Not specified		
Sand filtration	0–99	Activated sludge effluent		
Advanced wastewater treatment processes				
Ozonation	1-99	Activated Sludge effluent	Brazil, Europe, Japan	Ziylan & Ince (2011)
	86-100	Secondary effluent	France	Gabet-Giraud et al. (2010)
Ozonation/ultrasound and sonocatalysis	23–45	Not specified		Ziylan & Ince (2011)

Ozonation and catalytic ozonation	> 9–100		Europe, India, Japan, Turkey, USA	
UV irradiation	29	Not specified	Brazil, Europe, Japan	Ziylan & Ince (2011)
Photolysis (UV/ hydrogen peroxide)	52-100	Not specified	Europe, India, Japan, Turkey, USA	Ziylan & Ince (2011)
Dark and light Fenton	80-100			
UV/ TiO_2	>95			
Biomembrane	23-99	Treated effluent	Brazil, Europe, Japan	Ziylan & Ince (2011)
Microfiltration and RO	91-100	Secondary treated effluent	Australia	Watkinson, Murby & Costanzo (2
Reverse osmosis	62–97	Secondary treated effluent	France	Gabet-Giraud et al. (2010)
Ultrasound	24–100	Not specified	Europe, India, Japan, Turkey, USA	Ziylan & Ince (2011)

Activated sludge processes can achieve higher removal efficiency than simple biological filters, as shown in Table 1. Removal rates for pharmaceuticals can vary [19], depending on sludge age, activated sludge tank, temperature, and hydraulic retention time. [20] Advanced wastewater treatment processes, such as ozonation, membrane treatment, and advanced oxidation, can achieve higher removal rates (up to 100%) for pharmaceuticals compared with conventional processes. For example, another bench-scale study showed that advanced oxidation processes can achieve up to 100% removal of diclofenac.[21]

Predicting removal rates for pharmaceuticals is feasible within wastewater treatment processes for substances with very similar chemical structures. Challenges arise when attempting to predict removal rates across different wastewater treatment facilities. Beta-blockers, in particular, exhibit highly variable removal rates, and these rates can differ significantly depending on the specific wastewater treatment facility.

For instance, beta-blockers like betaxolol, bisoprolol, carazolol, and metoprolol show notable removal by activated sludge processes, with reported removal rates ranging from 65% to about 90% [20,22]. However, results for other beta-blockers like sotalol and propranolol, where removal rates are less than 20% and approximately 32% are reported in different studies [20,23]. This variability highlights the practical difficulties in predicting removal rates across diverse wastewater treatment facilities.

Overall, the existing treatment processes face several drawbacks, including the generation of toxic by-products, the incomplete destruction of APIs to comply with stringent PNEC values, high operating and energy costs due to the frequent replacement of equipment, and limited applicability to only specific groups of APIs.

2.2 Catalytic Hydrogenation

Catalytic hydrogenation is a highly effective water treatment process that offers superior selectivity and efficiency compared to traditional methods, without using any chemicals.[24,25] This process results in the production of substances that are either non-toxic or significantly less toxic and easily biodegradable.[26] This is a crucial aspect for the potential application of this process in WWTPs, as it eliminates the need for additional wastewater treatment to remove any toxic by-products that may be produced. This also has financial implications, making the process more cost-effective and efficient. The catalytic reactions of hydrogenation are also rapid reactions that allow short residence times and smaller reactors, reducing both the operations and installation costs.[27]

AOPs, widely applied in treating industrial wastewater from sectors like pulp and paper, dyeing, and petrochemicals, effectively address the presence of harmful and stubborn organic pollutants.[28,29] Catalysts play a crucial role in AOPs, offering benefits such as heightened reaction rates, the feasibility of compact reactors, shorter reaction times, and enhanced efficiency.[30,31,32] Heterogeneous catalysis holds an edge over homogeneous catalysis by eliminating the need for an extra step in the process—specifically, the recovery of the catalyst. Catalytic wet air oxidation (CWAO) decomposes more easily even the refractory substances and reduces the stringency reaction conditions.[27]

Based on some publications [27,30,31], noble metals such as Rh, Pd, and Pt have higher catalytic activity and resistance to metal leaching than base metal oxide catalysts. A strong oxidizing agent like hydrogen peroxide will generate hydroxyl radicals with high oxidative power and can also be used in CWAO to further reduce the stringency of reaction conditions.[32] Hydrogen peroxide due to its low cost can be used as a source of the OH radicals, in the presence of a catalyst (Rh, Pt, Pd) using hydrogen, in excess of oxygen/air, and can produce hydrogen peroxide in situ. In situ production of hydrogen peroxide reduces, also, the cost of the operation. Results of some publications show that in situ production of hydrogen peroxide has actual effects on the CWAO of pharmaceuticals.[27]

The effects of the nature of the active phase as well as the feed gas composition have been examined, and the results strongly suggested that the maximum conversion of paracetamol of 90% was reached in just 30 min of reaction over 1 wt.% Rh/Al_2O_3, when using pure hydrogen in the feed. Toxicity tests that followed showed a dramatic decrease in the toxicity of the product solutions, indicating that catalytic hydrogenation of pharmaceuticals might be a promising method for the elimination of their toxicity, as can be used for the degradation of wide spectrum organic compounds in aqueous solutions since the method is non-selective.

3 Design of a Pilot System for the detoxification of pharmaceutical wastewater from a pharmaceutical industry in Cyprus

The specific objectives of this study are to install such a system in a large pharmaceutical industry in Europe and thus to avoid APIs release in the wastewater sewage system, convert about 1,5 kg of APIs to nontoxic compounds, save 3,650 m^3 of potable water annually, reuse and recycle clean water for manufacturing plants or use for irrigation purposes, minimize the system's environmental footprint using renewable energy sources, transfer the project's results to other pharmaceutical companies across Europe, communicate and promote public awareness at local and regional levels, draft policy recommendations to the EU and create an effective value chain through the socio-economic impact of the proposed actions.

The proposed reactor initial design is based on published experimental data.[27,30,31,32] Some modifications of the initial design are expected after the replication of these studies with real wastewater solutions. Ultimately, the whole pilot system is designed according to the specific requirements of the pharmaceutical industry.

The pharmaceutical facility's equipment cleaning is expected to generate approximately 10 m^3/day, hence the proposed system is designed with a capacity of 10 m^3/day. The main components of the pilot system are a mixing tank where the effluents from pharmaceutical facilities are mixed, a Reverse Osmosis (RO) system, with a capacity of 420 L/h, that minimizes the volume of the wastewater going through the catalytic reactor by 80-90% close to 370 L/h. This approach minimizes both the size and cost of the reactor. A water electrolysis unit operating with renewable energy sources, especially solar energy. The concentrated stream from the RO system, approximately 50 L/h or 1.2 m^3/day, will be driven to and treated in the catalytic reactor. In this reactor, the pharmaceutical compounds, at room temperature (25 ^{0}C), under atmospheric pressure (1.3 atm), and in the presence of a catalyst will be hydrogenated and converted to non-critical organic matter, the reaction time is 30 min-2 hours. As a result of the hydrogenation process applied to pharmaceutical compounds, water with very low or no toxicity is produced, suitable for irrigation purposes, heat exchange systems, or cleaning. The energy consumption of the RO system is expected around 3 kWh/m^3 inlet or 30 kWh/day and the energy consumption of the catalytic reactor is around 5 kWh/m^3.

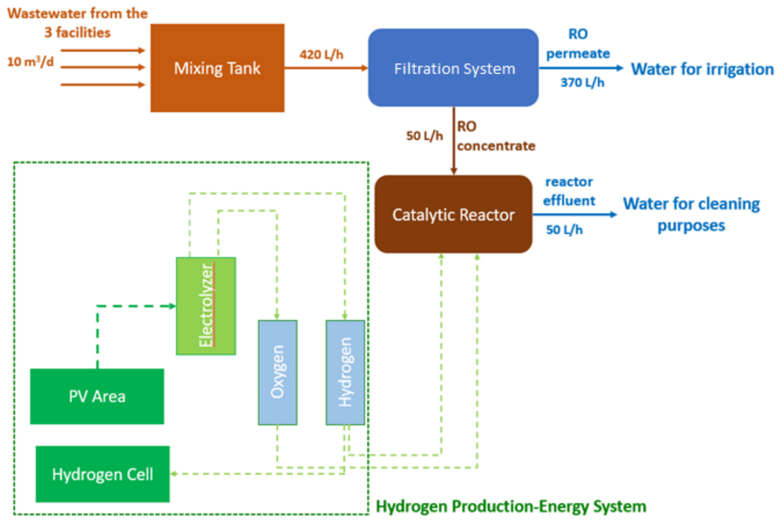

Fig. 1: Process flow Diagram

The catalytic reactor is an autoclave Continuous stirring tank reactor (CSTR) equipped with a catalyst basket. For the catalytic experiments, a special flow apparatus suitable for three-phase catalytic experiments (solid-liquid-gas) was used. To maximize the contact area between the solid-liquid-gas phase and minimize the possible external mass transfer phenomena the reactor's inlet and outlets as well as the catalytic basket designed adequately. The catalytic reactor was designed to work in a batch mode of 60-100 L/h, with low gas flow close to 1-2ml/min. The liquid phase (pharmaceutical wastewater known concentration of APIs), solid phase, and gas phase hydrogen/oxygen gas mixture were under continuous flow at about 1.3 atm total pressure and 25^{o}C. The design and specifications of the catalytic reactor are derived from the outcomes of bench-scale tests that were conducted.[24] The system will fully operate with renewable energy (solar).

The system focuses on the reduction of pressures from chemical pollutants in the water environment by reducing emissions of priority substances and other chemicals identified as river basin-specific pollutants at the source, through the use of appropriate substitutes or alternative technologies.

The system aims to design a novel technology for the treatment of pharmaceutical wastewater. Its operation requires no water consumption, thus saving 10 m^3 of potable water daily, in its place the same quantity of recycled water will be used. This means that 3,650 m^3 of potable water will be saved per year and about 5,220 g of APIs will not be released to the urban wastewater. The method utilised in this project can operate under mild temperature (i.e., environmental) and pressure (i.e., atmospheric) conditions, a fact that greatly reduces operating costs.

3.1 Monitoring Protocol

To monitor and evaluate the progress of the designed system, as well as the environmental impact of the proposed technology, a monitoring protocol is required to be established. The impact and the progress of the system will be evaluated by measuring specific indicators throughout its development and implementation.

The pharmaceutical industry generates process wastewater containing a variety of pollutants. The composition of pharmaceutical wastewater is complex, and it usually has a high concentration of organic matter, high toxicity, high conductivity, and is difficult to degrade. Even after secondary treatment, there are still trace amounts of suspended solids and dissolved organic matter.[33] Basic physicochemical parameters that are recorded to characterize pharmaceutical wastewater are the mentioned indicators pH, conductivity, the concentration of chloride ions, Biological Oxygen Demand (BOD_5), Total Suspended Solids (TSS), Chemical Oxygen Demand (COD), turbidity, concentration of total Nitrogen, the concentration of total Phosphorus, toxicity of wastewater, and concentration of pharmaceutical substances.

The design of the system is based on the detoxification of some pharmaceutical substances which are listed on the 4th Watch List under the Water Framework Directive.[34] A mechanism that provides high-quality monitoring information on the concentrations of potentially polluting substances in the aquatic environment to support future prioritization exercises in line with Article 16(2) of Directive 2000/60/EC Water Framework Directive and improves the protection of the aquatic environment and human health via the environment. The designed system focuses on the detoxification of Lincomycin, belongs to lincosamides, Lorazepam belongs to benzodiazepine, Dexamethasone Phosphate, Co-amoxiclav, Cloxacillin Sodium, Hyoscine Butylbromide, Diazepam, Dicloxacillin, Lincomycin, Amikacin, Amoxicillin/Clavulanic Acid, Amoxicillin.

The design and operation of the system are focused on wastewater with physicochemical characteristics that are presented in Table 2:

Table 2: Physico-chemical characterization of tested effluents.

Parameter	**Value close to**
BOD_5 (mg/l)	12-1055
Cl^- (mg/l)	12-6100
Conductivity (μS/cm)	100-12000
pH (20 ºC)	4.5-9
TP (mg/l)	0.1-436
TN (mg/l)	1.6-130
COD (mg/l)	4-73600
TDS (mg/l)	1.2-215
TSS (mg/l)	0.1-428
TU50 (5min, 15min,30min) Microfox	<1
Turbidity (FAU)	2-1640

The water quality in the RO permeate stream, which constitutes approximately 80-90% of the initial wastewater stream, will closely resemble that of distilled water. As for the RO retentate stream, it will share similar physico-chemical characteristics with the RO permeate stream, with the exception of higher concentrations and toxicity of APIs. The goal is to reduce the toxicity of pharmaceutical substances by approximately 70-90% through treatment in the catalytic reactor.

The conversion of selected API is studied over monometallic catalysts of Rh using different reducing feed gas compositions, as the conversion of the APIs is clearly affected by the nature of the active phase of the catalyst. The catalytic performance of the selected active phase is examined further and in detail, at different reaction times and different concertation of APIs. The toxicity of the product solution is studied before and after every reaction and for a range of APIs concertation, with the aim of verifying that the produced water follows the requirements for water reuse based on regulation (EU) 2020/741 of the European Parliament and the Council.

4 Conclusions

Wastewater from pharmaceutical industries ends up initially in the city's central sewage system and then in the WWT. Generally, WWST are not able to completely remove all pharmaceutical compounds.

Enhancing the efficiency and effectiveness of solutions and treatment options for recycled or reclaimed water involves implementing specific strategies. These strategies include the development of concepts for alternative water supply, wastewater treatment, and the reuse, recovery, and recycling of resources. Implementing source control methods and cost-effective on-site technologies to address the discharge of emerging pollutants and pathogens into wastewater treatment systems. Establishing water treatment innovation hubs in regions lacking appropriate sewer systems and sanitation facilities. These hubs should focus on smart technologies and decentralized systems, particularly for alternative water sources. Finally, implementing systematic approaches to prevent the loss of water, energy, and resources in industrial production and water/wastewater infrastructure.

This study aims at the development, testing, and demonstration of an innovative system for the treatment of wastewater produced by the pharmaceutical industry. The system will detoxify APIs, that would otherwise pass through the sewage system causing the well reported environmental problem associated with APIs accumulation. Furthermore, this system will return purified water of high quality to be re-used by the industry and will be suitable for being replicated, transferred, or mainstreamed.

The system will be able to be applied to the pharmaceutical industry in Cyprus and other pharmaceuticals, and chemical industries producing paints, cosmetics, chemicals for industry and laboratory use, petrochemicals, polymers, plastics, and specialty chemicals. manufacturing facilities in the Europe (EU) and around the world.

The proposed technology can be applied also, to already existing and operating new WWTPs as an additional tertiary treatment, to eliminate or considerably decrease the toxicity of the effluent of the plant or detoxify the effluent to be able to be biologically treated. The technology can be applied to urban WWTPs as well as smaller WWTPs for smaller communities, hospitals, and nursing homes. It must be highlighted that the proposed solution will be examined (on an industrial scale) for the first time in the European Union and globally. Experimental data and outcomes of our bench scale test will soon published.

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Material Science and Engineering

Metal-organic frameworks (MOFs) as novel adsorbents for alternative fuel gas storage - A short review

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Abstract. This comprehensive review examines recent research on key aspects of metal-organic frameworks (MOFs). Their chemistry, crystalline structure, ease of production, yield optimization, gas adsorption-delivery mechanisms, and performance are included. The potential for greater applicability in light of a wider utilization of MOFs as novel and effective adsorbents for storage of compressed natural gas and hydrogen is also considered. Using clean energy sources is essential for achieving zero net-carbon emissions to solve serious global warming and climate change problems. In this regard, natural gas and hydrogen are becoming well-known potential alternative car fuels. However, they should first be produced and then also stored till consumption, to accomplish sustainable transportation. Though, the volumetric energy density of hydrogen and natural gas (mostly methane) is significantly lower than that of gasoline. This presents a major obstacle to compressed gas storage in fuel cells for alternative vehicles. To overcome this hurdle and achieve a driving range comparable to that of conventional vehicles, an enhancement in the onboard gas storage capacity is required. One way to increase the energy density is storage of gas onto a solid surface via physical adsorption. For this purpose, MOFs stand out for their advantageous adsorption characteristics, particularly because of their high pore volume, specific surface and gas affinity adsorption sites, thus promoting future energy storage and cleaner energy solutions.

Keywords: Natural Gas, Hydrogen, Low-pressure Gas Storage, Metal Organic Frameworks (MOFs), Alternative Vehicle Fuels

1 Introduction

Natural gas and hydrogen are increasingly obtaining traction as possible alternative vehicle fuels to cope with global warming and climate change, with extreme weather phenomena including rising sea levels, drought, and deforestation posing a threat to human health and survival [1,2]. Indeed, a zero-carbon future necessitates the utilization of clean energy sources, in accordance with current climate change mitigation policies that call for immediate, dramatic, and transformative adaptation activities, especially in terms of lowering greenhouse gas emissions for sustainable development [3,4].

Natural gas, in particular, can be viewed as the fuel that can aid in the transition of the energy mix to one fully dominated by hydrogen-based, carbon-neutral clean energy. However, these alternative vehicle energy sources must not only be produced, but also stored before being utilized to achieve entirely sustainable transportation, as they exist in the gaseous phase with high entropy at usual atmospheric conditions.

Despite the promising future of hydrogen as an energy source, some technological challenges must first be resolved. Although hydrogen technologies using renewable energy sources have been developed to achieve a sustainable energy cycle, a major barrier to the adoption of hydrogen technology is the storage process.

Actually, both hydrogen (H2) and natural gas (mostly CH4) have lower volumetric energy densities than gasoline, posing a substantial issue in terms of storing compressed gas in alternative vehicle fuel cells. To overcome this obstacle and achieve a driving range comparable to that of traditional automobiles, more onboard gas storage capacity is required. Storage of gases onto a surface via physisorption via intermolecular weak van der Waals interactions is one essential strategy for enhancing energy density. Then, gas desorption can be easily conducted by employing appropriate pressure or heat [5,6].

So far, numerous materials with high chemical and thermal, structural stability, tailorable porosity, lightweight, efficient reversibility, and ease of manufacture have been considered as promising adsorbents for the storage of different gases, like hydrogen and natural gas. Carbon-based nanostructures, including multi-walled carbon nanotubes, peat, coconut shell-based molded active carbons, activated carbon fibers, as well as titanium-decorated polycrystalline graphene sheets, and even metal-decorated beryllium carbide have been reported as low-cost, environmentally benign, and high-performing storage options for both processes, adsorption and desorption [7-12]. Moreover, nanocluster synthesis from nanoparticle sources was reported for applications in hydrogen fuel cells and also metal addition in inorganic nanoclusters to improve gas adsorption capacity, such as in the design of novel gallium nitride nanoclusters via encapsulation with alkali metals [13]. For reversible hydrogen gas storage, materials based on decorated all-boron B38 nanocluster, anionic LaH8−, C20, C15M5, and H2@C15M5 (M = Al, Si, Ga, Ge), and PtPd nanoclusters have been reported [14-17].

MOFs in particular, represent a new category of inorganic-organic solid hybrid materials studied for that purpose in recent years due to their excellent adsorption capabilities. Especially: i. their versatile chemical composition that can be tweaked during and after synthesis for increased adsorption performance, and ii. their microstructure with a high pore volume, specific surface and adsorption sites with gas affinity are being taken into consideration in order to assess their use for improved hydrogen and methane (natural gas) adsorption and storage in specially designed tanks at temperatures closer to ambient ones and at relatively low pressures in comparison with those obtainable in liquefied storage applications.

2 MOFs as novel gas adsorbents

For the first time, the term "metal-organic framework" was mentioned in 1994 [18]. Since then, numerous MOFs have been reported in the literature, each consisting of a network of metal cations connected by organic linkers: Cu-BTC, a highly porous metal coordination open-framework polymer made up of Cu-based clusters and benzene tricarboxylate ligands, was first created [19]. Also, the MOF-5 structure was developed, consisting of Zn-based cations/clusters and benzene dicarboxylate ligands [20]. MOFs are now made from components like triethylamine, terephthalic acid, zinc acetate dihydrate, chloroform, and dimethylformamide, among others. Usually, the organic linkers are molecules with a negative charge, such as ditopic or polytopic organic carboxylates, bound to metal cations forming nodes, thus creating strong MOF crystalline architectural microstructures [21-23].

In comparison to commonly utilized microporous inorganic materials like zeolites, MOFs exhibit significantly greater specific surface areas and pore volumes, with highly tailorable pores ranging from 0-3 nm up to 10 nm, which can bridge the space between microporous zeolites and mesoporous silicas.

In fact, due to their huge specific surface area (usually between 1000 and 10,000 m2/g), molecular dimensions, diversified microstructures, and adaptable functionalities, MOFs have significant advantages for gas separation and selectivity [24,25]. Indeed, an extraordinary porosity with a pore volume in the range of 0.04-4.40 cm3/g has been reported [26,27]. Different approaches, such as metal ion exchange, can improve the chemistry of their pores. The possibility to control the structure and properties of MOFs is achieved by modifying their chemical nature and pore size without altering their basic topology or chemical functionality. The isoreticular (same network topology) principle arose from the capability to change the performance of MOF microstructures by employing an extended form of the organic linker initially used, without modifying their intrinsic topology. The application of this principle facilitated the development of MOFs with lower densities (0.13 g/cm3) due to larger pore apertures [20]. Such organic linkers, when properly functionalized, can also aid in improving target molecule selectivity [28-30]. Moreover, because they have lower heats of adsorption and heat capacities, these materials are able to conduct physical or weak chemical adsorption, demanding less regeneration energy.

MOFs are manufactured using various densification methods that influence their final stability and textural properties: initially, the interaction of hydrated metal salts with combined organic ligands in relatively expensive organic solvents at 100-150°C was used in solvothermal synthesis procedures [31-33]. Different processing routes have been explored in recent years, not only to increase adsorption properties but also to take material/system costs and environmental impacts into consideration. Indeed, the cost of adsorbents is a significant obstacle to their practical application in gas storage beyond thermal management requirements for the system [34]. For instance, opportunities to cut MOF costs by shortening the required time for synthesis and significantly reducing the solvent amounts have been reported using mechanochemistry methods, including grinding assisted by liquids or ions, aimed at achieving improved molecular mobility via the introduction of stoichiometric liquid phase quantities to a solid-state reaction, also assisted by catalytic effects [35-37]. Aqueous synthesis methods, which substitute water for the far more expensive and environmentally harmful traditional use of organic solvents, were also recently established and represent yet another alternative to conventional synthesis [38-40]. Furthermore, by using a chemical reduction approach, synthesized MOFs can be intercalated with carbon black, Pd/activated carbon, and carbon nanomaterials to improve hydrogen adsorption capabilities [41].

3 Hydrogen / Natural gas storage in onboard low-pressure MOF-based fuel tanks

Among several adsorbent materials, MOFs are increasingly being studied for enhancing hydrogen/natural gas solid-state storage capabilities in onboard low-pressure adsorbent-based fuel tanks. Indicatively, the increasing attention related to hydrogen storage into MOFs is illustrated by the notable number of publications, especially over the last 5 years, as illustrated in Fig. 1.

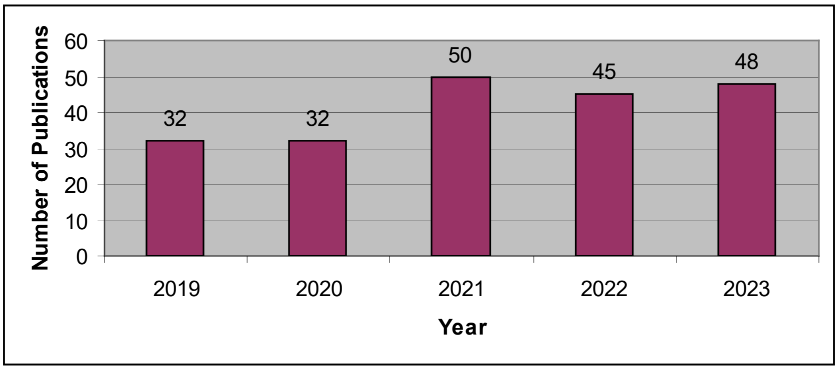

Fig. 1. Journal article results from the last five years using the keywords “hydrogen AND storage AND MOFs” via Scopus

Such systems, with their amenability to scale-up, have the potential to lower the cost of onboard tanks as well as to reduce the technical complexity of high-pressure compressors at the station. They also facilitate the development of a fuel delivery infrastructure, which is key to making transportation greener [42,43]. Given the increasing use of natural gas (methane) and hydrogen, and in view of their ample deployment, the US Department of Energy has introduced specific technical goals to compete with traditional fuels such as gasoline, specifically in onboard adsorption-based vehicle tank storage applications. Selected technical performance targets for hydrogen are summarized in the following Table 1.

Table 1. Technical performance targets: hydrogen adsorption-based onboard storage for light-duty fuel cell vehicles [44]

Storage Parameter	2020	2025	Ultimate
Gravimetric capacity (usable specific energy from H_2) (kg H_2/kg)	0.045	0.055	0.065
Volumetric capacity (usable specific energy from H_2) (kg H_2/L)	0.030	0.040	0.050
Ambient temperature (°C) of operation	-40/60 (sun)	-40/60 (sun)	-40/60 (sun)
Min/max delivery temperature (°C) for H_2	-40/85	-40/85	-40/85
Min/max delivery pressure (bar) from storage system	5/12	5/12	5/12
Onboard efficiency (%)	90	90	90
System fill time (min)	3-5	3-5	3-5

Balancing between a pore volume containing gas adsorption sites and a large specific surface area with high affinity for physisorption, MOFs can improve gravimetric and volumetric density. Therefore, they can hold and store significant volumes of hydrogen and natural gas at moderately low pressures in order to meet the above-mentioned DOE's target specifications.

In fact, the outstanding properties of MOFs have lead to their considerable investigation in several research works, as advanced porous adsorbents for hydrogen and natural gas (methane) storage. In the beginning, efforts were made to identify MOFs with optimal spacing between pore surfaces for high gas uptake. Although this method is an established strategy for identifying adsorbents with high gas capacities, several materials studied based on this criterion did not necessarily exhibit high gas uptake. Therefore, for discovering stable and effective storage media, some specific MOF structures have been proposed. Specifically:

For hydrogen solid-state storage, some materials are good candidates, depending on their structure and chemistry. Relevant data reported in literature are summarized in Table 2.

Table 2. Data for Hydrogen Storage into MOFs [45-48]

MOF Type	Temperature	Pressure	Gas
MOF-5	77 K	0,8 bar	4.5 wt%
		> 10 bar	1.6 wt%
		20 bar	4.5 wt%
		> 80 bar	5.1 wt%
		170 bar	11.5 wt%
	298 K	20 bar	1 wt%
		67 bar	0.2 wt%
HKUST-1	77 K	1 bar	1.25 wt%
		1 bar	1.6 wt%
		1 bar	2.5 wt%
	298 K	65 bar	0.35 wt%
	303 K	35 bar	0.47 wt%
	353 K	35 bar	0.34 wt%
ZIF-8	77 K	860 mmHg	6.92 mmol/g
		55 bar	3 wt%
	298 K	55 bar	0.1 wt%
MOF-177	77 K	0.9 bar	1 wt%
		1 bar	1.5 wt%
		90 bar	7.5 wt%
		100 bar	19.6 wt%
	87 K	1 bar	0.75 wt%
	297 K	46 bar	0.37 wt%
	298 K	40 bar	0.35 wt%
		100 bar	0.62 wt%

Particularly efficient MOFs appear to be those that include open metal sites, lighter and extra metal cations into the framework (which positively influence hydrogen-framework interactions), ultra-high void fraction and specific surface area in the framework, optimized pore size (small pores seem more appropriate for hydrogen molecule uptake), and also diversified topologies (for instance, the 'she' topology in the isoreticular she-MOF-x series for hydrogen adsorption at cryogenic conditions) [49-56]. One promising method recently reported for quick, safe, and reversible hydrogen storage is cryoadsorption on the inner surface of zeolitic imidazolate frameworks (e.g. ZIF-8), a family of very porous MOFs exhibiting exceptional mechanical, chemical and thermal stability [57,58].

On the other hand, for effective methane storage, such adsorbents include isoreticular MOFs based on Zn4O, M2(bdc)2(dabco) (M= Ni, Co, Zn) frameworks, copper carboxylates groups, MIL (Materials of Institute Lavoisier) series, and water stable Zr-based MOFs. For example, MOF-177, a structure comprising a complex called $[Zn4O6]^{6+}$ and ligand molecules known as 1,3,5-benzene-tribenzoic (BTB) ligands, has exhibited hydrogen adsorption capacity beyond the amount expected under certain conditions. The framework consists of Zn4O clusters located at the corners, bound to organic ligand molecules, specifically benzotriazoate (BTB) in the case of this typical MOF-177 framework. An interpenetrating framework structure is generally preferred, as it preserves the adsorption sites without blocking them although it may reduce the pore volume and create a complex pore structure [59-66]. Furthermore, hydrogen/methane mixtures adsorption onto different MOFs was also reported [67-69]. Relevant data are summarized in Table 3.

Table 3. Data for Natural Gas Storage into MOFs [70-75]

MOF Type	Temperature	Pressure	Gas
MOF-5	273 K	0.015 P/P_0	2.3 mmol/g
		0.025 P/P_0	3.4 mmol/g
	298 K	40 bar	550 g/L
HKUST-1	298 K	1 atm	0.67 mmol/g
		1 atm	1.55 mmol/g
		5.8 - 65 bar	190 $\text{cm/cm}^{3}{}_{(\text{STP})}{}^{3}$
		35 bar	160 $\text{cm/cm}^{3}{}_{(\text{STP})}{}^{3}$
		35 bar	227 $\text{cm/cm}^{3}{}_{(\text{STP})}{}^{3}$
		35 bar	255 $\text{cm/cm}^{3}{}_{(\text{STP})}{}^{3}$
	303 K	35 bar	94 v/v
NU-125	220 K	-	32 mmol/g
	298 K	5.8-65 bar	174 $\text{cm/cm}^{3}{}_{(\text{STP})}{}^{3}$
		58 bar	228 $\text{cm/cm}^{3}{}_{(\text{STP})}{}^{3}$
MIL-53	303 K	35 bar	155 $\text{cm/cm}^{3}{}_{(\text{STP})}{}^{3}$
		35 bar	165 $\text{cm/cm}^{3}{}_{(\text{STP})}{}^{3}$

4 Concluding

The research papers that were examined and discussed highlight the intrinsic chemistry of MOFs, porous microstructure design, technical simplicity, and optimization of the production process, as well as gas adsorption-desorption mechanisms and performance as significant factors in view of increased applicability and broader implementation of this category of materials. These factors are crucial for the development of potentially efficient novel adsorbents for natural gas and hydrogen storage in onboard low-pressure MOF-based fuel tanks.

With the potential to address the challenges of gas storage, MOFs offer promising solutions for achieving efficient and safe storage of hydrogen and natural gas, which is vital for their widespread adoption as a source of clean energy and reducing dependence on fossil fuels. By continuing research and development efforts in the area, we can pave the way towards an environmentally friendly and economically sustainable economy. The use of MOFs represents an important step in shaping the future of energy storage and promoting sustainable and greener energy solutions.

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Sustainable Development

Implementation of an activated sludge model to simulate Thriasio Wastewater Treatment Plant operation in West Attica, Greece

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Abstract: In the last decades, the use of activated sludge mathematical models has proved to be a useful tool for the simulation both of the design and performance of activated sludge systems in wastewater treatment plants (WWTPs). In this study, Activated Sludge SIMulation Program (ASIM) was used to verify operational performance and effluent characteristics of Thriasio WWTP, in conformity with 91/271 E.E.C, Urban Wastewater Treatment Directive (UWWTD) for discharge in a sensitive water body. Thriasio WWTP is located at a coastal site neighbouring Elefsina Bay in West Attica, Greece, and has a nominal capacity of 117,000 population equivalent (p.e.).

In this context, ASIM was used to simulate operational performance of WWTP for its current operational mode as a case study and its conformity to effluent criteria. Simulation results that were derived for the range of incoming wastewater flows and loads of the last three years indicated that the activated sludge system has a satisfactory performance for carbon oxidation, nitrogen and phosphorus removal, meeting all the effluent criteria. To this respect, ASIM proved to be a useful tool to verify operational performance and predict the effect of influent wastewater flows and loads variation on system behavior. To enhance ASIM applicability on Thriasio WWTP, it would be appropriate as future work to include plant specific data related to wastewater fractionation and biomass kinetics.

Keywords: Activated sludge models, ASIM, Thriasio WWTP

1 Introduction

The region of Attica has a current population of around 3.8 million people, which constitutes almost 40% of the total population of Greece [1]. Most of the population in the Attica region is concentrated at the capital city of Athens. Greater Athens area is currently served according to the Greek National Database that monitors compliance to 91/271 E.E.C, Urban Wastewater Treatment Directive [2], http://astikalimata.ypeka.gr/, with three Biological Nutrient Removal (BNR) activated sludge plants in operation: Psyttalia WWTP (5,630,000 p.e., design capacity), Metamorphosi WWTP in the north (500,000 p.e.) and Thriasio WWTP in the west with a design capacity of around 117,000 p.e. (Figure 1). Future wastewater treatment plants to be developed in East Attica in the next couple of years include Rafina-Artemida and Marathon WWTPs with capacities of 135,000 and 51,400 p.e. respectively. In addition, Koropi-Paiania WWTP which is currently under normal operation has a constructed capacity of about 100,000 p.e. [4].

The area of interest, Thriasio Pedio region, lies to the northwest of Athens and comprises the municipalities of Aspropyrgos, Elefsina, Mandra and Magoula of the Western Attiki Prefecture. The catchment is relatively flat and has an area of about 50 km^2. The domestic population, based on the National Census of 2021, is around 79,000 inhabitants [1]. The Thriasio Pedio region is a heavily polluted area, industrialized and environmentally considered as one of the most sensitive areas in Greece. The receiving water body for the domestic and industrial wastewater produced in the catchment area is the Elefsina Bay, which has been designated by the Greek State as a sensitive area since 1999, in accordance with the requirements of 91/271 EEC, Urban Wastewater Treatment Directive, UWWTD [3].

Since 2012, Thriasio WWTP with a design capacity of 117,000 p.e./21,000 m^3/d as average daily flow, has been under operation by Athens Water Supply and Sewerage Company (EYDAP S.A). Its general layout is given in Figure 2. The current operational mode, includes pretreatment works (coarse screening, fine screening, grit removal) and biological nutrient removal in two plug-flow activated sludge bioreactors having an operational volume of 7,032 m^3 (out of four constructed bioreactors with a total volume of 16,532 m^3) followed by sedimentation of influent wastewater in a settlement tank.

Downstream processes after biological treatment and secondary clarification, include tertiary treatment by chemical coagulation, gravity filtration and ultraviolet (U.V.) disinfection. Treated effluent is discharged into the Elefsina Bay from the outlet pumping station, via a 1.5 km outfall at a depth of around -14m. In case of emergency events (i.e. shock loads, power failure, flooding, etc.), the total raw sewage inflow is bypassed and after receiving coarse screening and chlorine disinfection is discharged into the sea, via a 1 km length second outfall pipe at a depth of around -10m.

As far as sludge treatment processes are concerned, surplus activated sludge is thickened and dewatered to produce a sludge cake of around 15% DS content. This sludge cake is transported to the drying facility of the Psyttalia WWTP for further treatment (i.e. thermal drying, with a final DS content of around 92%).

Constructed works in Thriasio WWTP include primary sedimentation of influent wastewater and anaerobic sludge digestion facilities, according to the detailed design for plant construction [5]. However, due to the low influent wastewater flows and pollutants' loads entering WWTP (about 20-25 % of its design capacity), the above facilities are bypassed. Thus, Thriasio WWTP is being operated as an extended aeration activated sludge system with high solids retention times (in general, SRTs > 10-15 days).

As activated sludge modelling is considered nowadays as a significant tool to simulate WWTPs performance [6-8], Activated Sludge SIMulation Program (ASIM) was used in the present study to simulate Thriasio WWTP operation. ASIM is a user friendly simulation software program that was developed by the Swiss Federal Institute of Aquatic Science and Technology, EAWAG [8, 9]. It is acknowledged as one of the most reliable simulation programs for the activated sludge process with worldwide application [7-8, 10]. Besides, it has been used previously with success to simulate Greek WWTPs either for design purposes (i.e. the newly constructed Koropi-Paiania WWTP) or to validate operational performance such as the Larisa WWTP [11, 12]. The objectives of ASIM application for Thriasio WWTP were to simulate plant operational performance for its current operational mode as a case study and its conformity to effluent criteria. Therefore, the purpose of the simulation was to assess ASIM reliability as a prognostic tool, by comparing simulation results with the plant operational data. On this basis ASIM could be used, at a future step, to assess system behaviour on potential changes in wastewater flows and loads entering WWTP in terms of evaluating alternative operating scenarios.

2 Description of the Activated Sludge System

The treatment standards adopted for the design of the Thriasio WWTP reflect the nature and requirements of the receiving water body (i.e. Elefsina Bay of Saronikos Gulf), which is an enclosed sensitive water body. These standards are summarized in Table 1, according to the approved environmental terms for Thriasio WWTP operation [13]. They are stricter in terms of 5-day Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD) and Total Suspended Solids (TSS) effluent concentrations than those required by the 91/271 EEC UWWTD for sensitive receiving water bodies Their attainment requires the adoption of an appropriate biological nutrient removal treatment scheme followed by tertiary treatment to achieve an enhanced removal of suspended solids, nitrogen, phosphorus and coliform bacteria.

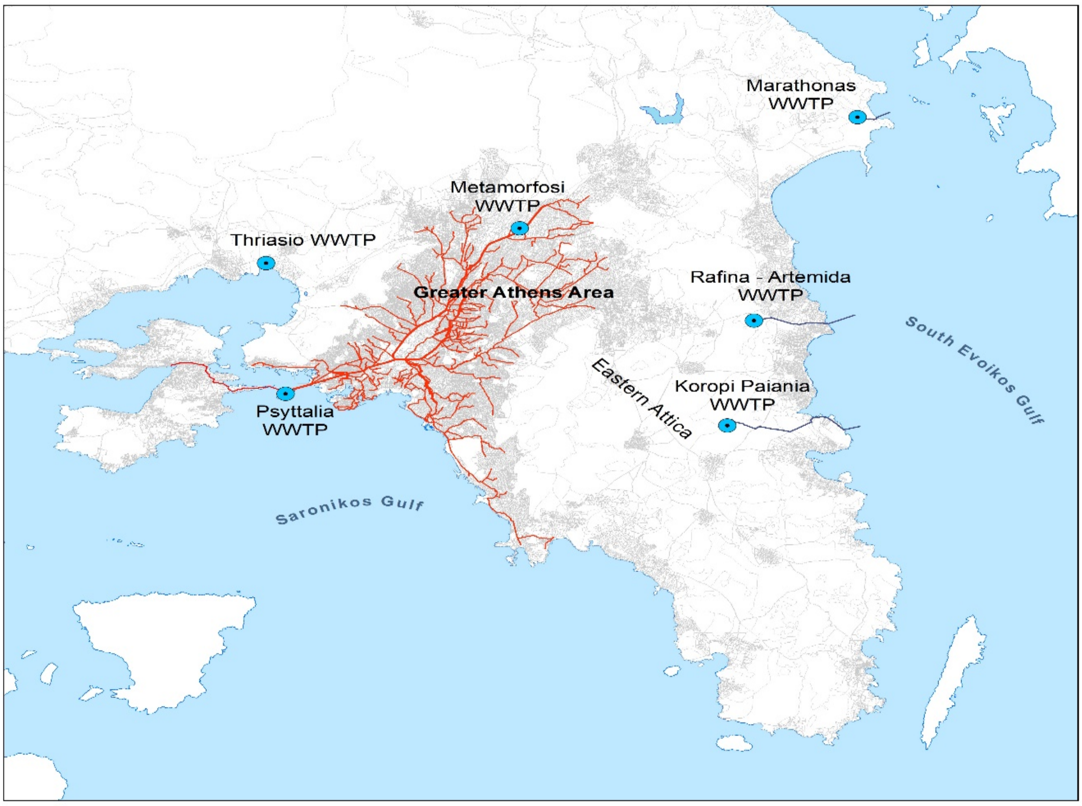

Fig. 1. Existing WWTPs with sewerage network of the Greater Athens area and future WWTPs in East Attica [4]

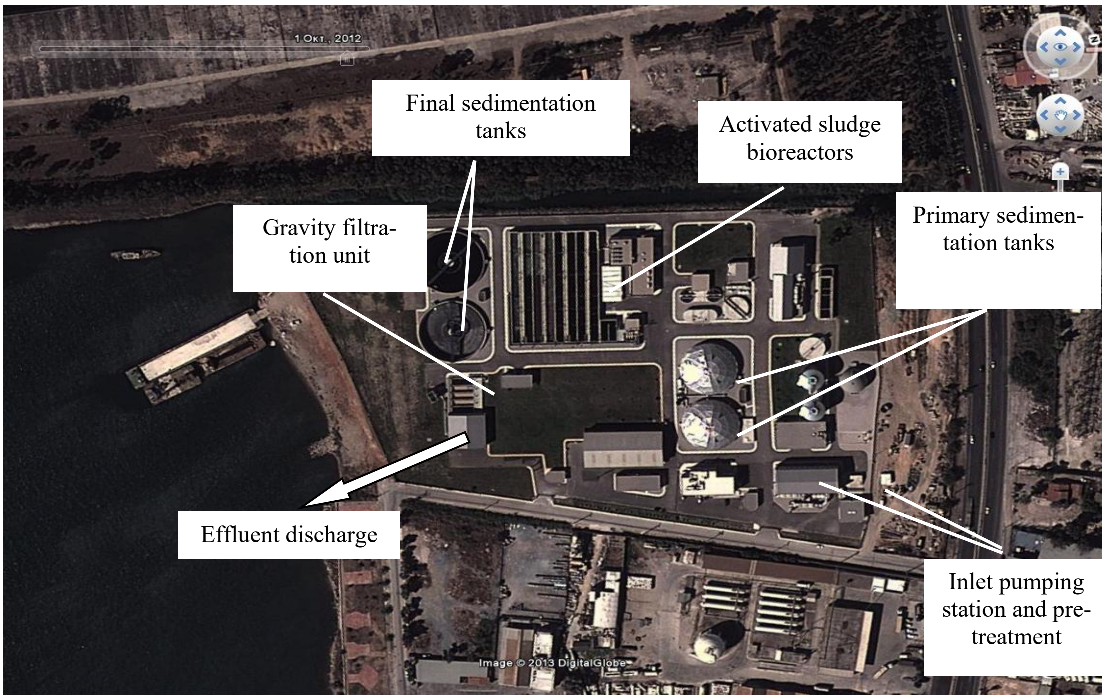

Fig. 2. General layout of Thriasio WWTP

The activated sludge biological process for N and P removal is a typical A^2O activated sludge system (anaerobic-anoxic-aerobic), modified with the inclusion of a pre-anoxic zone for return activated sludge (RAS) denitrification. The activated sludge flow scheme includes two bioreactors in operation (no 1 and 2) that receive half of the influent wastewater flow and operate in parallel with their compartmentalization given in Figure 3. Besides, the total volumes of bioreactors and of individual compartments are given in Table 3. The process scheme applied is generally known as the Johannesburg configuration developed in South Africa [5, 14, 15].

As can be seen in Figure 3, each bioreactor is a plug-flow system being compartmentalized with an anaerobic-anoxic-aerobic sequence in twelve tanks in series. This activated sludge configuration is capable of achieving almost complete carbonaceous and nitrogen removal via nitrification/denitrification at about 95% removal rates. Besides, biological phosphorus removal is accomplished in the anaerobic/aerobic zones of the bioreactors to achieve total phosphorus (TP) concentrations in the outlet of the activated sludge system well below 3 mg/l. In order to further reduce TP concentrations to lower than 1 mg/l, a supplementary chemical precipitation unit with aluminium sulphate (alum) is involved.

3 Mathematical Modelling of Activated Sludge Plants

Many mathematical models for the activated sludge process have been used in the last decades, to simulate seasonal system behaviour under various temperature conditions. These models can simulate different complex activated sludge flow schemes under steady-state or dynamic conditions, performing organic carbon removal and nitrogen/phosphorus removal. These are usually based on the development of a series of process rate equations which describe the fate of various components. These equations are then incorporated into mass balance equations to be solved for the systems being modelled, given that a biokinetic model is defined with its stoichiometry and the kinetic data for the components involved.

In the history of activated sludge modelling, a core model incorporating the above principles was that developed in 1987 by International Association on Water Pollution and Research Control (IAWPRC, currently International Water Association, IWA) [16]. This original model was named Activated Sludge Model No 1 (ASM 1).

ASM 1 is capable of predicting performance of single-sludge systems carrying out carbon oxidation, nitrification and denitrification. The model includes eight fundamental processes of importance in single-sludge systems: aerobic growth of heterotrophic biomass, anoxic growth of heterotrophic biomass, aerobic growth of autotrophic biomass, decay of heterotrophic biomass, decay of autotrophic biomass, ammonification of soluble organic nitrogen and hydrolysis of entrapped particulate organic matter under aerobic and anoxic conditions. Process rate equations for each of these processes are defined by ASM 1 model, and all kinetic expressions and stoichiometry are presented in a matrix format. Since 1987, several modifications of ASM 1 such as ASM 2, ASM 2d and ASM 3 were developed, either to include more processes such as Enhanced Biological Phosphorus Removal (EBPR) or provide greater flexibility [17].

Table 1. Thriasio WWTP effluent criteria

Parameter	**Maximum permissible concentration**	**Percentage of conformity (%)**
BOD_5	15 mg/l	95%*
COD	100 mg/l	95%*
TSS	10 mg/l	95%*
Total nitrogen (TN)	10 mg/l	UWWTD **
Total phosphorus (TP)	1 mg/l	UWWTD **
Fecal coliforms (FC)	100 FC/100 ml	Arithmetic mean ***

* Percentage of conformity for daily composite samples according to 91/271/EEC

** 91/271/EEC, UWWTD

*** Mean value of 30 consecutive days for grab samples

Table 2. Design parameters and operational values of the activated sludge system for the period 2021-2023 (mean monthly values)

Parameter	**Design values**	**Operational values (2021-2023)**
1) Flows/loads to bioreactors		
Average daily flow, Q (m^3/d)	23,740	5,361-6,858
Average daily BOD_5, kg/d	5,780	904-2,078
Average daily COD, kg/d	11,850	1,962-4,129
Average daily TSS, kg/d	4,455	845-2,044
Average daily TN, kg/d	1,092	296-486
Average daily TP, kg/d	242.5	21-70
2) Operational parameters of the activated sludge system		
Total bioreactors' volume V_{tot} (m^3)	16,532 (4,133 x 4)	7,032 (4,133+2,899)
Number of bioreactors	4	2
Hydraulic retention time, HRT (hrs)	13-16.7	26-39
Temperature (°C)	15-28	18-24
MLSS (mg/l)	3,180-3,900	3,586-7,207
F/M loading (kg BOD_5/kg MLSS.d)	0.09-0.11	0.03-0.06
Solids retention time, SRT (days)	9-10.5	9,5-37
SAS, Q_w (kg SS/d)	4,511-6,350	963-5,121
VSS fraction to TSS (%)	70%	70%
Return sludge flow ratio (Q_r/Q)	0.65-0.92	0,86-1.44
Internal recycle flow ratio (Q_R/Q)	3.70	3.70

As mentioned above, in the context of activated sludge modelling one of the most useful variants is the Activated Sludge Simulation Program (ASIM), [10]. In the case of ASIM unlike other activated sludge simulation programs where the biokinetic model used is fixed, it allows to choose the biokinetic model from a list of IWA models (ASM1, ASM 2, ASM 2d, ASM 3, etc.) or to define a fit-for-purpose new biokinetic model for the simulations.

In the present study, ASIM was implemented to simulate Thriasio WWTP operation under steady-state conditions. The use of ASIM had the objective to simulate current operation of the plant with regard to its operational parameters and conformity to effluent criteria.

4 Simulation of Thriasio WWTP with ASIM

For the purpose of the simulation, input data was required as follows:

1. Definition of the biokinetic model;
2. Activated sludge flow scheme;
3. Influent pollutants' concentrations/wastewater composition and;
4. Definition of kinetic and stoichiometric parameters

4.1 Definition of the biokinetic model

ASM 1 was used as the biokinetic model for the simulation of Thriasio WWTP. Regarding biological phosphorus removal in the anaerobic/aerobic zones of the bioreactors, TP effluent concentrations were derived based on the daily estimated quantities of surplus activated sludge (SAS). It was assumed that the phosphorus percentage in surplus activated sludge (SAS) may vary between 1% to 5% (0.01-0.05 kgP/kgVSS), depending on the COD/TP influent wastewater ratio [19].

4.2 Activated sludge flow scheme

Thriasio WWTP activated sludge flow scheme and bioreactors' compartmentalisation is presented in Figure 3. As can be seen in Figure 3, the influent wastewater flow is split to the bioreactors no 1 and 2 which operate in parallel. Bioreactors total volumes as well as volumes of individual anaerobic/anoxic/aerobic compartments are given in Table 3. Biological stage of WWTP comprises two bioreactors in operation (out of four constructed tanks) with a total operating volume of 7,032 m^3. This includes, one full bioreactor with volume 4,133 m^3 plus another bioreactor with modified its aerobic zones with volume 2,899 m^3 as shown in Table 3. In each bioreactor, the second compartment D1/AN is facultative and may operate either as a second anaerobic compartment or as a first anoxic compartment. Besides, the first compartment in the aerobic zone D4/A1 is also facultative and may operate either as a fourth anoxic compartment or as a first aerobic compartment.

More specifically, as presented in Figure 3 the current operational mode of bioreactor no. 1 includes one anaerobic compartment (AN), three anoxic compartments (D1/AN, D2 and D3) and eight aerobic compartments (D4/A1 to A8).

Regarding bioreactor no. 2, the current operational mode includes one anaerobic compartment (AN), three anoxic compartments (D1/AN, D2 and D3) and five aerobic compartments (A4 to A8). Compartments D4/A1, A2 and A3 are bypassed and the wastewater flow from anoxic compartment D3 passes to aerobic compartment A4.

Return activated sludge from the settlement tank to bioreactors no. 1 and 2 passes through a pre-anoxic tank with a volume of 634 m^3 to provide denitrification of nitrates contained in the sludge. This is essential since a requirement to have an effective biological phosphorus removal is to have nitrate nitrogen ($NO_3 - N$) concentration in the anaerobic zone below 0.5 mg/l. Mixed liquor internal recycle is carried out from the last aerobic compartment (A8) of bioreactors no. 1 and 2 to the fist anoxic compartment (D1/AN), in order to enhance the nitrification-denitrification process and hence biological nitrogen removal.

4.3 Influent concentrations – wastewater composition

Mean influent wastewater flows and pollutants' loads entering the activated sludge scheme, such as the 5-day Biochemical Oxygen Demand, Chemical Oxygen Demand, Total Suspended Solids, Total Nitrogen and Total Phosphorus (BOD_5, COD, TSS, TN & TP respectively) for the last three years 2021-2023 are given in Table 2. Main operational parameters of the activated sludge system such as sludge loadings (Food to Microorganisms: F/M ratios), mixed liquor suspended solids concentrations (MLSS), solids retention times (SRTs) and surplus activated sludge (SAS) production are also presented. Influent wastewater entering Thriasio WWTP is of domestic origin with COD/BOD_5 ratio in the range of 1.5-2.3. Regarding organic carbon and nitrogen fractionation with respect to the rate and extent of their degradation, this input data was estimated based on typical data obtained previously in Greek WWTPs [20, 21]. This was essential, since there is a lack of such kind of information in Thriasio WWTP. Based on the above assumptions, total influent COD is split to 50% soluble (S) and 50 % particulate matter (X). For inert soluble and particulate COD (S_i and X_i respectively), it was assumed that they constitute 6 % of total COD. Hence, the percentage of readily biodegradable COD, S_S and slowly biodegradable COD, X_S were taken as 44 % of total COD. Input values used for organic carbon and nitrogen fractionation with respect to their biodegradability are summarized in Table 4.

4.4 Definition of kinetic and stoichiometric parameters

Input data for kinetic and stoichiometric parameters for the activated sludge at T = 20 °C were default values proposed in ASM 1. These values are given in Table 5. They have been generally verified from relevant observations in Greek WWTPs, where a nitrification inhibition at about 15% is possible [20, 21].

Biological processes of growth and decay for heterotrophic and autotrophic biomass as well as hydrolysis of entrapped particulate organic matter under aerobic and anoxic conditions are temperature dependent. Dependence of the values of kinetic parameters of these processes on temperature variation is modelled based on the well-established Arrhenius equation [18] as given in Table 6. Monthly temperature variation taken in Thriasio WWTP is given in Table 7.

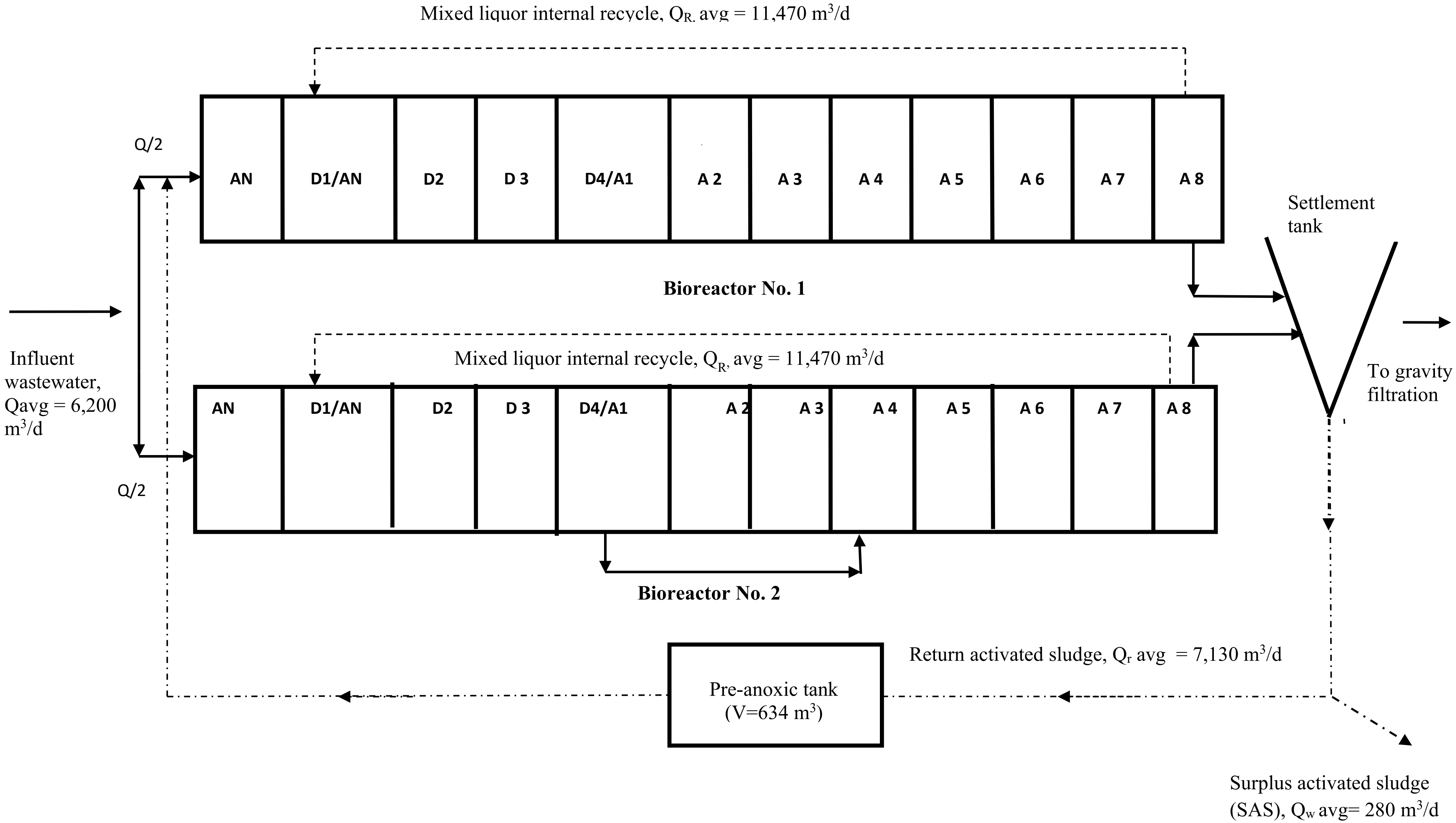

Fig. 3. Activated sludge flow scheme and bioreactors' compartmentalization

Table 3. Bioreactors volumes of anaerobic/anoxic/aerobic compartments and total volumes

Compartments	**Volumes (m^3)**	
	1st lane	**2^{nd} lane**
AN (anaerobic)	303	303
D1/AN (currently αnoxic)	303	303
D2 (anoxic)	227	227
D3 (anoxic)	411	411
D4/A1 (currently aerobic)	411	0
A2, A3, A4 & A5 (aerobic)	1,644 (411x4)	822 (411x2)
A6 (aerobic)	227	227
A7 & A8 (aerobic)	606 (303x2)	606 (303x2)
Total	**4,133 m^3**	**2,899 m^3**
Total bioreactors' volume	**7,032 m^3**	

Table 4. Wastewater fractionation used for the mathematical simulation

Parameter	**Operational values, mg/l (2021-2023)**
Total influent COD in the activated sludge system	331.36 - 666.67
Total influent nitrogen in the activated sludge system	55.22 - 78.36
COD fractions (mg/l)	
Total COD	331.36 – 666.67
Soluble COD, S	165.70 - 333.33
Particulate COD, X	165.70 - 333.33
Soluble readily biodegradable COD, S_s	145.80 - 293.33
Inert soluble COD, S_i	19.90 – 40.0
Particulate slowly biodegradable COD, X_s	145.80 - 293.33
Particulate inert COD, X_i	19.90 – 40.0

Nitrogen fractions (mg/l)	
Total nitrogen, TN	55.22 - 78.36
Ammoniacal nitrogen, S_{NH}	35.84 - 44.30
Soluble organic nitrogen, S_{ND}	9.69 - 17.03
Particulate organic nitrogen, X_{ND}	9.69 - 17.03

Table 5. Kinetic and stoichiometric parameters used for the mathematical simulation.

Parameters	**Units**	**Typical values, T=20ºC***
1. Kinetic parameters		
Heterotrophic biomass		
Maximum specific growth rate, μ_H	day^{-1}	6.0
Decay rate constant, b_H	day^{-1}	0.62
Monod saturation constant for substrate S, K_{sh}	gCOD/m^3	20.0
Monod saturation constant for oxygen, K_o	gO$_2$/m^3	0.20
Monod saturation constant for ammoniacal nitrogen, K_{NH}	gN/m^3	0.001
Monod saturation constant for nitrate nitrogen K_{NO}	gN/m^3	0.50
Correction factor for anoxic growth, n_g	Unitless	0.80
Autotrophic biomass		
Maximum specific growth rate, μ_A	day^{-1}	0.68
Decay rate constant, b_A	day^{-1}	0.12
Monod saturation constant for ammoniacal nitrogen, K_{NH}	n/m^3	1.0
Monod saturation constant for oxygen, K_o	gO$_2$/m^3	0.4
Maximum specific hydrolysis rate, K_h	gCOD/gCOD/day	3.0
Saturation constant for substrate X, K_X	gCOD/gCOD	0.03
Monod saturation constant for oxygen, K_o	gO$_2$/m^3	0.2
Ammonification rate, K_a	m^3/gCOD/day	0.08
Correction factor for anoxic hydrolysis. n_h	Unitless	0.25

2. Stoichiometric parameters		
Heterotrophic biomass yield, Y_H	gCOD/gCOD	0.62
Autotrophic biomass yield, Y_A	gCOD/gN	0.20
Mass of nitrogen per mass of COD in biomass, i_{XB}	gN/gCOD	0.086
Mass of nitrogen per mass of inert COD, i_{XI}	gN/gCD	0.01
Fraction of inert COD in biomass, f_P	gCOD/gCOD	0.080

Table 6. Dependence of kinetic parameters of biological processes on temperature variation

$c(T) = c(20^{o}C) * e^{[\theta *(T-20)]}$	**X_H**	**X_{Nitr}**	**Units**
θ for μ_{max} (growth)	0,069	0,1	$(^{o}C)^{-1}$
θ for b (decay)	0,1	0,095	$(^{o}C)^{-1}$
θ for k_h (hydrolysis)	0,11 (aerobic/anoxic)		
$c(T)$ = biological process rate at T°C, c= μ_{max}, b ή k_h			
$c(20^{o}C)$ = biological process rate at 20°C			
θ = temperature coefficient			

Table 7. Monthly temperature variation used for the mathematical simulation

Mean monthly temperature of the activated sludge system											
Jan.	Feb.	Mar.	Apr.	May	June	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
19°C	19°C	19°C	20°C	21°C	22°C	23°C	24°C	24°C	23°C	21°C	18°C

5 Results

Simulation of Thriasio WWTP operation was carried out for the mean monthly daily influent wastewater flows to bioreactors for the last three years 2021-2023. (Figure 4). Besides, the pollutants concentrations in the bioreactors for BOD_5, COD, TSS, TN & TP are given in Figures 5 and 6. Monthly temperature variation used is given in Table 7.

According to the information provided by EYDAP S.A. relevant Department which operates Thriasio WWTP, dissolved oxygen (DO) concentration in the aerobic zones of the bioreactors was taken at 2 mg/l. Also, the average recycled flows percentages (return activated sludge and mixed liquor internal recycle) are given in Table 2.

Simulation results are presented in Figures 7 to 13 and relate to:

- operational parameters of the activated sludge system for various sludge loadings (F/M ratios), SAS production (Figure 7) and MLSS concentrations Figure 8)
- effluent characteristics in terms of organic carbon, suspended solids, nitrogen and phosphorus concentrations (BOD_5, COD, TSS, NH_4-N/NO_3-N, TN & TP), are given in Figures 9 to 13.

6 Discussion

Based on the simulation results, the following key findings are derived:

Estimated values of the operational parameters are close to the obtained data from plant operation. Regarding effluent characteristics, estimated concentrations of main pollutants are in good agreement with measured data from plant operation;

According to the mathematical simulation, all parameters in the effluent satisfy the relevant criteria given in Table 1 for discharging to the sensitive water body of Elefsina Bay. Almost complete removal of organic carbon and suspended solids is achieved as well as very satisfactory nitrogen removal via nitrification-denitrification. Estimated concentrations of total soluble COD in the effluent (inert and readily biodegradable, $S_I + S_S$) vary between 20 – 41 mg/l. These values are quite close with measured data from plant operation (~ 17 – 27 mg/l).

Moreover, estimated values of total suspended solids (TSS) at the outlet of the activated sludge system are in the range of 7 - 11 mg/l, with an average value of 8 mg/l. By taking into account that about 50 % of total suspended solids from the outlet of the activated sludge system are removed via downstream gravity filtration, these values are being decreased to 3.5 – 5.5 mg/l for effluent TSS concentrations, which are very close to measured data.

Regarding, nitrogen removal, estimated effluent concentrations for ammoniacal nitrogen (NH_4-N), nitrate nitrogen (NO_3 – N) and total nitrogen (TN) are in good agreement with the corresponding measured values from plant operation. Estimated NH_4-N concentrations are well below 0.5 mg/l and TN concentrations are close to 10 mg/l. Elevated effluent concentrations for NO_3 – N and TN were estimated in the summer/autumn period (July-August and September to November). In this period, higher temperatures coupled with the maintenance of an adequate concentration of dissolved oxygen in the aerobic zone of the bioreactors (DO = 2 mg/l) leads to an enhanced production of nitrates through nitrification. As a consequence, total nitrogen (TN) concentrations in the effluent may exceed the maximum permissible concentration of 10 mg/l. It is therefore recommended to keep DO concentrations in the aerobic zone during this period in the range of 1.0 – 1.5 mg/l. For the winter/spring period, the maintenance of DO = 2 mg/l could be more appropriate. Estimated concentrations of nitrate nitrogen (NO_3 – N) of recycled sludge in the outlet of the pre-anoxic tank vary between 0.1 – 0.5 mg/l. Therefore, NO_3 – N concentrations in the anaerobic compartment of the bioreactors

(AN) are well below 1 mg/l and in many cases near zero. This justifies the adequacy of pre- anoxic zone for removing nitrate in recycled sludge. Estimated concentrations of total phosphorus (TP) in the outlet of the activated sludge system are generally below 3 mg/l, thus meeting the design criteria for the biological phosphorus removal process [5]. Further removal of phosphorus is accomplished via chemical precipitation with the addition of aluminum sulphate (alum) either upstream of the settlement tank or upstream of gravity filters. This is essential to reach the effluent criterion of TP < 1 mg/l as measured data indicates.

In summary, application of ASIM to simulate Thriasio WWTP proved to be a consistent and practical tool, which verified the plant operational performance. In this context, it should be mentioned that although activated sludge modelling is well established worldwide as a significant tool to simulate WWTPs operational performance it has very limited application in Greece. This is attributed to the general lack of plant specific data in Greek WWTPs (wastewater characterization, kinetics data, etc.). An exemption to this is Psyttalia WWTP, which is the main wastewater treatment plant that serves the Greater Athens area – being one of the largest in size WWTPs in Europe and worldwide. In recent years, activated sludge modeling with GPS-X simulation software which is similar to ASIM program was implemented [21]. The objectives were to simulate operational performance of the activated sludge scheme for different operating scenarios related to the variation of flows and loads, mixed liquor temperatures and Solids Retention Times, SRTs. These results obtained verified the operational performance of Psyttalia WWTP and system response to various operating conditions, such as the results obtained in this study.

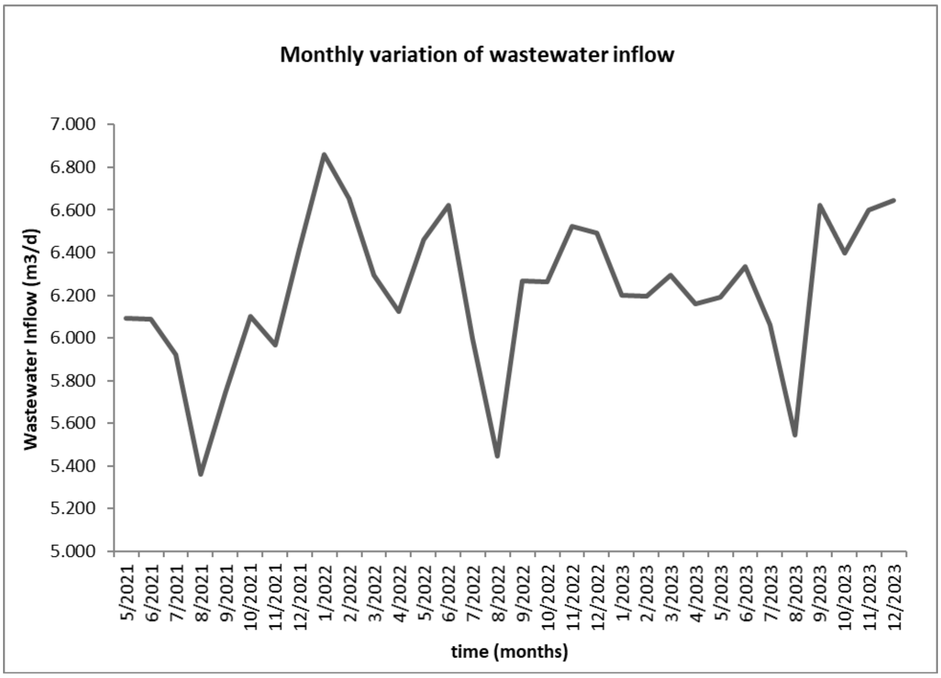

Fig. 4. Monthly variation of wastewater inflow (m^3/d), 2021-2023

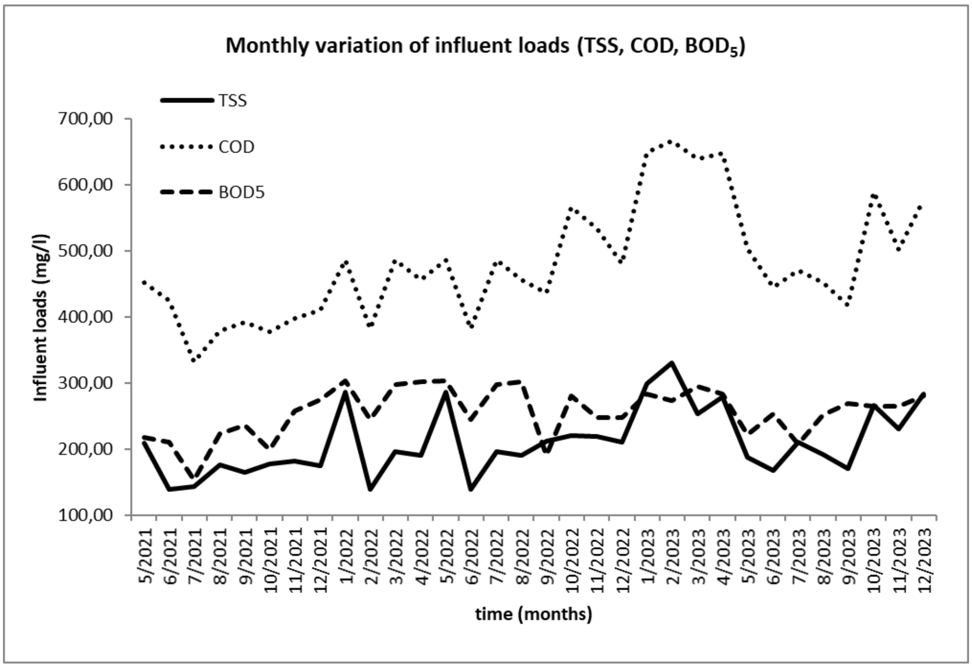

Fig. 5. Monthly variation of influent loads (TSS, COD, BOD$_5$), 2021-2023

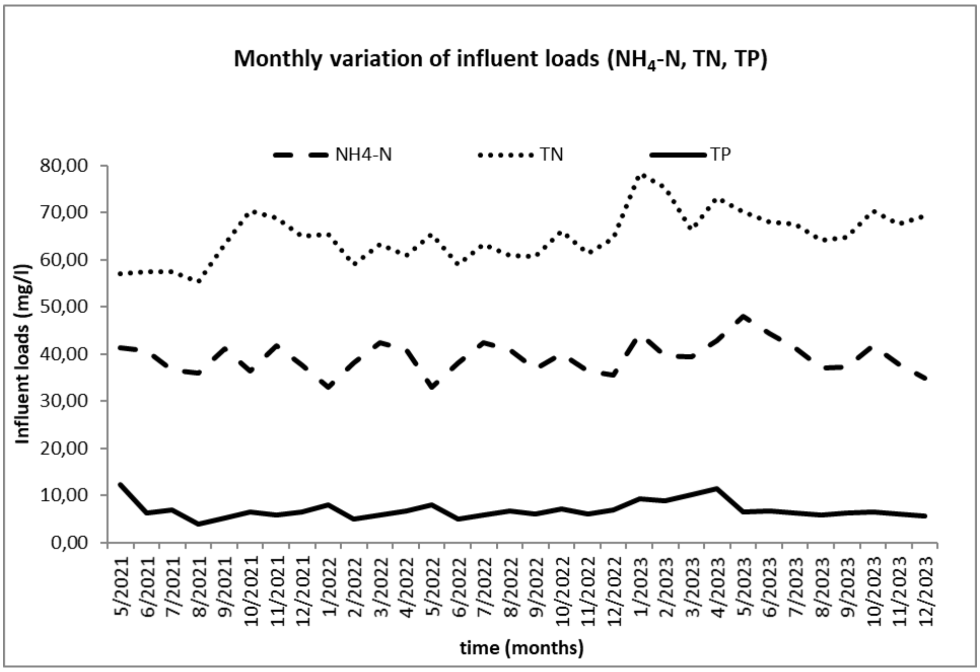

Fig. 6. Monthly variation of influent loads (NH_4-N, TN, TP). 2021-2023

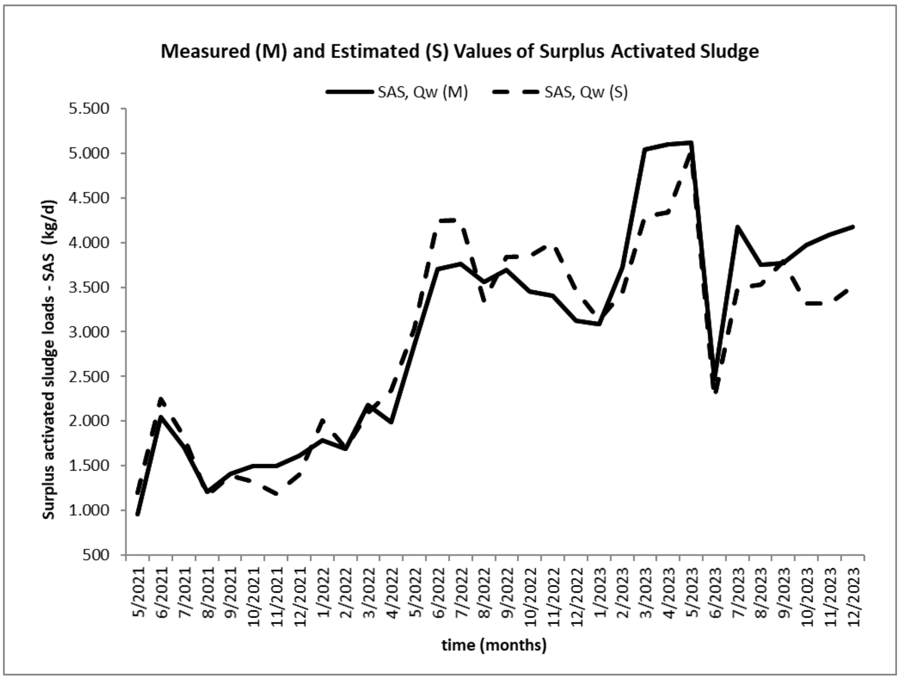

Fig.7. Measured (M) and Estimated (S) values of Surplus Activated Sludge

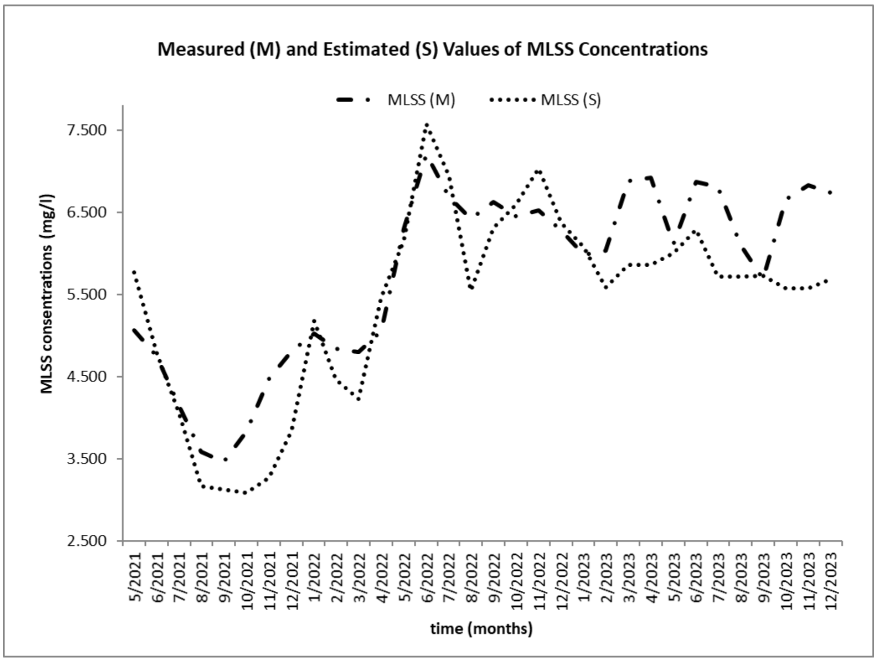

Fig. 8. Measured (M) and Estimated (S) values of MLSS concentrations

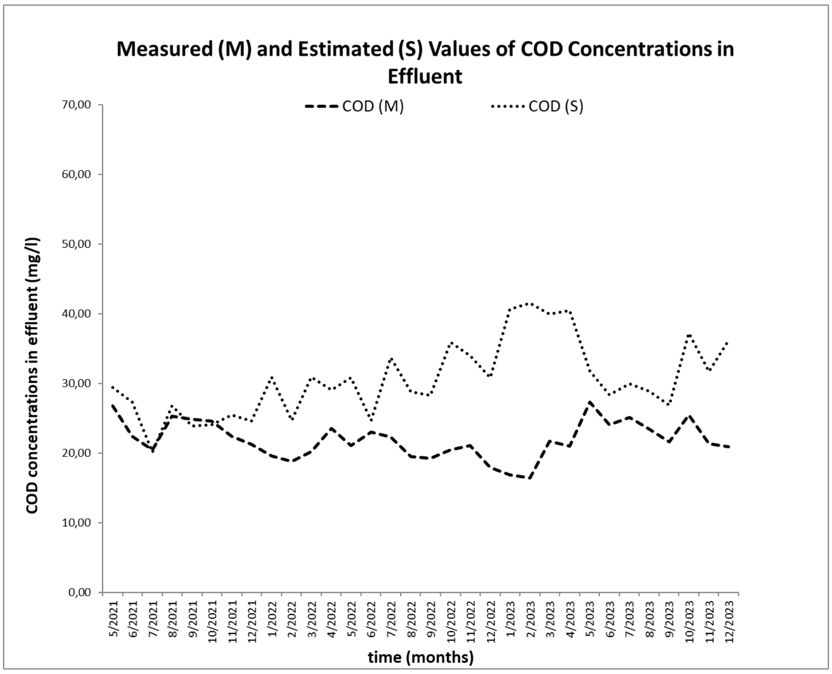

Fig. 9. Measured (M) and Estimated (S) values of COD concentrations in effluent

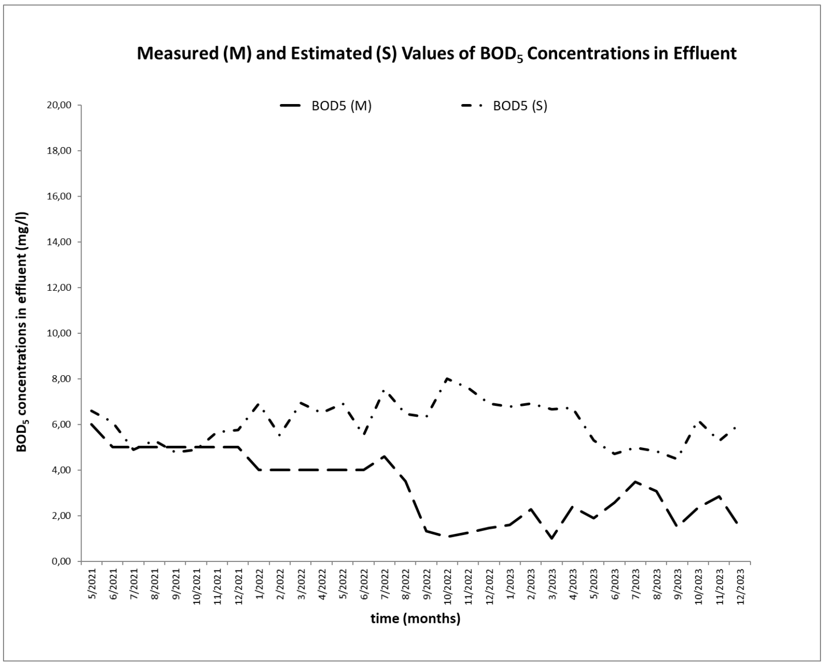

Fig. 10. Measured (M) and Estimated (S) values of BOD_5 concentrations in effluent

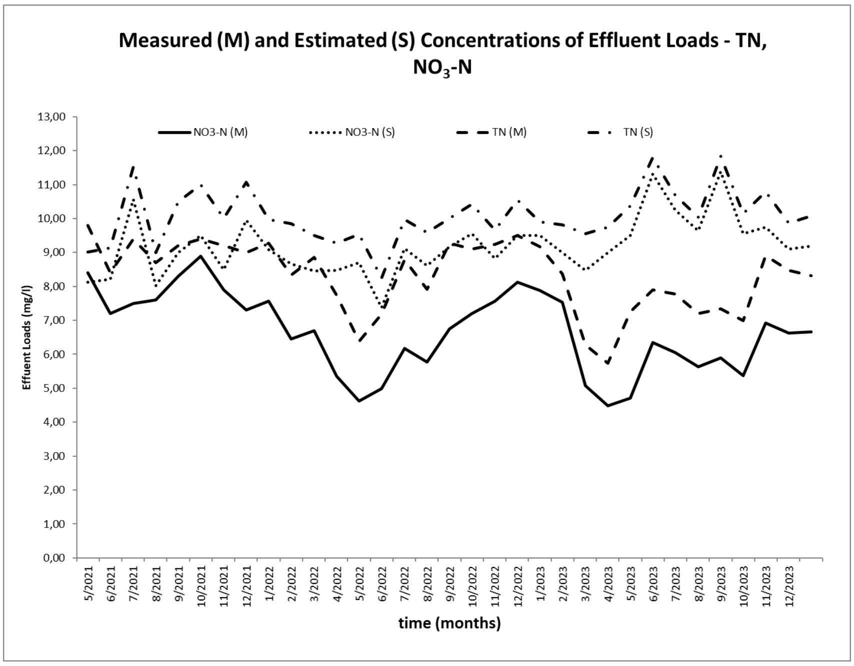

Fig. 11. Measured (M) and Estimated (S) values of TSS concentrations in effluent

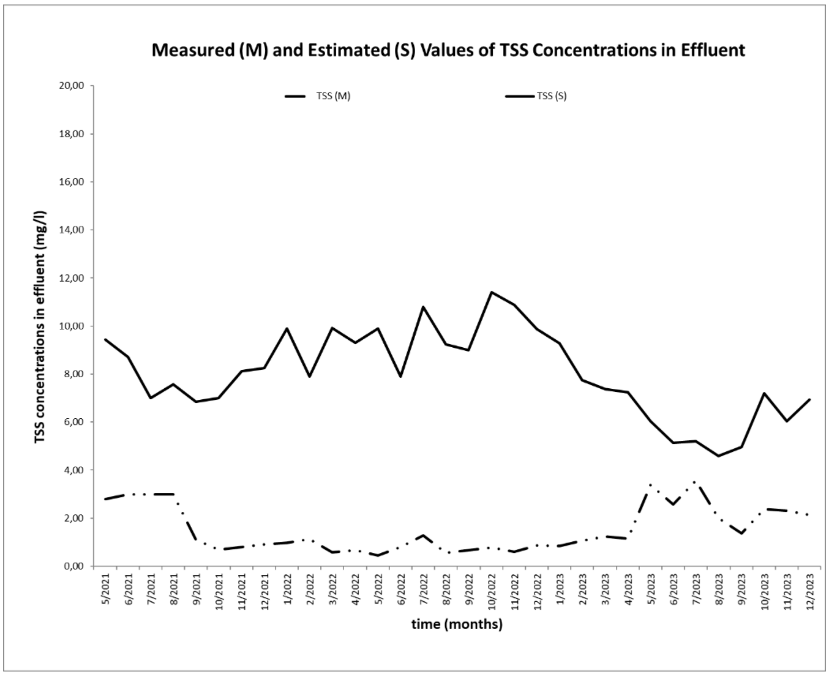

Fig. 12. Measured (M) and Estimated (S) values of effluent loads – TN, NO_3-N

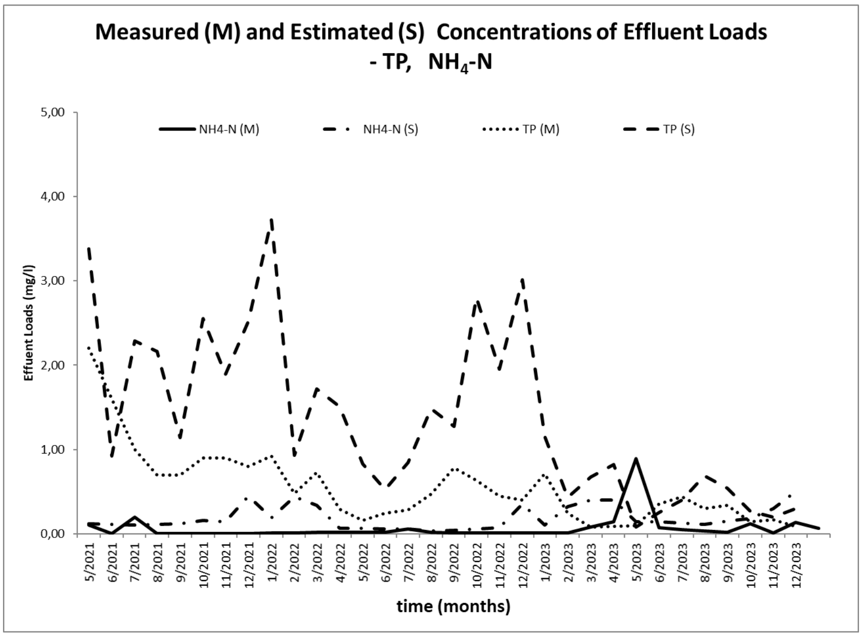

Fig. 13. Measured (M) and Estimated (S) values of effluent loads –NH4-N & TP

7 Conclusions

Activated Sludge SIMulation Program (ASIM) was used to simulate the operation of Thriasio WWTP which is a biological nutrient removal activated sludge plant. Estimated values from mathematical modelling for the operational parameters are in good agreement with the observed operational data. Estimated values of the concentrations of effluent parameters are also close with observed operational data. Overall, the activated sludge system has a satisfactory performance for carbon oxidation, nitrogen and phosphorus removal meeting all the effluent criteria. Regarding biological nitrogen removal, the activated sludge system achieves total nitrogen concentrations (TN) generally less than 10 mg/l, thus fulfilling the effluent criterion for nitrogen removal. Besides, biological phosphorus removal achieves total phosphorus (TP) concentrations in the outlet of the activated sludge system less than 3 mg/l and with chemical removal less than 1 mg/l, thus fulfilling the effluent criterion for phosphorus additional removal.

The simulation of the activated sludge system had the purpose to simulate plant performance for the hydraulic flows and loads of the last three years 2021-2023, in terms of meeting effluent criteria for carbon oxidation, nitrogen and phosphorus removal. Input data for the simulation, related to wastewater fractionation and the values of kinetic/stoichiometric parameters for the biomass are based on relevant information obtained from other Greek WWTPs. Besides, default values were used as they are defined in Activated Sludge Model No 1 (ASM 1).

In summary, simulation with ASIM proved to be a useful tool to predict and verify the operational performance of Thriasio WWTP. Therefore, future work may focus on optimizing the operational performance of the activated sludge scheme by evaluating different operating scenarios. These could investigate for instance system behaviour on the variation of flows and loads, mixed liquor temperatures and different SRTs. To this respect, it is expected that ASIM applicability to Thriasio WWTP could be enhanced with the provision of plant specific data for the needs of the simulation, related to wastewater fractionation and biomass kinetics which are not currently available.

Acknowledgements

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Sustainability analysis for scandium recovery from secondary sources

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Abstract. Primary aluminium industry is one of the largest industries associated with high greenhouse gas emissions. It is reported that in 2022, the aluminium production emitted nearly 270 Mt of direct CO_2 in the atmosphere. To achieve the European goals of zero emissions by 2050, a reduction of 4 % annually is essential. The industry needs to take a turn towards less impactful production practices, focusing on the valorisation of residues for promoting sustainability. Bauxite residue from alumina production represents a remarkable source of Rare Earth Elements (REEs). This study offers valuable insights into the environmental and economic aspects of processes related to resource Scandium (Sc) extraction and processing in Greece, Romania and Turkey. In this frame, a comparative analysis of the environmental impact of the extraction process of REEs from Bauxite Residues (BR) in the regions mentioned above is presented. The results show that an up to 23 % greenhouse gas emissions reduction can be achieved, while the environmental categories of human health risks, aquatic toxicity potential, and terrestrial ecotoxicity potential are improved by applying hydrothermal processes and direct leaching to BR. While the stages of Sc extraction remain consistent, variations in the chemical compositions of BR underscore the influence of local factors. The findings also emphasize the importance of tailoring extraction processes to local conditions and compositions for scandium extraction. These insights can guide industry decisions and contribute to responsible resource management in the future.

Keywords: Extraction of Scandium; Bauxite Residue (BR); Rare Earth Elements (REEs); Life Cycle Assessment (LCA); Aluminum refineries; Circularity

1 Introduction

The primary aluminum industry is a high energy intensive industry, responsible for more than 3 % of total global emissions [1]. Following the electricity and steel industries, primary aluminum industry is the third largest source of greenhouse gas emissions. It is reported that in 2022, the aluminium production emitted nearly 270 Mt of direct CO2 in the atmosphere [2]. According to the International Aluminium Institute, the annual production of aluminum was 69 million tons in 2022, with China being the world-leading producer accounting for 57 % of the global production [1]. However, in order to achieve the transition towards a climate-neutral economy by 2050, the global direct emissions from aluminium production should decline at nearly 4 % per year up to 2030 [3]. In this scope, the aluminium industry needs to explore and apply near zero emissions technologies to reduce emissions from both primary and secondary aluminium production as well as to increase scrap collection and recycling [3]. To realize the scale and resource-intensive nature of primary aluminium production, it is essential to understand the significant quantities of bauxite required. To produce 1 ton of aluminium, 4-5 tons of bauxite are required [4]. Firstly, the mining of raw ore takes place and is followed by the extraction of metal through a series of long-established and vertically integrated industrial processes [5].

Bauxite residue (BR) is a waste product of the alumina refining in the Bayer process. Historically, BR was often stored in large impoundment areas, which could lead to environmental impacts due to the risk of dam failures and environmental contamination. Currently, there are four major disposal routes, which include the marine and slurry disposal, dry stacking, and dry cake stacking. Since the 1980s, there has been a shift away from lagoon-type disposal towards dry stacking, as this method can reduce the potential for leakage, while also reducing space required for storage and improving the recoveries of soda and alumina. Marine disposal does not require land storage, but may result in the release of hazardous metals into the marine environment, which can increase seawater turbidity due to residue dispersion and formation of colloidal compounds [6], [7]. Dry stacking is widely used for BR disposal at large alumina refineries, as it is able to reduce the potential for the caustic liquor leakage into the surrounding environment, to minimize the required land area, and maximize the recoveries of soda and aluminium. In the dry stacking method, the residue slurry is thickened to 48–55% solids and then deposited in layers on a sloping surface, allowing rainwater to run off. This method leads to minimizing the liquid stored in the disposal area, lowering the risk of leakage, and improving structural integrity of the disposal site [8].

However, stockpiling of materials with such a large volume bares environmental risks, thus valorizing bauxite residue is essential. The exploitation of BR will not only benefit the environment but also serve as a source of valuable metals. It is reported that BR contains significant concentrations of critical metals [9], such as aluminium, iron, titanium, as well as some Rare Earth Elements (REEs). Among them scandium (Sc) has the most economic value, accounting for more than 90 % of the total value, due to its difficulties associated with its extraction and purification [10]. Because of its widespread availability, BR is considered a promising secondary resource for valuable metals [10].

Rare earth elements are Critical Raw Materials (CRMs) that have gained attention over the last few years thus, the demand for these elements is continuously growing. A shift towards a sustainable economy can be achieved because they could be applied in clean energy technologies, thus reducing our reliance on fossil sources. However, their production, their supply chain, for instance, the geological characteristics of a mineral deposit, mineral type and composition, and the methods of extraction lead to environmental impacts [11]. As a REE, Sc has attracted the interest of researchers in the recent years due to its high value. Its unique physical and chemical properties make it suitable for applications in solid oxide fuel cells (SOFC's) and in high-strength aluminium alloys as well as in many advanced manufacturing industries [12]. Because of its various applications and limited supply, Sc is considered to be a critical raw material [13]. The global supply and consumption of Sc is approximately 10 to 25 tons per year. China is the largest producer of Sc (66 % of global Sc production) followed by Russia (26 %) which has been the second significant supplier to global markets, especially Europe, and Ukraine (7 %) [14]. As for the extraction of Sc, in nature it can be found only in small volumes thus, the industrial mining for primary extraction is unaffordable. Currently, Sc is mainly produced as a by-product during the processing of various ores or it is recovered from previously processed tailings or residues, such as BR [10], [15].

The chemical composition of BR varies and depends on the origin of the bauxite ore and the operating conditions during the Bayer process [10]. A typical BR material contains 5-60 % iron oxide (Fe_2O_3), 5-30 % aluminium oxide (Al_2O_3), 0.3-15 % titanium dioxide (TiO_2), 2-14 % calcium oxide (CaO), 3-50 % silicon dioxide (SiO_2) and 1-10 % Na_2O [16]. Also, traces of arsenic, beryllium, cadmium, chromium, copper, gallium, lead, manganese, mercury, nickel, potassium, thorium, uranium, vanadium, zinc, and a wide range of rare earth elements can be found in BR. Certain components do not dissolve during the Bayer process, remaining as part of the BR. Others dissolve in the Bayer process solution, where they either accumulate within the solution, precipitate in the residue, or form aluminum hydroxide in the final product. The extent to which elements are extracted into the solution or transformed in the bauxite residue depends on the processing conditions [16]. Iron oxides, mainly in the form of hematite in BR, represent almost half of the BR mass, therefore their effective separation can increase the basic metal and REEs content in the residue by 60-70 %. This can be achieved with the hydrothermal transformation of the poorly magnetic hematite to high magnetic susceptibility magnetite and apply magnetic separation to the formed magnetite residue. Prior experimental evidence has shown that the conversion of hematite to magnetite can be achieved during the Bayer process with the addition of $FeSO_4$ or 2 % iron powder in the Bayer liquor. The magnetite transformation exceeded 80 % of all the iron-bearing minerals in BR after 40 min of digestion, which was amenable to recovery of the iron minerals in a weak magnetic field. The conversion of hematite to magnetite in BR, followed by the recovery of basic metals and REEs from the non-magnetic fraction, is a highly attractive BR valorisation option.

In this frame, two main processes are studied, hydrothermal transformation and direct leaching. Hydrothermal transformation aims to convert the hematite found in BR into magnetite through hydrothermal processes and subsequently separating this magnetite from BR using magnetic methods. This process offers the potential to create a concentrated mixture of basic metals and REEs from BR, which can then undergo direct leaching. Additionally, this process yields a high-iron magnetic fraction that has diverse applications, such as in pigments and ceramics. This innovative method represents a new and valuable approach to recovering metal values from BR and making productive use of the resulting residue. Then direct leaching takes place and higher acid concentrations, exceeding 3M along with elevated solid-to-liquid (S/L) ratios are utilized in order to avoid silica dissolution. In addition, high S/L ratios, greater than the conventional 5 % S/L ratio are utilized to enhance the concentration of REEs and Sc in the leaching solution.

The scope of this study is the environmental assessment of the extraction of REE from BR in three regions, Greece, Romania and Turkey. As for the capacity production in each refinery the Aluminium of Greece (AoG) facility has a yearly production capacity of more than 190,000 tons of aluminium and 860,000 tons of alumina being the largest vertical producer of aluminium and alumina in the EU [17]. Alum Tulcea stands as the exclusive alumina refinery in Romania, with a production capacity of 600,000 tons per year [18]. The ETI Aluminium plant in Turkey, also known as the Seydişehir Aluminium Plant, occupies an impressive indoor area of approximately 12,000,000 square meters, making it the largest modern aluminium manufacturing facility in the country. In terms of production, it holds an annual capacity of 120,243 tons of round ingots and 80,000 tons of primary aluminium [19].

The study is based on the environmental and economic impact of efficient processing of the remaining BR residue to achieve maximum extraction and recovery of Sc and REEs as well as the production of a marketable magnetite concentrate corresponding to about 35 % of the processed BR quantity. To this end, a Life Cycle Assessment (LCA) is performed, to analyse the environmental impacts from the treatment technology of BR of the above regions. A life cycle impact assessment (LCIA) was completed using the Grave-to-Cradle model, and the following environmental impact categories were reported: global warming potential, abiotic depletion potential, freshwater aquatic ecotoxicity potential, human toxicity potential and terrestrial ecotoxicity potential. The results of this research emphasize the importance of generating reliable data for increasing application of LCA as a proven tool for sustainable development, supporting decisions for the industrial sector.

2 Materials and methods

2.1 LCA Methodology

To evaluate the environmental impact of the extraction of Sc in three different countries, an LCA was performed, following the standardized procedures described by ISO 14040:2006 and 14044:2006/A1:2018 [20], [21] and the International Life Cycle Data (ILCD) Handbook [22]. The LCA framework consists of: (1) the goal and scope definition; (2) the Life Cycle Inventory (LCI) preparation; (3) the Life Cycle Impact Assessment (LCIA); and (4) the interpretation of the results. The LCA was conducted with the commercial software package, Sphera LCA FE database. The calculation of the impacts was based on the CML (Centrum voor Milieukunde Leiden) 2001 standard developed by the Centre of Environmental Science of Leiden University.

2.2 Goals, Scope and Functional unit

The primary objective of this LCA study is to conduct a comprehensive assessment of the environmental potential of end-of-life processes for Sc extraction, achieved through innovative leaching and recovery treatments. Furthermore, it seeks to identify hot spots, optimize processes, and provide a quantified assessment of the environmental impacts of the new technologies and final materials in comparison with conventional scenarios. The scope of this study is the end-of-life management and treatment of BR. The functional unit (FU) was the treatment of 1 ton of BR feed.

2.3 Scenario Description and System Boundaries

A " Grave-to-Cradle " analysis was conducted to assess the scandium extraction from bauxite residue in three different cases. The first case is associated with the AoG plant in Greece, the second with the Alum Tulcea in Romania and the third case refers to ETI Aluminium plant in Turkey. Each scenario includes the following four stages for Sc extraction process as well as for the separation of iron oxide as a product Fig. 1.

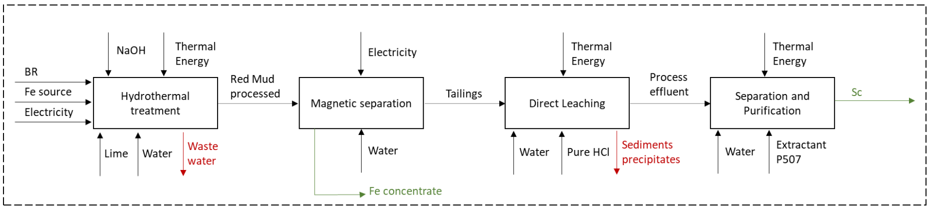

Fig. 1. System boundaries of the LCA scenario

Stage 1: Hydrothermal Treatment

In the initial stage of the process, hydrothermal treatment operations are carried out. The primary inputs include BR, which has undergone bauxite digestion and drying for a cleaner by-product, lime, water (deionized), iron sulphate, and sodium hydroxide. These materials are then hydrothermally treated and as a consequence hydrated alumina is generated. The process occurs at high temperature (250 °C), 480 psi pressure and at rotation speed of 400 rpm for 180 minutes. As a result, the output BR undergoes a substantial reduction in impurities, which increases the Fe2O3 content.

Given that the BR is a highly alkaline (pH = 10–12.5) by-product and the addition of the sodium hydroxide to the hydrothermal treatment operations, the generation of an alkaline waste water is inevitable. This stage serves as a crucial preparatory step to make the raw material compliant to further processing.

Stage 2: Magnetic Separation & Drying

The next stage involves wet magnetic separation and drying processes. At this process, the input consists primarily of processed red mud and water, as well as electricity, associated with the use of a magnetic drum separator. Regarding the output products, it is noted that Fe concentrate contains a higher percentage of Fe2O3 compared to the input and in a larger volume in comparison with the tailings, indicating the successful removal of other minerals through magnetic separation.. Through the application of magnetic separation and subsequent drying, the materials are separated into two distinct products: a concentrated iron (Fe) product (iron oxide) and residual tailings, which will be further processed in the next stage.

Stage 3: Direct Leaching

In the third stage, known as direct leaching, the tailings from the previous stage are further processed. The feed at this stage includes the tailings, pure hydrochloric acid (HCl) and water. The leaching process is conducted in leaching glass reactors of 1L for 60 minutes at a temperature of 120°C, with a rotation speed of 500 rpm. As a result, it is obtained as a product an aqueous solution containing up to 85 % Sc and various other elements and solid residues (sediments precipitates), which are considered as a by-product.

Stage 4: Separation and Purification

The final stage of the Sc extraction process involves separation and purification. The objective in this stage is to purify Sc from the input materials. Thus, solvent extraction process is applied, in which Sc transfers from one solvent to another owing to the difference in solubility. The solvent extractant reagent used in the procedure is P507. Water and thermal energy source are also added.

2.4 Assumption and Limitations

Prior to the LCA modelling, main assumptions and limitations were clarified in order facilitate the procedure. The main assumptions/limitations are presented below:

- Industrial-scale treatment may not reflect the actual conditions of smaller-scale or pilot-scale operations, which can have significantly different environmental impacts. It is crucial to consider how the scale of the operation might influence resource consumption, energy use, and emissions
- The geographical characteristics can greatly impact the environmental performance of the BR treatment process. This analysis focuses on the specific geographic location of the refineries and is being aware that the results may not be readily transferable to different locations due to varying conditions
- Transportation can be a significant contributor to the overall carbon footprint, especially for plants located far from the source of raw materials. Although for this analysis the transportation of materials to plant and of the intermediate products inside the plant are not considered
- While this analysis assumes a consistent process efficiency level, it acknowledges that in reality, processes can experience variability due to equipment performance or optimization efforts. Recognizing this limitation is essential for understanding the potential dynamic nature of the environmental impact

2.5 Life Cycle Impact Analysis

In this LCA study five impact categories are examined, which were selected according to the scope of the study, as well as to comply with ISO 14040 and 14044 standards containing the broadest set of midpoint categories. The impact categories are summarized in Table 1.

The CML 2001 standard is a method for evaluating the environmental consequences of a product or process throughout its entire life cycle. It was developed by the Center of Environmental Science of Leiden University and was published in a guide to the ISO standards in 2001 [23].

Table 1. LCIA impact categories

Impact Category	Selected Indicator	Unit
Climate Change	Global Warming Potential (GWP) (CML 2001)	kg CO_2 eq
Abiotic depletion	Abiotic Depletion Potential (ADP) (CML 2001)	kg Sb eq
Freshwater Aquatic Ecotoxicity	Freshwater Aquatic Ecotoxicity Potential (FAETP) (CML 2001)	kg DCB eq
Human Toxicity	Human Toxicity Potential (HTP) (CML 2001)	kg DCB eq
Terrestrial Ecotoxicity	Terrestrial Ecotoxicity Potential (TETP)	kg DCB eq

3 Life Cycle Inventory

Life Cycle Inventory (LCI) refers to all the inputs and outputs data of the system, consisting of material flows, energy and emissions. To ensure the credibility of the data, the processes provided by the Sphera database were used. The quantities of material and energy flows for the production processes are obtained from laboratory analysis.

The chemical composition of BR differs in each scenario due to its origin; thus, Table 2 derives from material characterization results. The output product of the second stage, Fe concentrate, contains a higher percentage of Fe2O3 than the initial concentration in BR. In the first case (GR), the concentration of Fe2O3 has been increased from 45.58 % to 56.35 %, in the second case (RO) from 39.18 % to 62.56 % and in the last case (TR) from 35.25 % to 40.04 % respectively. That increase indicates that the hydrothermal treatment process was successful and the impurities have been reduced compared to the feed.

Table 2. Chemical composition of BR

BR Composition	Case 1 - GR (%)	Case 2 - RO (%)	Case 3 - TR (%)
Fe_2O_3	45.58	39.18	35.25
Al_2O_3	15.32	17.37	17.52
CaO	9.19	4.88	4.84
TiO_2	5.70	2.20	4.62
Cr_2O_3	0.24	0.10	0.09
Na_2O	1.76	6.71	6.98
SiO_2	9.72	11.53	14.63
P_2O_5	0.25	0.32	0.15
SO_3	0.89	1.04	0.74
V_2O_5	0.17	0.14	0.07
MgO	0.46	0.02	0.18
LOI	10.26	16.27	14.12

The LCI data for Case 1 (GR), Case 2 (RO) and Case 3 (TR) are summarized in Table 3, Table 4, Table 5 respectively. Although the process and the reagents are common in all cases, the input flow differs, due to the different chemical composition of BR. In all cases, the reagents usually come from a common supplier, while the energy supply depends on the location of the plant. Thermal energy is provided to the system in the form of NG, HFO, LFO and energy consumption is estimated in MJ. In Case 1 (GR), 4,726.83 MJ thermal energy is required, and is deriving from Greece’s electricity grid mix. Fossil fuels have the biggest share in Greece’s energy supply. The required thermal energy in Case 2 (RO) accounts for 4,726.7 MJ and is provided by the energy grid mix, which is composed mainly of hydrocarbons and coal. In Case 3 (TR) 5,798 MJ thermal energy is required and is provided by Turkey’s electricity grid mix. Fossil fuels, including coal, natural gas, and oil, account for the majority of the energy supply.

Table 3. LCI data for Case 1, AoG plant (GR)

Flow	Quantity	Unit
Inputs		
BR	1,000.00	kg
Fe Source	576.00	kg
NaOH	23.50	kg
Water	37.62	m^3
Electricity	318.80	MJ
LFO	131.40	MJ
NG	2,441.43	MJ
HFO	2,154.00	MJ
Lime	30.30	kg
Pure HCl acid	95.40	kg
Extractant P507	2.37	kg
Outputs		
Waste water	1,681.00	L
Fe concentrate	541.00	kg
Sediments Precipitates	81.50	kg
Sc	0.16	kg

Table 4. LCI data for Case 2, Alum Tulcea plant (RO)

Flow	Quantity	Unit
Inputs		
BR	1,000.00	kg
Fe Source	560.00	kg
NaOH	23.50	kg
Water	37.53	m^3
Electricity	318.80	MJ
LFO	90.20	MJ
NG	4,404.00	MJ
HFO	232.50	MJ
Lime	30.30	kg
Pure HCl acid	94.70	kg
Extractant P507	2.36	kg
Outputs		
Waste water	1,681.00	L
Fe concentrate	558.00	kg
Sediments Precipitates	81.50	kg
Sc	0.16	kg

Table 5. LCI data for Case 3, ETI Aluminium plant (TR)

Flow	Quantity	Unit
Inputs		
BR	1,000.00	kg
Fe Source	386.00	kg
NaOH	23.50	kg
Water	37.83	m^3
Electricity	318.80	MJ
LFO	191.70	MJ
NG	2,451.30	MJ
HFO	3,155.00	MJ
Lime	30.30	kg
Pure HCl acid	138.00	kg
Extractant P507	3.46	kg
Outputs		
Waste water	1,681.00	L
Fe concentrate	464.00	kg
Sediments Precipitates	117.16	kg
Sc	0.23	kg

4 Results

The LCIA results for the different scenarios are shown in Table 6 and in Figure 2. The results showed the environmental impact associated with the Sc and Iron recovery processes in Greece, Romania and Turkey. The analysis considered both the efficiency of the processes proposed as well as the energy contribution related to geographical conditions.

In terms of GWP, Case 1 (GR) has a total of 722.72 kg CO_2 eq, which is approximately 82.50 kg CO_2 eq lower compared to Case 3 (TR), while Case 2 (RO) has an even lower GWP of 619.91 kg CO_2 eq. These differences reflected in percentages are respectively 10.2 % and 23 %, for Case 1 (GR) and Case 2 (RO), lower, compared to Case 3 (TR). According to the contributing processes the hydrothermal treatment is the main process responsible for the environmental impacts, accounting for approximately 54.7 % in AoG scenario, 55.6 % in ALUM, while in the ETI scenario, separation and purification process is the main contributor (44.9 %). Direct leaching and magnetic separation, on the other hand, each account for less than 10 % of the total GWP, emphasizing their relatively lower impact on global warming potential.

Considering ADP, Case 1 (GR) shows the lowest overall ADP, with a total of 0.000886 kg Sb eq. It is followed closely by Case 2 (RO), which exhibits a slightly higher ADP value of 0.000887 kg Sb eq, while, Case 3 (TR) stands out with the highest ADP value of 0.000923 kg Sb eq, suggesting a potentially more significant impact on abiotic resource depletion. Therefore, both Case 1 (GR) and Case 2 (RO) have lower ADP percentages compared to Case 3 (TR), with decreases of about 4 % and 3.9 %, respectively. In all cases, the magnetic separation process consistently stands out as the most significant contributor to the overall ADP of each plant, comprising 47.2 % in AoG and ALUM plants and 45.3 % in ETI, of the total ADP. Following closely behind is the hydrothermal treatment process, while the separation and purification stages have a minimal impact less than 1 % in all cases.

When it comes to Freshwater Aquatic Ecotoxicity, Case 3 (TR) has the highest total FAETP of 5.6 kg DCB eq, suggesting the highest potential impact on FAETP, while Case 1 (GR) follows with a total FAETP of 4.4 kg DCB eq Case 2 (RO) has the lowest total FAETP of 2.8 kg DCB eq and compared to Case 3 (TR) is substantially lower by 50.5 % approximately.

The separation and purification phase in the first Case (GR) accounts for 44.3 % of the total FAETP, followed by the hydrothermal treatment process (43.5 %). However, in the second Case (RO) hydrothermal treatment dominates with a contribution of 68.0 %, while the rest processes contribute to approximately 10 % each.

As for human toxicity it is obvious that Case 3 (TR) has the highest total HTP among the three cases, with a total of 113.1 kg DCB eq. Case 1 (GR) has a lower total HTP compared to Case 3, with a total of 43.9 kg DCB eq and Case 2 (RO) has the lowest HTP impact with the value of 25.2 kg DCB eq, exhibiting 77.7 % decrease compared to Case 3 (TR). In the first and in the third Scenario separation and purification stage is the main contributor, representing approximately 50.0 % and 75 % of the total HTP respectively, underscoring its potential impact on human toxicity. In the second Scenario hydrothermal pretreatment plays a crucial role contributing 55.6 % of the total HTP.

In terms of Terrestrial Ecotoxicity Potential Case 1 (GR) has a total of 2.01 kg DCB eq, which is by approximately 0.85 kg DCB eq lower compared to Case 3 (TR). Additionally, Case 2 (RO) has a total TETP of 1.43 kg DCB eq, indicating a decrease of approximately 50.3 % compared to Case 3 (TR). In Case 1 (GR) and Case 2 (RO) hydrothermal pretreatment dominates TETP, while in Case 3 (TR) separation and purification plays the most important role.

Table 6. LCIA results for all cases in terms of the selected indicators for impact categories

Indicators for impact categories	**Case 1 - GR**	**Case 2 - RO**	**Case 3 - TR**
GWP (kg CO_2 eq)	722.72	619.91	805.21
ADP (kg Sb eq)	0.000887	0.000887	0.000923
FAETP (kg DCB eq)	4.42	2.77	5.60
HTP (kg DCB eq)	43.90	25.19	113.10
TETP (kg DCB eq)	10.26	16.27	14.12

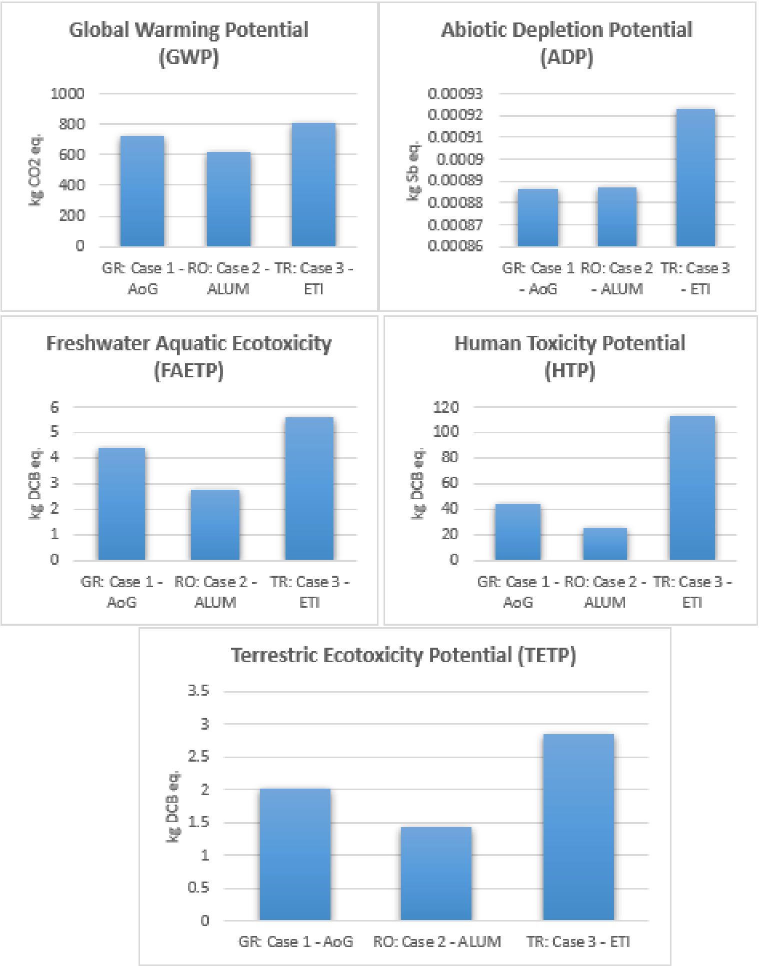

Fig. 2. LCIA results for all cases in terms of GWP, ADP, FAETP, HTP, TETP

5 Discussion

Proper handling of BR is a major challenge for the EU aluminium industry, raising concerns for the impact on both the environment and human health, as well as spatial limitations related to the sheer volume of residues. In 2019, the BR production in the EU was about 6.8 Mt/y [24]. The amount of stockpiled BR in the form of a dry matter was more than 250 Mt by the same year, raising concern for the availability of BR disposal space. The AoG refinery in Greece for example is responsible for 0.75 Mt dry BR production per year, requiring 1 km2 of land for its annual deposit. Alum in Romania accounts for 0.54 Mt and ETI in Turkey accounts for 0.44 Mt dry BR production [24].

In addition, landfilling is restricted by specific regulation for both non-hazardous and hazardous BR. According to the EU categorization of waste documentation [25], BR resulting from the alumina refining process is classified either as Non-Hazardous or Hazardous waste depending on the origin [26]. The classification can only be determined after the necessary test work has been undertaken [27]. If BR is considered non-hazardous, it is landfilled in accordance with the Directive 1999/31/EC, which mandates that non-hazardous waste must be disposed of in landfills, equipped with a natural or artificial geological barrier [26]. Additionally, these landfills should incorporate an artificial sealing liner above the geological barrier and a drainage layer at the top to ensure the protection of soil and water. Also, the same Directive indicates that the landfill regulations to the geological barrier can be limited when either the collection and treatment of leachate is not essential or it has been ascertained that the landfill has not potential hazard on the environment [26].

When BR contains hazardous substances, treatment of waste before its landfilling is required. The most appropriate treatment, including the stabilization of the organic fraction of waste, is applied, in order to reduce, as far as possible, the adverse effects of landfilling on the environment and on human health [28]. In addition, the Directive (EU) 2018/850, which is an amendment of the Directive 1999/31/EC on the landfill of waste, implies that as of 2030, all waste suitable for recycling or other recovery, shall not be accepted in a landfill with the exception of waste for which landfilling delivers the best environmental outcome [28].

According to research, disposal of BR in residual material landfill is one of the most hazardous approaches considering the radiological impact to biota for freshwater, marine and terrestrial ecosystems, due to prolonged release of radioactive substances [29]. Furthermore, landfilling may affect areas larger and distant from the actual deposits through deposition of fine dust particles, in particular in dry stacking. Therefore, soil is a valuable – yet often ignored – resource that needs protection, particularly for industrialized and more densely populated areas.

In contrast, utilization of BR can significantly reduce their impact while also producing valuable products such as construction materials. According to research, 1 kg of BR can be utilized for the production of 2.47 kg of bricks or 22.4 kg of cement, mixed of course with other raw materials. These approaches significantly minimize the impact in the ecosystem while not significantly affecting the impact on human health. In that sense, assessing the economic viability of these and other BR recycling approaches is essential to establish them as a valuable alternative to the outdated technique of landfilling.

As of now, economically efficient integrated technologies available for the total recycling of BR on a large industrial scale pose a challenge. However, the valorisation of BR contributes to the reduction of the management costs of RM. The cost for purchasing high purity Sc ranges from 4,219 € up to 4,876 € per 1 kg in the market [30]. Producing 1 kg Sc with the approaches analyzed above is estimated to cost 1,710 to 2,857 €, depending on the examined region. Although the process is common in all cases, the input of reagents differs according to the chemical composition of BR. In addition, thermal energy plays a significant role in the cost sharing and its price depends on the location of the plant, while each country has its own set price. The same applies with water and electricity, while the rest of the reagents usually come from a common supplier. According to the supplier, as well as the location of the supplier, the prices vary. Also, the amounts purchased, for instance if it is in wholesale or retail price, plays an important role. The purity of the reagent is a significant contributor to the price too, while as purity increases price rises accordingly.

The impact of landfilling and the potential of recycling gives ground to reopen the discussion on alternative sustainable pathways for BR handling in EU. The escalating production of BR, coupled with the limitations in disposal space, highlights the urgency for sustainable solutions. Transitioning from outdated landfilling methods to innovative recycling and valorization techniques mitigates ecological risks while presenting opportunities for creating value-added products like construction materials. Promoting research on these different approaches can establish their potential and benefits, incentivizing investments, fostering collaboration between industry stakeholders and regulatory bodies. This way, EU can advance towards a more sustainable and circular approach to BR management in line with its goal on sustainability and promoting the circular economy.

6 Conclusions

The novel extraction route analyzed in the study enables the extraction of Sc content from BR. To assess the overall environmental impact of the valorisation of BR, LCA is a powerful tool which can provide the most accurate results. The LCA conducted in this study investigates three different cases of Sc extraction through innovative BR treatment in Greece, Romania, and Turkey. The recovery of Sc was estimated up to 85%. The deviations between the three regions, highlights the adaptability and potential for improvement in these processes. While the stages of Sc extraction remain consistent, variations in the chemical compositions of BR underscore the influence of local factors. Turkey's red mud contains lower concentrations of Fe2O3, necessitating tailored treatment methods. This underscores the importance of considering local conditions and compositions when designing sustainable extraction processes.

The environmental impact assessments for the three cases reveal several findings. Scenario 2 (RO) consistently demonstrates the lowest environmental burdens and potential impacts across various environmental impact categories, such as GWP, FAETP, HTP, and TETP, indicating reduced greenhouse gas emissions, aquatic toxicity potential, human health risks, and terrestrial ecotoxicity potential accordingly. It is considered the most environmentally sustainable scenario because a 23% reduction in greenhouse gas emissions in comparison with the other cases can be achieved. Scenario 1 (GR) also shows reduced environmental impacts compared to Scenario 3 (TR) exhibiting 45 % lower ADP values and 61. 2 % lower HTP values compared to the third case. Important reductions were also reported in greenhouse gas emissions, indicating a 10.2 % reduction in GWP and a 21.1 % reduction in FAETP compared to case 3. Furthermore, the choice of extraction method significantly influences the environmental impact, with hydrothermal treatment process and separation and purification, playing the most important role in the majority of the environmental indicators.

It is expected that the environmental impacts may differ after full integration of the Sc production route in an aluminum plant and process optimization, while the reagents consumption can be reduced.

In conclusion, the necessity of exploring alternative, sustainable methods for managing BR becomes evident when considering the environmental impact of landfilling and the benefits of recycling. Moving from outdated landfill practices towards innovative recycling and valorisation approaches not only reduces ecological risks but also creates opportunities for the development of value-added products. These solutions will enable the EU to progress towards a more sustainable and circular approach to BR management, aligning with its goals of sustainability and the promotion of a circular economy.

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Sustainable management of end-of-life creosote-treated wood poles sawdust into red ceramics for environmental and health protection

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Abstract. In the current original research, sintered red ceramics, incorporated with creosote-impregnated timber (CIT) in the form of sawdust as a useful porous making additive, were manufactured and characterized. Actually, safe management of creosote-treated electricity and telecommunication poles waste and its utilization as a useful secondary raw material into materials of added-value, represents an important priority towards circular economy and equally a great challenge given potential health risks reported in association with reuse of creosote-containing materials. The full life cycle of creosote-treated electricity and telecommunication poles includes: the growth of trees on forested land, harvest of logs, milling to produce poles and lumber; then creosote treatment of poles and their use by the Electricity and Telecommunication Grids; and finally disposal in landfills or valorization as an energy source at the end of their use lives. This paper reports results of evaluation performed to determine the possibility of using end-of-life poles in the form of sawdust as additive (pore making agent) in building ceramic industry. End of Waste (EoW) criteria will be implemented to assess the safe use of this waste by-product as secondary resource, for ensuring environmental and human health protection.

Keywords: Creosote-treated wood poles, end-of-life, sawdust, red ceramics, environmental, health protection, sustainability

1. Introduction

A combination of coal tar called creosote oil (tar oil) contains, among other things, chemicals from the phenol, cresol, and xylenol groups in different proportions, depending on the production method [1]. It belongs to the oldest impregnating substances used in the preservation of wood, since ancient times. It is a viscous oily liquid with a tar smell, which is produced by the dry distillation of coal [2]. This substance exhibits satisfactory penetration, minimal leakage and strong toxicity towards microorganisms [3]. Its disadvantages are that it gives the wood a dark brown shade and a strong smell, for which are responsible the drops of oil that appear on the surface of the wood, as a result of which it is not amenable to painting or adhesive substances.

Creosote [4] is a brownish-black oily liquid and is a distillation product of coal tars which themselves are by-products of the high-temperature destructive distillation of bituminous coal to form coke. Creosote is the intermediate cut, ranging from 200 to 355ºC.

Creosote is a complex mixture of hundreds of distinct substances, including bi- and polycyclic aromatic hydrocarbons (PAH's), phenols as well as heterocyclic, oxygen-, sulphur- and nitrogen-containing substances. On average 35-43% of creosote remains unidentified. Creosote typically contains more than 300 compounds that are categorized into five main classes of compounds, as follows [5]:

- Aromatic hydrocarbons including polycyclic aromatic hydrocarbons (PAHs, up to 90% of creosote), benzene, toluene and xylene
- Phenolics including phenols, cresols, xylenols and naphthols (1 to 3 % of creosote)
- Nitrogen-containing heterocyclics including pyridines, quinolines, acridines, indolines, carbazoles (1 to 3 % of creosote)
- Sulphur-containing heterocyclics including benzothiophenols (1 to 3 % of creosote)
- Oxygen-containing heterocyclics including dibenzofurans (5 to 7.5 % of creosote)

European creosotes must comply with EN 13991. In Directive 2011/71/EU this was specified as "Grade B or Grade C creosote as specified in European Standard EN 13991:2003".

Wood as a biological material is attacked by fungi, bacteria, insects, marine organisms wood-eating organisms, which find food and shelter in it. Impregnation of wood with creosote oil (creosote or tar oil) is a method based on in oil-soluble petrochemical fractions (creosote oils), which is widely used to protect pillars of electricity and telecommunication networks from the attacks described above. The under pressure impregnated wood (forest or black pine) has a dark black to brown color, unpleasant smell, especially when it is "fresh", and has excellent dimensional behavior and very extended life time.

However, wood treated with creosote contains several toxic substances. It is still in use in almost all of Europe, even in Scandinavia, although it was predicted that from in 2004 this technique would be phased out. The CIT is a hazardous waste, after its withdrawal from train lines and Electricity distribution as well as Telecommunication Grids. Wooden poles Impregnated with Creosote may offer a lifecycle of more than 40years.

Material Safety Data Sheet (MSDS) [6] for creosote-treated wood in its disposal considerations, proposes that because the smoke and ashes from burning treated wood can contain harmful compounds, it is not recommended to use it in open fires, stoves, fireplaces, or domestic boilers. Alternatively, creosote-treated wood may be incinerated only in commercial or industrial burners or grate-fired boilers and fluidized bed combustion kilns, in accordance with local, regional and national regulations. However, this necessitates that the wood be prepared (shredded) to ensure full incineration and that the temperature at which it is burned is high enough [7].

It should be noticed that reuse of materials that were previously treated with creosote pose a potential danger for environmental and human health, as they contain harmful polycyclic aromatic hydrocarbons (PAHs), nitrogen-containing heterocyclic compounds and other already mentioned substances. Actually, a significant percentage of the creosote total weight is made up of several PAHs, which are considered to be important pollutants and potential carcinogens [8-11]. PAHs can leach into the surrounding water from creosote-treated wood as well as the nitrogen heterocycles that leach more quickly and intensely than the PAHs). Moreover, creosote can contaminate soil in preservation facilities. Because of storage, procedures, tools, and waste treatment of chemicals that are part of the composition of creosote, older wood preservative sites have extensive soil, sediment, and sludge pollution, which makes remediation of these sites more difficult. Thus, risks for human, animal and environmental/ecological health arise from preservatives like creosote that build up in soil and then bioaccumulate in fruits and vegetables [12-15].

Nevertheless, both industries and researchers have tested and experimented with industrial symbiosis solutions that enable the utilization of waste from other industries in ceramic manufacturing [16-20]. Waste valorization technologies in building ceramic industry, are mostly at diverse stages of their maturity (TRL2-3 to TRL7-8) [21]. Sawdust is a common porous making agent in the building ceramic industry [22-26].

In the present research work, safe management of waste poles impregnated with creosote oil, at the end of their life, in the form of sawdust as porous making agent in red ceramics is investigated, complying with the EoW criteria, in accordance to circular economy principles, in the context of sustainable development. For that purpose, clay-based ceramic bodies containing CIT in the form of sawdust were formed, sintered and characterized.

2. Materials and Methods

2.1 Raw Materials

In this study, three different clays A, B and C (received from Central Greece) were utilized. A clay blend, consisting of 50% of clay type A, 33% of clay type B, and 17% of clay type C, commonly utilized for making standard ceramics (Terra SA), was employed for creating prototype (pr) clay samples and samples containing 8% CIT. The chemical analysis of the clays was conducted based on the EN 196-2 standard, and the findings are outlined in Table 1.

Table 1. Chemical analysis of the clayey raw materials

	Composition (%)										
Clay	**Loss on Ignition (LOI)**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**TiO_2**	**$CaCO_3$ (eq)**	**CO_2**
A	11.9	49.4	12.9	7.1	8.6	4.9	2.9	1.6	0.8	14.7	6.5
B	9.9	52.8	13.5	7.6	6.3	4.3	3.2	1.6	0.9	-	-
C	16.5	51.0	8.5	4.7	11.6	3.9	1.5	1.4	0.6	24.5	10.7

In Fig. 1, the Creosote-treated wood at the end of its life, which was used in this research, is presented. The impregnated region (wood mavro) is clearly distinguished from the inner region of the pole (wood leuko) – 70% and 30% respectively.
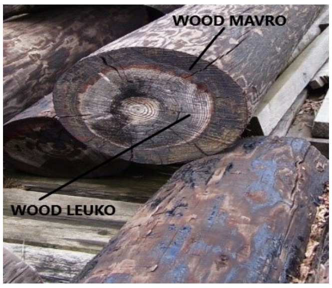
Fig. 1. Creosote-treated wood waste 70% 'mavro' (black) – 30% 'leuko' (white)

In Fig. 2, shredded wood from the above mentioned regions has been used for GC/MS volatile components analysis.

Fig. 2. (a) Shredded wood 'leuko'; (b) Shredded wood 'mavro'

2.2 Ceramic specimen fabrication and characterization

Ceramic bodies were produced by incorporating 0% and 8%wt. CIT sawdust (mixed mavro and leuko) in the aforementioned clay mixture. The particle size distribution of the incorporated CIT sawdust lies between 1mm – 4mm. A schematic diagram of the proposed method is shown in Figure 3.

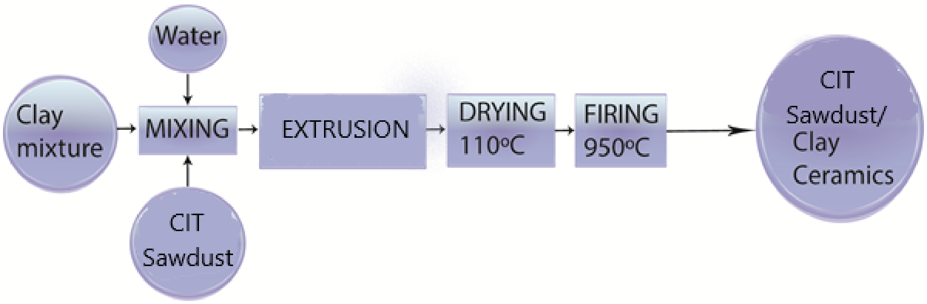

Fig. 3. A schematic representation of the process for the production of CIT sawdust/clay-based red ceramic specimens.

The clay and sawdust blend was mixed with water to create the right malleable texture for shaping specimens with a manual cutter on a pilot-plant vacuum extruder. The specimen bars had a rectangular cross section and measured 80 mm × 43.5 mm × 18 mm. Test specimens were weighed to determine moisture content, then subjected to natural drying at room temperature for 12 hours and forced drying at 110°C until a constant weight was achieved. Test pieces that had been dried were subjected to a controlled temperature increase in a programmable electric chamber furnace, reaching a peak temperature in just 15 minutes to reduce energy spending. The temperature of 950°C was the final sintering temperature that was adopted.

The water absorption and three-point bending strength measured by modulus of rupture (MOR), were assessed on fired samples following the ASTM C67 guidelines. The Anter Unitherm Model 2022 measured the thermal conductivity coefficient (k) at 25°C using the guarded heat flow meter method. The examinations are conducted following the guidelines of ASTM E1530. The results show the impact of adding CIT waste sawdust to the clay mixture, and represent the average of measurements taken from 5, 7, and 3 specimens.

Determination of volatile components contained in CIT and clay/CIT mixture, before and after mixing with clay and sintering was investigated by GC/MS Analysis. Leachates were obtained by following the HS-SPME [27] method for the treated wood and the ceramic bodies containing 8 %wt CIT waste sawdust.

3. Results and Discussion

It was observed during specimen formation that the green clay mixture plasticity and extrusion behavior were influenced in a certain degree by the addition of 8%wt CIT sawdust.

The magnitude of weight loss, cold water absorption, modulus of rupture and thermal conductivity, resulting from the incorporation of 8 %wt CIT sawdust into clay mixture sintered at 950ºC, compared to 0 %wt CIT sawdust specimen are provided in Table 2. The specimen weight loss, cold water absorption, modulus of rupture and thermal conductivity, resulting from the incorporation of 8%wt CIT sawdust into clay mixture sintered at 950ºC, are diverged to a large extend in comparison to 0%wt CIT sawdust specimen. This is an expected consequence of the 8%wt CIT sawdust content in the clay mixture. It is apparent that the embodiment of CIT waste sawdust in considerable proportions (8%wt.) in the clay mixture, slightly deteriorates the modulus of rupture, whereas it decreases the thermal conductivity values, which is beneficial from the thermal insulation properties aspect.

An optimization study will determine the suitable %wt CIT sawdust in the clay mixture and the optimal particle size distribution of the incorporated CIT sawdust, so that article 6 (c) of Directive 2008/98/EC be fulfilled [28].

Determination of volatile components contained in the sintered specimen, compared to the volatile components contained in the CIT waste sawdust (see Table 3), proves that the volatile components are degraded during the sintering process, fulfilling 6 (d) of Directive 2008/98/EC. Thus, potential health risks reported in connection with applications of reused creosote-treated materials are here avoided.

Table 2. Characterization results on sintered ceramic specimens:
(a) Weight Loss (%) and Total Volume Shrinkage, TVS (%)

Tsint (ºC)	**CIT (% wt.)**	**Specimen**	**Sintering weight loss (%)**	**Variation (%)**	**Total Volume Shrinkage (%)**	**Variation (%)**
950	0	40	6,49		2,29	
	8	40	9,47	**45,92**	0,35	**84,69**

b) Water absorption WA (%) (Cold water), WA (%) (Boiled water),
3 – Point Bending MOR (MPa), Thermal Conductivity k (W/m*K)

Tsint (ºC)	CIT (% κ.β.)	Cold Water Absorption (%)	**Variation (%)**	**Boiled** Water Absorption (%)	**Variation (%)**	MOR (MPa)	**Variation (%)**	k (W/m*K)	**Variation (%)**
950	0	15,16		17,60		8,78		0,499	
	8	19,88	**31,13**	**23,51**	**33,58**	5,38	**38,72**	0,398	**20,24**

Table 3. GC/MS Analysis: volatile components of the CIT sawdust and the sintered specimen

No	RT (min)	Volatile compound	Area % LEUKO	Area % MAVRO	Area % Bricks 8% CIT sawdust
1	1.992	Propane	0.21	0.02	-
2	3.106	α-Pinene	27.08	0.05	-
3	3.688	(1R)-α-Pinene		0.03	-
4	4.536	D-Limonene	8.36		-
5	4.547	Indene		0.25	-
6	5.625	L-Fenchone	0.58		-
7	5.849	7-Methylbenzofuran	1.59		-
8	5.936	2-Methylbenzofuran		0.11	-
9	6.326	(+)-Fenchol	0.48		-
10	6.919	(+)-2-Bornanone	1.01		-
11	7.209	Camphor	0.47		-
12	7.267	3-Methyl-1H-indene		0.13	-
13	7.34	1-methyl-1,2-propadienyl-benzene	0.56		-
14	8.206	Naphthalene	13.45	3.18	-
15	8.748	α-Terpineol	6.62		-
16	9.664	Isoquinoline		0.35	-
17	9.739	α-Methylene-benzeneacetonitrile	0.88		-
18	10.388	2-Isopropyl-1-methoxy-4-methylbenzene	0.22		-
19	10.46	Quinoline		0.02	-
20	11.402	6-Methyl-benzothiophene	0.08		-
21	12.08	1-Methylnaphthalene	13.48	5.31	-
22	12.517	2-Methylnaphthalene	6.37	2.61	-
23	13.394	2-Naphthalenamine		0.03	-
24	14.087	7-Methylquinoline		0.11	-
25	14.381	α-Terpinyl acetate	0.38		-
26	14.914	Biphenyl	2.84	3.22	-
27	15.488	1-Ethylnaphthalene	0.88		-
28	15.741	2-Ethylnaphthalene	0.08	1.02	-
29	15.982	2,7-Dimethylnaphthalene	1.48	2.28	-
30	16.471	1,3-Dimethylnaphthalene	1.14	2.90	-
31	16.567	1,6-Dimethylnaphthalene	0.81	1.34	-
32	17.162	1,4-Dimethylnaphthalene	0.70	0.52	-
33	17.607	2,3-Dimethylnaphthalene	0.13		-
34	18.74	Acenaphthene	5.12	8.07	-
35	18.988	3-Methyl-1,1'-biphenyl	0.48		-
36	19.268	4-Methyl-1,1'-biphenyl	0.13		-
37	19.722	1-Isopropenylnaphthalene	0.14	1.62	-
38	19.944	Dibenzofuran	1.57		-
39	20.411	α-Muurolene	0.07		-
40	20.599	1,6,7-Trimethylnaphthalene	0.12	8.88	-
41	20.778	1,4,6-Trimethylnaphthalene	0.11	0.69	-
42	21.323	2,3,6-Trimethylnaphthalene	0.07	0.26	-
43	21.966	1,4,5-Trimethylnaphthalene	0.06		-
44	22.239	1H-Benzonaphthene		4.13	-
45	22.372	Fluorene	0.90	7.89	-
46	25.124	Fluorene-9-methanol		4.52	-
47	25.972	Diphenylketene		5.92	-
48	26.76	Ethionamide		2.48	-
49	27.614	9-Methyl-9H-fluorene		1.30	-
50	28.08	2-Methyl-9H-fluorene		1.38	-
51	28.358	2-Methyl-1,1'-biphenyl	0.31	0.51	-
52	29.946	4,5-Benzothionaphthene		2.78	-
53	31.564	Diethyl Phthalate	0.25	3.32	-
54	33.073	4-Methyldibenzofuran	0.09	5.60	-
55	35.711	4-Biphenylylcarboxaldehyde	0.06	4.66	-
56	39.733	Anthracene	0.10	10.78	-
57	45.348	Isobutyl phthalate	0.53	1.74	-

4. Conclusions

Recent trends in wood processing include safe use of wood preservatives, the development of wood modification methods, and the recycling and disposal of treated materials. In this framework, the incorporation of 8 %wt CIT sawdust into red ceramics was investigated in the present work. Sawdust influences in a certain degree the green clay body plasticity and extrusion behavior during specimen fabrication. The characterization results on sintered red brick products show that the embodiment of CIT waste sawdust in noticeable proportions (8%wt.) in the clay mixture sligthly impacts on strength values, while also decreases thermal conductivity, which will be beneficial to red brick thermal insulation behavior. An optimization study would be necessary to determine the optimal both %wt CIT sawdust in the clay mixture and particle size distribution of the incorporated CIT sawdust in the final ceramic product, in view of fulfilling the technical standards for specific applications and meeting the existing legislation requirements for building materials.

Particularly, the comparison of volatile components contained in the sintered specimen to those identified in the CIT waste sawdust, proves that the volatile components are degraded during the sintering process and, as a result, potential use of the final ceramic product will not cause any negative effects on the environment or human health.

A pilot-scale study (TRL 7–8) should follow the present laboratory scale research, to ensure that possible unburned volatile components in the flue gases will be traced and securely retained, satisfying and fulfilling the End of Waste (EoW) criteria for CIT sawdust through its proper incorporation in clay mixtures to produce high quality and environmentally safe red ceramic building materials while also avoiding overall environmental and human health risks. Furthermore, in addition to addressing current issues, the wood treatment sector should go forward to remediate environmental sites contaminated by wood preservation operations and also develop and embrace innovative recycling and valorization research advancements, practical solutions and supportive policies, towards a sustainable circular economy.

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