October 2023 vol. 22 No. 10

ISSN 1582-9596

Environmental Engineering and Management Journal

Founding Editor: Matei Macoveanu
Editor-in-Chief: Maria Gavrilescu
Guest Editor: Fabio Fava

"Gheorghe Asachi" Technical University of Iasi

October 2023 Vol. 22 No. 10 *ISSN 1582 - 9596*

Environmental Engineering and Management Journal

An International Journal

Founding Editor: **Matei Macoveanu**

Editor-in-Chief: **Maria Gavrilescu**

Leading the Ecological Transition
ECOMONDO 2022

“Gheorghe Asachi” Technical University of Iasi

Environmental Engineering and Management Journal

Environmental Engineering and Management Journal encourages initiatives and actions concerning the improvement of education, research, marketing and management, in order to achieve sustainable development. This journal brings valuable opportunities for those offering products, technologies, services, educational programs or other related activities, creating thus a closer relation with the request of the market in the fields of environmental engineering, management and education.

This journal address researchers, designers, academic staff, specialists with responsibilities in the field of environmental protection and management from government organizations (central and local administrations, environmental protection agencies) or from the private or public companies. Also, graduates of specialization courses or of the Environmental Engineering and Management profile, as well as other specialists may find in this journal a direct linkage between the offer and request of the market concerned with the protection of the environment and the administration of natural resources in the national and international context.

The journal was conceived as a means to develop scientific and technical relationships between people who offer and request solutions for environmental protection and conservation of natural resources, creating thus the premises to enhance the transfer of technology and know-how, the confirmation and implementation of ecological products and services.

Taking into consideration these aspects, we gladly welcome any persons or companies which correspond to the above-mentioned purposes and objectives to use our journal to identify potential collaborators.

For subscriptions and orders please contact us at:
OAIMDD (*Academic Organization for Environmental Engineering and Sustainable Development*), 73 Prof. Dimitrie Mangeron Blvd., PO 10, Box 2111, 700050 Iasi, Romania, CIF: 10150285

Phone/Fax: 0040-232-271759
E-mail: brindusa.sluser.at.gmail.com, mgav_eemj.at.yahoo.com

In LEI:
ALPHA BANK ROMANIA (ABR)
SWIFT Code: BUCUROBU
IBAN: RO87BUCU1032235333663RON
Beneficiary: OAIMDD-EEMJ
Address: PO 10, Box 2111, 700050 Iasi, Romania

In EURO:
ALPHA BANK ROMANIA (ABR)
SWIFT Code: BUCUROBU
IBAN: RO79BUCU1031215940036EUR
Beneficiary: OAIMDD-EEMJ
Address: PO 10, Box 2111, 700050 Iasi, Romania

Department of Environmental Engineering and Management and
EcoZone Publishing House - O.A.I.M.D.D.
73 Prof. Dimitrie Mangeron Blvd., 700050, Iasi, Romania
Phone/Fax: 0040-232-271759

Environmental
Engineering and
Management Journal

EDITORIAL BOARD

Founding Editor:

Matei Macoveanu, *Gheorghe Asachi* Technical University of Iasi, Romania

Editor-in-Chief:

Maria Gavrilescu, *Gheorghe Asachi* Technical University of Iasi, Romania

SCIENTIFIC ADVISORY BOARD

Maria Madalena dos Santos Alves
University of Minho, Braga
Portugal

Ecaterina Andronescu
University *Polytechnica* of Bucharest
Romania

Robert Armon
Technion-Israel Institute of Technology, Haifa
Israel

John Atkinson
State University of New York at Buffalo
USA

Adisa Azapagic
The University of Manchester
United Kingdom

William Brazile
Colorado State University
USA

Hans Bressers
University of Twente, Enschede
The Netherlands

Han Brezet
Delft University of Technology
The Netherlands

Dan Cascaval
Gheorghe Asachi Technical University of Iasi
Romania

Yusuf Chisti
Universiti Malaysia Terengganu,
Malaysia

Philippe Corvini
University of Applied Sciences Northwestern
Switzerland, Muttenz, Switzerland

Igor Cretescu
Gheorghe Asachi Technical University of Iasi
Romania

Silvia Curteanu
Gheorghe Asachi Technical University of Iasi
Romania

Andrew J. Daugulis
Queen's University Kingston
Canada

Valeriu David
Gheorghe Asachi Technical University of Iasi
Romania

Katerina Demnerova
University of Prague
Czech Republic

Gheorghe Duca
StateUniversity of Moldavia, Kishinew
Republic of Moldavia

Emil Dumitriu
Gheorghe Asachi Technical University of Iasi
Romania

Anca Duta Capra
Transilvania University of Brasov
Romania

Fabio Fava
Alma Mater Studiorum University of Bologna
Italy

Francesco Fatone
Marche Polytechnic University, Ancona
Italy

Lidia Favier
University of Rennes,
France

Eugenio Campos Ferreira
University of Minho, Braga,
Portugal

Silvia Fiore
Polytechnic University of Turin,
Italy

Cristian Foşalău
Gheorghe Asachi Technical University of Iasi
Romania

Anton Friedl
Vienna University of Technology,
Austria

Joan Garcia
Universitat Politècnica de Catalunya-Barcelona,
Spain

Anne Giroir Fendler
University *Claude Bernard* Lyon 1
France

Sabino de Gisi
Politecnico di Bari
Italy

Yuh-Shan Ho
Peking University
People's Republic of China

Nicolae Hurduc
Gheorghe Asachi Technical University of Iasi
Romania

Marcel Istrate
Gheorghe Asachi Technical University of Iasi
Romania

Ravi Jain
University of Pacific, Baun Hall Stockton
United States of America

Michael Søgaard Jørgensen
Aalborg University
Denmark

Nicolas Kalogerakis
Technical University of Crete, Chania
Greece

Thomas Lindhqvist
International Institute for Industrial Environmental
Economics, Lund University, Sweden

Andreas Paul Loibner
University of Natural Resources and Life Sciences,
Vienna, Austria

Tudor Lupascu
Academy of Sciences, Institute of Chemistry,
Kishinev, Republic of Moldavia

Gerasimos Lyberatos
National Technical University of Athens
Greece

Mauro Majone
Sapienza University of Rome
Italy

Teodor Malutan
Gheorghe Asachi Technical University of Iasi
Romania

Florica Manea
Polytechnic University of Timisoara,
Romania

Antonio Marzocchella
University of Naples Federico II,
Naples, Italy

Ecaterina Matei
Politehnica University of Bucharest
Romania

Marcela Mihai
Petru Poni Institute of Macromolecular Chemistry,
Iasi, Romania

José Mondéjar Jiménez
University Castilla-La Mancha, Cuenca
Spain

Shin' ichi Nakatsuji
University of Hyogo
Japan

Mircea Nicoara
Al.I.Cuza University, Iasi
Romania

Cristina Orbeci
University *Polytechnica* of Bucharest
Romania

Alexandru Ozunu
Babes-Bolyai University of Cluj-Napoca
Romania

Valentin I. Popa
Gheorghe Asachi Technical University of Iasi
Romania

Tudor Prisecaru
University *Polytechnica* of Bucharest
Romania

Gabriel-Lucian Radu
Polytechn ica University of Bucharest
Romania

Maria Angeles Sanroman
University of Vigo
Spain

Joshua Schaeffer
Colorado State University
USA

Bogdan C. Simionescu
Gheorghe Asachi Technical University of Iasi
Romania

Florian Statescu
Gheorghe Asachi Technical University of Iasi
Romania

Carmen Teodosiu
Gheorghe Asachi Technical University of Iasi
Romania

Saulius Vasarevicius
Vilnius Gediminas Technical University
Lithuania

Irina Volf
Gheorghe Asachi Technical University of Iasi
Romania

Environmental Engineering and Management Journal (Environ. Eng. Manag. J.) is included and indexed in:

CABI
Chemical Abstracts Service/SciFinder (ACS) (since 2002)
EBSCO Database (since 2002)
EVISA
ICAAP (International Consortium for Advancement of Academic Publications)
Index Copernicus Journal Master List (**ICV/2015=156.46**)
Journal Citation Reports® 2022 Edition (**IF=1.1**), (*Environmental Sciences*, Ranked **256 out of 274**; 5-Year Impact Factor: 0.9; Article Influence® Score: 0.093; Immediacy Index: 0.3; Normalized eigenfactor: 0.22304; **Quartile: Q4**); Journal Citation Indicator, JCI/2022: 0.18
Web of Science® (**H=41**)
MedSci
ProQuest (since 2002)
The National University Research Council (RO)
Science Citation Index Expanded™
SJR (SCImago Journal&Country Rank) (*Environmental Sciences*, **SJR index/2022=0.237**; Ranked **1175 out of 1708**, Quartile **Q3**, **H=42,** *Environmental Engineering:* Ranked **123 out of 175, Quartile Q3***; Management, Monitoring, Policy and Law:* Ranked **271 out of 382,** Quartile **Q3***; Pollution***,** Ranked **111 out of 156; Quartile: Q3**)
SCOPUS (since 2002), **Cite Score/2022=1.8, SNIP index/2022=0.289,** *Environmental Engineering:* Ranked **117 out of 184**

Home page: *http://www.eemj.icpm.tuiasi.ro;*
http://www.eemj.eu

Full text: *http://www.ecozone.ro, http://www.eemj.eu*

Founding Editor: Matei Macoveanu, Iasi (RO)
Editor-in-Chief: Maria Gavrilescu, Iasi (RO)

Environmental Engineering and Management Journal (EEMJ) is edited by
***Gheorghe Asachi* Technical University of Iasi and *EcoZone* Publishing House of the *Academic Organization for Environmental Engineering and Sustainable Development* (O.A.I.M.D.D.)**

Editorial and Production Office:
Department of Environmental Engineering and Management – *Cristofor Simionescu* Faculty of Chemical Engineering and Environmental Protection and EcoZone - O.A.I.M.D.D., 73 *Prof. Dimitrie Mangeron* Bd., 700050 Iasi, Romania
Phone: +40-232-278680, ext. 2259, 2137
Fax: +40-232-271759
e-mail: eemjournal.at.yahoo.com, eem_journal.at.yahoo.com, eemjeditor.at.yahoo.com, eemj_editor.at.yahoo.com, emj.office.at.yahoo.com, eemj_office.at.yahoo.com

Published 12 issues per year, **under the aegis of the *Gheorghe Asachi* Technical University of Iasi, Romania**
by *EcoZone* Publishing House of the *Academic Organization for Environmental Engineering and Sustainable Development* (O.A.I.M.D.D.), **http://www.ecozone.ro**

Annual subscription rate 2023 (12 issues)

	Print:	**Electronic full access:**	**Print+Electronic:**
EURO	575 per volume	575 per year	1000 per volume/year
Individual costs			
EURO	55 per issue	45 per issue	

Order directly to the Editorial Office, 73 *Prof. Dimitrie Mangeron* Bd., 700050 Iasi, Romania
Phone/Fax: Fax: +40-232-271759, e-mail: brindusa.sluser.at.gmail.com, eemj.office.at.gmail.com

Electronic, full text: Order or purchase on-line at: **www.eemj.eu, www.ecozone.ro**

Bank account (EURO):
ALPHA BANK ROMANIA (ABR)
SWIFT Code: BUCUROBU,
IBAN: RO79BUCU1031215940036EUR
Beneficiary: OAIMDD-EEMJ, Address: PO 10, Box 2111, 700050 Iasi, Romania

Bank account (LEI):
ALPHA BANK ROMANIA (ABR), IBAN: RO87BUCU1032235333663RON,
Beneficiary: OAIMDD-EEMJ

Environmental Engineering and Management Journal
October 2023 Vol.22, No. 10, 1679-1774
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

CONTENTS

Editorial
Leading the Ecological Transition ECOMONDO 2022.
The Green Technology Expo
Fabio Fava …… 1679
http://doi.org/10.30638/eemj.2023.142

The water stewardship approach towards resilient water use
Beatrice Bizzaro, Cristina Sala, Alessandra Magnani, Eugenio Capponi,
Chiara Rizzi, Gianluca Capodimonte…… 1681
http://doi.org/10.30638/eemj.2023.143

Co-hydrothermal carbonization of cavitated stabilized organic fraction
and landfill leachate: optimization of hydrochar characteristics
Alessandro Cardarelli, Pierpaolo Lombardi, Andrea Nicolini, Marco Barbanera …… 1689
http://doi.org/10.30638/eemj.2023.144

Green public procurement for a sustainable public administration
in a resilience context
Tiziana Crovella, Giovanni Lagioia, Annarita Paiano…… 1703
http://doi.org/10.30638/eemj.2023.145

Potential of aerobic stabilization in drastic sludge reduction: a full-scale experiment
Marta Domini, Andrea Volpi, Giorgio Bertanza…… 1717
http://doi.org/10.30638/eemj.2023.146

Horizontal subsurface flow phytotreatment for domestic wastewater treatment:
nitrification-denitrification efficiency tested on Bertalia-UNIBO pilot plant
Carmine Fiorentino, Maurizio Mancini…… 1729
http://doi.org/10.30638/eemj.2023.147

Remediation of dioxin-contaminated soils through thermal desorption and vapor management via thermal oxidizer at Biên Hòa airbase, Vietnam
Aline Jordens, Maël Makoudi, Hatem Saadaoui, Jan Haemers……………………………….……….. 1735
http://doi.org/10.30638/eemj.2023.148

Electrochemical recycling of red gypsum waste: The ELEDGE process
Francesco Negri, Francesco Gallo, Flavio Manenti ………………………………………………… 1745
http://doi.org/10.30638/eemj.2023.149

Synthesis of bio-based wood adhesive
Salise Oktay, Nilgün Kızılcan, Başak Bengü ……………………………………………………… 1753
http://doi.org/10.30638/eemj.2023.150

Management and possible valorisation of bioplastics separated from organic fraction of municipal solid waste
Giorgia Pellegrino, Paola Zitella, Alexia Boulanger, Barbara La Licata, Debora Fino ………………………………………………………………………………………… 1755
http://doi.org/10.30638/eemj.2023.151

Life cycle assessment of the production of natural and recycled aggregates for concrete: A case study in the province of Brescia
Andrea Piccinali, Irma Cavallotti, Giovanni Plizzari, Sabrina Sorlini…………………………… 1767
http://doi.org/10.30638/eemj.2023.152

Environmental Engineering and Management Journal

October 2023, Vol.22, No. 10, 1679-1680
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2023.142

"Gheorghe Asachi" Technical University of Iasi, Romania

EDITORIAL

Leading the Ecological Transition

ECOMONDO 2022

The Green Technology Expo

The papers collected in this special issue of *Environmental Engineering and Management Journal* were presented as lectures or posters at the scientific and technical conferences hosted by *Ecomondo 2022* held from the Italian Exhibition Group headquarter in Rimini, Italy, during 8-11 November 2022.

(http://en.ecomondo.com).

Ecomondo is one of the largest European exhibitions in the field of *Green and Circular Economy*, hosting annually over than 99,000 delegates from more than 140 different nations along with 1,500 industrial exhibition stands in 150,000 square meters and over than 100 conferences and workshops on policies, research and innovation, innovation funding opportunities, education, communication and entrepreneurship and international networking and partnership creation.

As with the previous editions, the aim of *Ecomondo 2022* was to explore and share recent industrial advances and opportunities in industrial technical waste production reduction, recycling and exploitation; sustainable agrifood and wood chains, biowaste collection and exploitation via integrated biorefinery schemes, with the production of biobased chemicals, materials and biofuels, including methane; industrial eco-design; industrial symbiosis, renewable and critical resources; water resources monitoring, protection and sustainable use in the civil and agrifood sectors; wastewater treatment and valorization with nutrients recovery and water reuse; marine resources protection and sustainable exploitation and port regeneration; sustainable remediation of contaminated sites and marine ecosystems; indoor and outdoor air monitoring and clean up; and circular and smart cities.

Some of the international workshops were focused on the emerging trends in the circular economy domains and on the role of digitalization and industry 4.0 enabling technologies in process efficiency, eco-design and waste collection in the major industrial value chains. Some other workshops were focused on the technical and regulatory constrains currently affecting the implementation of circular economy value chains in the sectors of electronic and electric products, automotive, construction and demolition, packaging materials and textile and fashion. A special focus was on the recycling of plastic waste, biodegradable plastics and the monitoring, prevention and mitigation of marine litter. Finally, *Ecomondo 2022* also hosted events on the priorities of the Mediterranean macro-region, in close cooperation with the EU commission, and in particular the water scarcity of the area, the Mediterranean Sea contamination (also due to marine litter) and its sustainable exploitation.

Ecomondo 2022 conferences hosted more than 700 oral communications, about 90 of them were then selected for full paper publications on this journal, the *Procedia Environmental Science, Engineering and Management* and the *Ecomondo proceedings*. This special issue contains some of such papers and provides some of the key information presented and discussed in the frame of some of the mentioned technical and scientific conferences of *Ecomondo* 2022.

We believe that this collection of papers will be useful to people who could not follow the edition of *Ecomondo 2022*. It is primarily towards them but it also aspires to provide permanent records in the promotion, adoption and implementation of the major priorities and opportunities of the green and circular economy in Europe and in the Mediterranean basin, with the conversion of some of the key local environmental challenges into new opportunities for a green and sustainable growth of the territories.

For additional info, please refer to the following link: https://en.ecomondo.com

Guest Editor:

Professor ***Fabio Fava***, *Alma Mater Studiorum - Università di Bologna*, Italy

Fabio Fava, born in 1963, is Full Professor of “Industrial & Environmental Biotechnology” at the School of Engineering of University of Bologna since 2005. He published about 250 scientific papers, 220 of which on medium/high IF peer-review international journals of industrial and environmental biotechnology and circular bioeconomy. He has more than 11000 citations, a H-index of 61 and an i10 index of 150 (Google Scholar) along with 215 papers quoted by Scopus. He is actively working in the fields of environmental, industrial and marine biotechnology and of the circular bioeconomy in the frame of a number of national projects and collaborative projects funded by the European Commission. Among the latter, he coordinated the FP7 collaborative projects NAMASTE, on the integrated exploitation of citrus and cereal processing byproducts with the production of food ingredients and new food products, and BIOCLEAN, aiming at the development of biotechnological processes and strategies for the biodegradation and the tailored depolymerization of wastes from the major oil-deriving plastics, both in terrestrial and marine habitats. He also coordinated the Unit of the University of Bologna who participated in the FP7 collaborative projects ECOBIOCAP, ROUTES, MINOTAURUS, WATER4CROPS, ULIXES and KILL SPILL.

Fabio Fava served and is serving several national, European and international panels, by covering, among others, the following positions:

- Member of the Scientific Committee of the European Environmental Agency (EEA), Copenhagen, for the "Circular economy and resource use" domain (2021-);
- Italian Representative in the "European Bioeconomy Policy Forum" and the "European Bioeconomy Policy Support Facility" of the European Commission (2020-);
- Senior Expert of the Italian delegation to the Programming committee Horizon Europe, Cluster VI: Food, bioeconomy, natural resources, agriculture and environment (European Commission, DG RTD)(2020-);
- Italian Representative and elected vice chair in the "States Representatives Group" della Public Private Partnership "Circular Biobased Europe" (CBE JU), Brussels (2021-);
- Italian Representative in the BLUEMED WG of the EURO-MED Group of Senior Officials (EU Commission DG RTD and Union for Mediterranean) (2017-) and in the initiative on sustainable development of the blue economy in the western Mediterranean the "Western Mediterranean Initiative" WEST MED, promoted by the EU Commission (DG MARE) in close cooperation with 10 countries of the area (2016-);
- Italian Representative in the "Working Party on Biotechnology, Nanotechnology and Converging Technologies" of the Organization for Economic Co-operation and Development (OECD, Paris) (2008-);

Finally, he is the scientific coordinator of the International Exhibition on Green and Circular economy ECOMONDO held yearly in Rimini (Italy)

Environmental Engineering and Management Journal

October 2023, Vol. 22, No. 10, 1681-1687
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2023.143

"Gheorghe Asachi" Technical University of Iasi, Romania

THE WATER STEWARDSHIP APPROACH TOWARDS RESILIENT WATER USE

Beatrice Bizzaro[1]*, Cristina Sala[1], Alessandra Magnani[1], Eugenio Capponi[1], Chiara Rizzi[2], Gianluca Capodimonte[2]

[1]HPC Italia S.r.l., Via Francesco Ferrucci 17/A, 20145, Milan, Italy
[2]Philip Morris International - Operations, Avenue de Rhodanie 50, 1007, Lausanne, Switzerland

Abstract

Climate change is altering patterns of weather and water all around the world and, uneven water distribution is amongst the most compromising aspects. Water-related challenges may have serious impacts on a country in terms of economic losses, livelihoods, and political stability. The need to safeguard the water resource is becoming a growing necessity for many multinational companies which often operate in vulnerable and water-stressed environments.

The water stewardship approach and the Alliance for Water Stewardship (AWS) Certification is offering a standardized solution to sustainable water management by implementing a 360-degree approach that acts both in local and territorial contexts and it is applicable to all organization and industrial sectors. AWS is the first internationally recognized Standard for sustainable and resilient water use: the certification allows companies to reduce their water footprint, through external engagement and synergic cooperation between parties. Consequently, issues are address not only inside the site's physical boundaries but also directly on and with the catchment context through a stakeholder inclusive process. In the following article, we aim to illustrate the benefits and mitigation actions implemented by a multi-national company following the water stewardship approach and the standardized framework given by the AWS Standard. By implementing the AWS Standard, it is possible for companies to safeguard their surrounding territories and communities, formalize and optimize their commitment into water saving and increase the environmental international awareness through mitigation actions recognized and adopted by AWS.

Key words: catchment, multi-stakeholder governance, stewardship, sustainability, water security

Received: May, 2023; Revised final: September, 2023; Accepted: September, 2023; Published in final edited form: October, 2023

1. Introduction

The world is dealing with numerous interconnected crises that have increased the level of uncertainty around the globe. In this context, natural resource calamities are amongst the top 10 global risks as reported by the United Nations in 2022 (World Economic Forum, 2022). In this paper we will focus on those risks known to provoke water crises, and on potential mitigation solutions that water demanding companies can potentially apply to avoid one of the most critical, upcoming situations of our time.

In the last 15 years, water-related challenges have been exacerbating due to a multitude of factors linked to climate change, population growth and consequent overexploitation and mismanagement (Carvalho and Van Tulder, 2022). Demand of fresh, potable water is constantly increasing, especially in emerging economies, as is competition and pressure from agriculture, manufacturing, and energy sectors. This can be highlighted by the fact that from 1900 to 2010, global freshwater consumption has grown by over 600% (UNESCO, 2021). Freshwater resources are very limited.

---

* Author to whom all correspondence should be addressed: e-mail: beatrice.bizzaro@hpc.ag; Phone: +39 0245488990

We currently relay on less than 1% feasibly usable freshwater reserves on Earth. The lack of availability and resilient management of water resources can have major negative impacts on both social, economic and development aspects of a country (Moreno-Pinzani, 2021). For this reason, water crises must be considered a shared responsibility: they involve a multitude of causes and consequences and will potentially impact a huge number of people and sectors, for which no single solution is available (Carvalho and Van Tulder, 2022).

Before thinking about how to act, it must be understood that water can be extremely complex to deal with. A given water source never feeds one actor alone, but a multitude of different stakeholders located in a common catchment area. Companies often find themselves operating in areas subjected to water-related vulnerabilities, many of which remain unperceived, especially in the short term. According to the Carbon Disclosure Project's (CDP, 2020) Global Report, the cost of inaction on water risks, especially for the manufacturing sector, is up to five times the cost of action. Consequently, the need of resilient management strategies to avoid physical, reputational, and regulatory water risks that may affect business productivity, is becoming impellent for all multinational companies, especially those operating in vulnerable and water-stressed environments.

Based on new, growing awareness and understanding that water risks affect not only single sites, but a multitude of different key figures in a common territory, the term water stewardship was born. This emerging paradigm sustains that water-related issues can only be fully addressed and mitigated through external engagement (Morrison and Schulte, 2014) and synergic cooperation between parties. Consequently, water stewardship practices aim to address issues not only inside but especially outside a site's physical boundary, thus engaging and acting directly on and with the catchment context in a long-term multi-stakeholder pathway.

2. Baseline approach and methods

2.1. Clarification of concepts

The first global water conference organized by the United Nations in Mar del Plata, Argentina, in 1977, was the first steppingstone towards concrete and meaningful discussions in formalizing a standardized approach in ensuring sustainable continuity in water resource use. However, it was only after the United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro, Brazil, also known as the Rio Conference in 1992, that the concept of Integrated Water Resource Management (IWRM) was truly formalized and put into practice. The IWRM is defined as an approach which promotes the co-ordinated, synergic development and management of water and related resources in order to maximize economic and social well-being in an equitable manner, without compromising the sustainability of vital ecosystems. On these principles the IWRM approach has been discussed and taken into consideration by all the following water-related summits and conferences, but the major challenge has remained its effective implementation on-the-ground (Rahaman and Varis, 2005).

We can say that the Alliance for Water Stewardship (AWS) Standard System (here forward Standard) is a paradigm deriving and strictly connected to the IWRM approach, as it is defined as the use of water that is environmentally sustainable, socially equal, and economically beneficial, achieved through a stakeholder inclusive process that involves site and catchment-based activities (Magnani et al., 2020). The AWS Standard is focused on implementing actions in a *catchment area*, a physical area of land which the site relies upon for its water supply and discharge, including the upstream and downstream areas which may be impacted by the site's activity. A catchment area is defined considering both surface water and groundwater if the site is relying on multiple water sources.

2.2. Baseline approach

It is safe to say that we are all touched, either directly or indirectly, by water risks. Some countries may face them at more dramatic scale, whilst others may still live in idyllic short-term situation in which water is still readily available and free. Numerous water-intensive multi-national companies are however acting fast and now, especially those that have numerous water-demanding operational activities scattered in vulnerable areas world-wide. They are committing to long-term sustainable water management and stewardship practices to safeguard and positively impact their territories' water resources and ensure a supply that is secure, especially in the long run.

The question is, how are they managing to do this? In the last 10 years, many companies have been implementing an innovative, globally recognized, how-to framework for stewardship implementation, defined as the AWS Standard. The Standard is designed around a Plan-Do-Check-Act management concept subdivided into 5 phases (or Steps), focused not only on the operational site but also on the supply chain and territorial context that surround it. The scope is to not only reduce a site's water footprint but contribute through the engagement of public and private sector stakeholders to the identification and mitigation of shared water challenges, which would otherwise remain unperceived if focus of actions were limited only to a site's four walls.

2.3. Methods

To fully understand how a particular operational site may implement the Standard in its everyday activities and as a long-term commitment, it is necessary to explain and detail further the Standard structure itself. As previously anticipated, the

Standard is subdivided into 5 main steps which are, in turn, subdivided into criteria and indicators which must be fulfilled and applied with standard compliance. The degree of compliance may vary from a basic, core level, to more advance levels of water stewardship maturity (Gold or Platinum levels). Standard implementation also implies a path of continuous improvement, evaluation of achievements against targets and implementation of ameliorative actions over time.

The methodology on which the Standard relies upon for water stewardship achievement can be classified into two main categories (Figs. 1, 2):

1 Outcome compliance
2 Standard Step indicator implementation

Although the two are interconnected and strictly reliant upon each other, the fulfilment of a particular standard step does not automatically imply the obtainment of a specific outcome.

Fig. 1. The Alliance for Water Stewardship (AWS) Standard Steps categories designed around a Plan-Do-Check-Act management concept

Fig. 2. The Alliance for Water Stewardship (AWS) Standard Outcomes categories for water stewardship achievement

At this stage, a detailed description of each category must be undertaken.

2.3.1. Outcome compliance

The 5 AWS Outcomes represent the fundamental steppingstones of optimum water stewardship practices that benefit the site as well as the catchment area. They do not correspond to a particular Step but are a result of correct Standard implementation:

- *Good Water Quality Status*: active contribution to ensuring optimum water quality in relation to the site (i.e., respect of legal threshold levels for outgoing wastewater/incoming water) and the catchment area based on credible data from environmental agencies, academic studies and/or direct sample collection
- *Sustainable Water Balance*: active contribution to ensuring sustainable water use in relation to the site (i.e., respect of legal abstraction limits) and the catchment area based on water balance studies
- *Good Water Governance*: active contribution to water/wastewater management in the catchment area (i.e., protection, monitoring, treatment, policy framework etc.) synergically with institutions, public sectors, and government agencies, as well as other organizations
- *Secure Important Water-Related Areas* (IWRAs): active contribution to assessing, monitoring, restoring and/or maintaining the status of specific water-related areas of environmental, cultural, community and/or economic importance
- *Water, Sanitation and Hygiene* (WASH): active contribution to providing, improving and/or maintaining the provision of safe water, sanitation and hygiene for employees and local catchment communities in need.

2.3.2. Standard step indicator implementation

The Standard indicators have a particular focus and scope based on the 5 Steps that they are bound to comply with:

- Step 1 indicators are all about collecting and analyzing data from the site, indirect water use of its service/raw material providers, the catchment area of interest, and stakeholders in relation to the 5 Outcomes (quality, quantity, governance, WASH and IWRAs), water risks, and shared challenges as well as mitigation actions and opportunities.
- Step 2 indicators are focused on developing three principal aspects related to water stewardship:
  - public commitment;
  - system for maintaining and tracking water-related regulatory compliance;
  - developing a strategy and plan with actions (technological and/or socioeconomic), goals and targets linked to the 5 Outcomes with the scope of addressing the water risks/challenges identified in Step 1.
- Step 3 indicators are based on providing evidence of the ‘doing’ to verify conformance and/or achievement of the following:
  - actions to implement to achieve goals/targets (Step 2);
  - 5 outcomes;
  - water rights and legal prescriptions;

- indirect water use;
- stakeholder engagement.

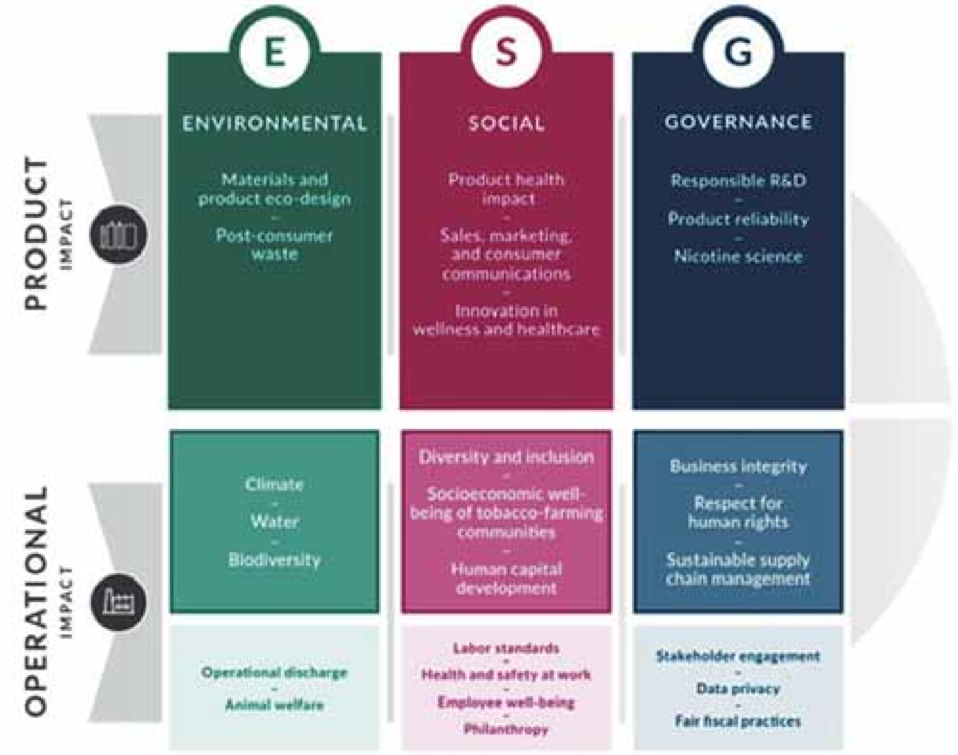
- Step 4 indicators regard evaluating and measuring performance (both positive and negative) of what has been achieved (so far) based on planned actions and targets (Step 2), as well as water-related emergency incidents or compliance violations. Stakeholders must be direct contributors to this Step as they provide valuable insights and suggestions for improvements. Based on evaluation results, the plan (Step 2) must be adapted and integrated accordingly.
- Step 5 indicators regard the communication and disclosure part of the Standard, which must be executed with the scope of publicly sharing internal governance, water risks and shared challenges (Step 1), planned actions (Step 2) and performances (Step 4), stakeholder synergies and (if applicable) any significant water-related compliance violations.

Based on this framework, focused on complying with 5 specific AWS Outcomes and implementing the indicators belonging to the 5 Standard Steps, any type of site, anywhere in the world, may formally and credibly implement with an adequate level of maturity, a successful and resilient water stewardship *modus operandi.*

3. Case studies

To portray the relevant array of results which arise from Standard implementation, we will illustrate a case study of a multi-national manufacturing company that operates in the tobacco industry. Philip Morris International (PMI) has, since 2018, incorporated water stewardship and the AWS Certification as a fundamental pillar of its sustainability initiatives and core of its business strategy. PMI believes that working efficiently goes hand in hand with resiliently safeguarding and managing the environment (Philip Morris International, 2021a). This year, PMI has received, for the third consecutive year, a triple A rating from CDP on its performance in protecting forest, tackling climate change, and water security.

By conducting annual and dynamic materiality assessments to identify, assess and prioritize Environmental, Social, and Governance (ESG) topics of interest (Philip Morris International, 2021b) (Fig. 3), PMI has shed light on the growing and fundamental importance of sustainable water management and stewardship for its operations. The reason is that water is vital in PMI's activities: from tobacco cultivation to manufacturing, all products require water. PMI's 2021 Materiality Assessment additionally identified water as an emerging environmental issue in terms of potential outward impact, on society and plant, and inward impact on PMI's operations (Philip Morris International, 2021a) (Fig. 4). PMI's agricultural supply chain accounts for approximately 50% of PMI's total water footprint, while approximately 40% comes from other raw material producers and approximately 5% from direct manufacturing operations (Philip Morris International, 2022).



	ENVIRONMENTAL	SOCIAL	GOVERNANCE
PRODUCT IMPACT	Materials and product eco-design - Post-consumer waste	Product health impact - Sales, marketing, and consumer communications - Innovation in wellness and healthcare	Responsible R&D - Product reliability - Nicotine science
OPERATIONAL IMPACT	Climate - Water - Biodiversity	Diversity and inclusion - Socioeconomic well-being of tobacco-farming communities - Human capital development	Business integrity - Respect for human rights - Sustainable supply chain management
	Operational discharge - Animal welfare	Labor standards - Health and safety at work - Employee well-being - Philanthropy	Stakeholder engagement - Data privacy - Fair fiscal practices

Fig. 3. Top ranking Environmental, Social, and Governance (ESG)'s topics for Philip Morris International (PMI) (Philip Morris International, 2021a)

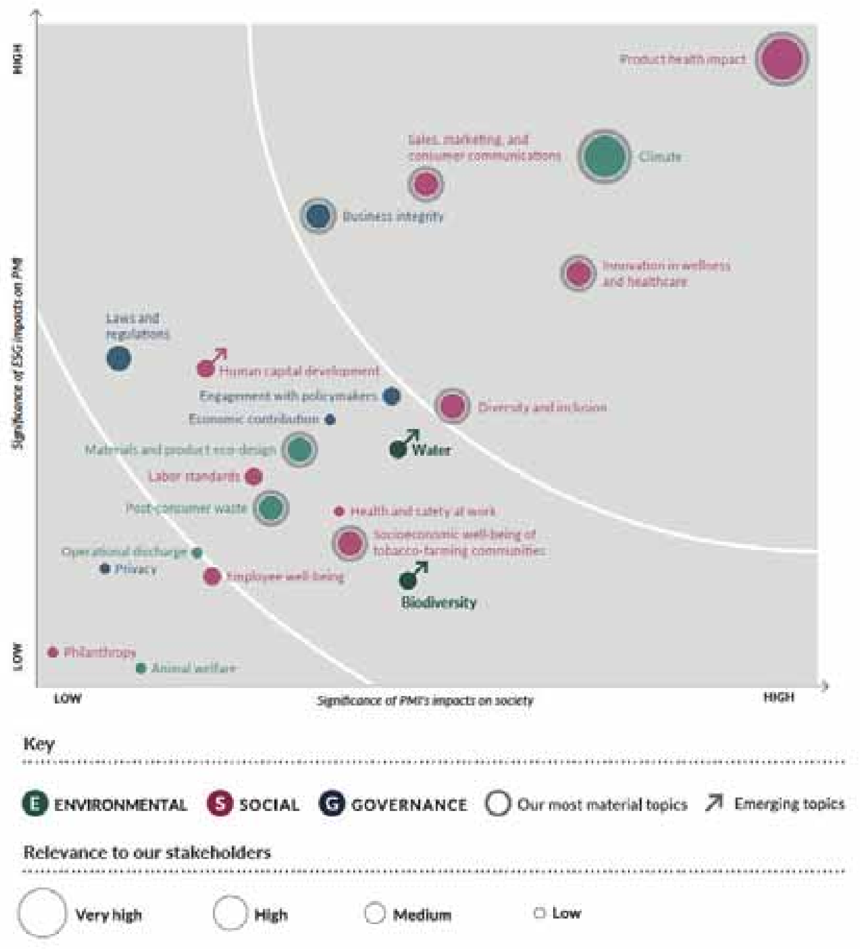


Fig. 4. Materiality matrix illustrating the results of Philip Morris International (PMI)'s Sustainability Materiality Assessment and identifying water as an emerging environmental issue (Philip Morris International, 2022)

Consequently, the global goal of implementing the AWS Standard to all relevant manufacturing facilities by 2025 (Philip Morris International, 2022), was a strategic decision to mitigate and reduce not only a facility's water footprint, but also the indirect water use of its raw material producers. In 2018 the first AWS pilot site deployed in Brazil. Following its success, 17 manufacturing facilities followed the Certification roadmap (Argentina, Brazil, Czech Republic, Greece, Indonesia, Italy, Korea, Mexico, Netherlands, Philippines, Portugal, Romania, Serbia, Switzerland, Turkey, Jordan, and Poland - from the AWS Certified list) with more to come in the upcoming years.

Implementing the Standard and achieving Certification allowed PMI to formalize its commitment to water stewardship principles, reduce its water footprint in manufacturing facilities and throughout its supply chain, engage with local stakeholders in a more robust, transparent, and cooperative way with the scope of raising awareness and synergically contributing to mitigating and addressing shared water risks and challenges. The implementation of the Standard framework has also led to the completion of annual global water-risk assessments with the scope of deep-diving into local, more granular scenarios for identifying hotspots of greater water-related vulnerabilities and prioritizing intervention to higher risk areas (Philip Morris International, 2022).

It would be difficult, if not impossible, to report all the results and best practices that have arisen and daily arise from each single PMI facility that has achieved AWS Certification. Consequently, we have decided to report a small array amongst the many global examples. Each Certified site has become, in their local catchment contexts, advocates for water stewardship with the scope of continuously improving their performances and outcomes. In the section below, we will discuss the performance of three PMI facilities: Philip Morris Manufacturing and Technology Bologna (PM MTB), in Italy, Philip Morris Polska S.A. (PMPL), in Poland, and the Philip Morris Philippines (PMFTC) facility in Marikina, in relation to the 5 AWS outcomes (Philip Morris Polska, 2021):

- Good Water Quality Status: Since 2021, PMPL is undertaking detailed investigations on the quality status of the groundwater, by implementing dedicated on-site tests. The scope is to monitor the quality status of the groundwater bodies on which the site relies upon for its water provision (Philip Morris Polska, 2022). PMFTC has also acted in safeguarding the water quality of its surface water bodies. In collaboration with the local government, the Community Environment and Natural Resources (CENRO), neighbouring companies from an industrial complex, and a local NGO, PMFTC supported the installation of trash traps along a main river, the San Juan. Two of these traps, which help prevent surface water pollution, as well as blockages that may cause flooding, have already been installed by the local government. PMFTC and its community partners consulted third party engineers, who improved the design of the traps. Through a local NGO, the company also provided the infrastructure to install a third trash trap along the river and has plans to put additional ones in place (Philip Morris Philippine, 2022).

- Sustainable Water Balance: PM MTB has been investing in innovative water recycling and reuse technologies with the aim of reducing its potable water withdrawal. From 2019, approximately 29% of PM MTB's total water consumption comes from recycled waters. In 2021, PM MTB ameliorated its water consumption even further by optimizing its on-site wastewater treatment plant, resulting in an additional potable water saving of approximately 58,000 m^3. Furthermore, PM MTB is also continuing its investments in water consumption monitoring, which has reached a coverage of 100%. This has significantly contributed to the prompt identification of water losses and, consequently, to timely mitigation and corrective actions (Philip Morris Manufacturing & Technology Bologna, 2022).
- Good Water Governance: Since responsible water stewardship requires collective actions, PMFTC identified and engaged with key internal and external stakeholders, including employees and third-party workers, as well as local communities, academics, and regulators. To promote responsible water stewardship, PMFTC ran comprehensive awareness campaigns that included a webinar, in which local companies participated in round table discussions with leaders of local barangays (small communities or villages), a seminar for in-house contractors, and a water conservation art contest aimed to raise awareness within local communities. Extensive communications efforts across several digital channels and announcements on local bulletin boards complemented the awareness campaign (Philip Morris Philippine, 2022).
- Secure Important Water-Related Areas (IWRAs): To protect and maintain healthy ecosystems and important green areas, PMPL conducts annual tree planting programmes and has installed, over the years, beehives directly on-site. Forty-three trees have been planted between 2019 and 2021 to enrich the green areas within the site boundaries, thus also promoting bee pollination and the development of local biodiversity. Extensive campaigns with employees, for example in occasion of world earth day, have also been conducted to increase awareness and know-how regarding environmental preservation and sustainability. Such campaigns included the construction and installation of bird nesting boxes, to encourage the repopulation of bird species, the conduction of educational webinars on the urban animals found within the site premises, and the planting of herb gardens (Philip Morris Polska, 2022).
- Water, Sanitation and Hygiene (WASH): Access to water, sanitation, and hygiene is a key factor in the AWS certification process. To equip local communities, PMFTC has donated the first two handwashing facilities at Tanauan Vegetable Trading Post to provide residents better access to WASH facilities. PMFTC also implemented awareness campaigns on the importance of good potable water quality within the local communities (Philip Morris Philippine, 2022).

Based on the success stories and global results achieved to date, PMI will continue to implement a long-standing approach of sustainable water management and stewardship actions at an international scale. The scope will be to continue to engage stakeholders, identify and address water challenges, risks, and create catchment resilience, throughout PMI's supply chain and manufacturing operations.

The long-term objectives that PMI is striving to achieve through the implementation of sustainable management practices and the Standard framework, will be to save a total of 10 million m^3 of freshwater by 2030, address shared water challenges both in its tobacco and non-tobacco supply chain as well as in production activities, reinforce good agricultural practices, and improve current tools to better monitor and understand water volumes that need to be restored to achieve a net positive balance on-site and in the catchment (Philip Morris International, 2021a).

4. Conclusion

Applicability of the AWS Standard framework is structured in such way to fit and comply with any type of water user anywhere in the world. This flexibility permits the Standard to be implemented voluntarily by any organisation, even if not productive or water demanding, with the scope of formalizing a commitment and an implementation scheme for internationally recognized water stewardship practices.

By implementing the Standard and, consequently, water stewardship practices, water management is brought to another level by stepping outside of an organization's physical boundary and bringing into the picture various actions and actors such as stakeholders, water use in the supply chain, WASH and IWRAs, assessment of shared water-related challenges and resilient mitigation interventions to address vulnerabilities and ensure a long-term water security. Consequently, issues are address not only inside the site's physical boundaries but also directly on and with the catchment context through a stakeholder inclusive process.

The case study of PMI highlights how a multinational company can incorporate the Standard framework as an international ambition and fundamental steppingstone towards the achievement of long-term sustainability goals in relation to water. The benefits and mitigation actions implemented by several PMI facilities following the water stewardship approach and the standardized framework given by the AWS Standard, allowed the companies not only to minimise their local water footprint, but also cooperate in a more robust, durable, and synergic way with their local stakeholders to manage and concretely mitigate shared water issues and challenges within the same catchment context. PMI's journey in water stewardship is still ongoing, but PMI facilities all over the world are on the right path to transforming the way that they deal with water.

The AWS and its water stewardship approach could potentially be the light at the end of the tunnel, an innovative, long-term solution to the widespread water crises that we all, sooner or later, will lean towards. We are seeing a significant transformation in a number of companies and organizations, but the hope is that many others will embark on this path toward a more sustainable future and security for water.

References

Carvalho D.M., Van Tulder R., (2022), Water and sanitation as a wicked governance problem in Brazil: An Institutional Approach, *Frontiers*, **4**, 781638, https://doi.org/10.3389/frwa.2022.781638.

CDP, (2020), A wave of change. The role of companies in building a water-secure world, CDP Global Water Report, On line at: https://www.cdp.net/en/reports/downloads/5577

Magnani M., Rizzi C., Iannacci M.G., Brancone-Capponi E., Bizzaro B., (2020), Alliance for Water Stewardship: a network of sustainable water stewards, *Environmental Engineering and Management Journal*, **19**, 1677-1681.

Moreno-Pinzani M.A., (2021), Water management in agricultural production, the economy, and Venezuelan Society, *Frontiers*, **4**, 624066, https://doi.org/10.3389/fsufs.2020.624066.

Morrison J., Schulte P., (2014), The CEO Water Mandate. Shared Water Challenges and Interests: The Case for Private Sector Engagement in Water Policy and Management. Discussion Paper, *Pacific Institute*, *The World's Water*, **8**, 19-33.

Philip Morris International, (2021a), Integrated Report, On line at: https://www.pmi.com/integratedreport2021

Philip Morris International, (2021b), Materiality Assessment, On line at: https://www.pmi.com/resources/docs/default-source/pmi-sustainability/pmi-2021-sustainability-materiality-report.pdf

Philip Morris International, (2022), Towards a net positive impact on nature, PMI's ambition on biodiversity and water, On line at: https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&cad=rja&uact=8&ved=2ahUKEwiAn6Stm-P9AhUewQIHHfuYAFYQFnoECAsQAQ&url=https%3A%2F%2Fwww.pmi.com%2Fresources%2Fdocs%2Fdefault-source%2Fpmi-sustainability%2Fpmi_water_biodiversity_ambitions_2022.pdf&usg=AOvVaw3MYGzgXAZCUllsVd2LAGmD

Philip Morris Manufacturing & Technology Bologna, (2022), Water Stewardship. Report on Water Performance of Philip Morris in Italy, On line at: https://www.pmi.com/resources/docs/default-source/italy-files/water-stewardship-report_ita-2022-final.pdf

Philip Morris Philippine, (2022), Leading on water stewardship in the Philippines, On line at: https://www.pmi.com/sustainability/case-studies/leading-on-water-stewardship-in-the-philippines

Philip Morris Polska, (2021), Report on Water Performance of Philip Morris in Poland, On line at: https://www.pmi.com/resources/docs/default-source/poland-market/water-report-pmpl-en.pdf?sfvrsn=4d2cddb4_4

Philip Morris Polska, (2022), Report on Water Performance of Philip Morris in Poland, On line at: https://www.pmi.com/resources/docs/default-source/poland-market/water-report.pdf?sfvrsn=abcc5db6_

Rahaman M.M., Varis O., (2005), Integrated water resources management: evolution, prospects and future challenges, *Sustainability: Science, Practice and Policy*, **1**, 15-21.

UNESCO, (2021), The United Nations World Water Development Report 2021. Valuing Water., 11-16, On line at: https://unesdoc.unesco.org/in/documentViewer.xhtml?v=2.1.196&id=p::usmarcdef_0000375724&file=/in/rest/annotationSVC/DownloadWatermarkedAttachment/attach_import_db06f7c4-b33f-4833-be56-bbf54afdee3f%3F_%3D375724eng.pdf&locale=en&multi=true&ark=/ark:/48223/pf0000375724/PDF/375724eng.pdf#WWDR%202021%20EN%20report.indd%3A.56356%3A2357

World Economic Forum, (2022), The Global Risks Report 17th Edition Insight Report, 93-95, Online at: https://www3.weforum.org/docs/WEF_The_Global_Risks_Report_2022.pdf

Environmental Engineering and Management Journal October 2023, Vol. 22, No. 10, 1689-1702
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2023.144

"Gheorghe Asachi" Technical University of Iasi, Romania

CO-HYDROTHERMAL CARBONIZATION OF CAVITATED STABILIZED ORGANIC FRACTION AND LANDFILL LEACHATE: OPTIMIZATION OF HYDROCHAR CHARACTERISTICS

Alessandro Cardarelli[1]*, Pierpaolo Lombardi[2], Andrea Nicolini[3], Marco Barbanera[1]

[1]Department of Economics Engineering Society and Business Organization (DEIM), University of Tuscia, Largo dell'Università s.n.c., Loc. Riello, 01100 Viterbo, Italy
[2]Ecologia Viterbo srl, Via Atto Tigri, 11, 00197, Roma, Italy
[3]CIRIAF (Inter-University Research Center on Pollution and Environment "Mauro Felli"), Biomass Research Centre, University of Perugia, Perugia, Italy

Abstract

The problem of municipal solid waste (MSW) management is becoming an issue more and more relevant. Hydrothermal carbonization (HTC) is an emerging path to address the concerns arising from the management of MSW, promoting a from-waste-to-resource action plan. In this study, the HTC was performed by using the stabilized organic fraction (SOF) of the MSW to evaluate the hydrochar characteristics and to determine the optimum temperature and residence time of the HTC process. Preliminary tests were achieved with SOF and two different liquid substrates, the landfill leachate (LL) and the concentrate fraction (CF) of landfill leachate from the reverse osmosis plant, respectively. The HTC was performed at different process temperatures and residence times, while the solid-to-liquid ratio was maintained at 1/10. Furthermore, the influence of hydrodynamic cavitation (HC) to enhance the homogenization of SOF and liquid substrate before the HTC was studied. Response Surface Methodology (RSM) was applied to determine the best HTC process conditions (process temperature and residence time) based on the experimental campaign developed through the Central Composite Face-Centered Design (CCF-CD). By statistical analysis, it was possible to understand how the process variables influenced the fixed carbon content, deashing efficiency and mass yield (considered as responses of the model). The optimum condition for the HTC process was at 232°C and 2.65 h. The preliminary results showed that the hydrochar from HTC of the cavitated blend of SOF and LL is a valid mixture for the production of eco-sustainable plasters to be used in the building sector in a circular economy approach.

Key words: HTC, hydrochar, hydrodynamic cavitation, municipal solid waste, response surface methodology

Received: May, 2023; Revised final: July, 2023; Accepted: August, 2023; Published in final edited form: October, 2023

1. Introduction

Approximately 232 million tonnes of municipal solid waste, or 517 kg per capita, were produced in 2020 in the UE27. In the three years 2018–2020, there was an increase of 3.7% in production overall (Eurostat, 2023). In 2021, in Italy, the production of municipal waste involved a quantity of about 30 million tons, the solution of which final mainly involves landfilling. Such a solution not only occupies more and more valuable space but also causes air, water and soil pollution by discharging carbon dioxide carbon (CO_2) and methane (CH_4) into the atmosphere and chemicals and pesticides in the land and the groundwater. This, in turn, is harmful to human health, as well as the environment.

Mechanical Biological Treatment (MBT) is widely used as a form of pretreatment to landfill or incineration. It is an essential phase of the waste cycle since allows, through a process of selection (mechanical) and treatment (biological), to:

- recover a further part of recyclable materials;

---

* Author to whom all correspondence should be addressed: e-mail: a.cardarelli@unitus.it

- make an appropriate selection of waste to be sent for incineration/waste-to-energy plant, obtaining a lower emission of pollutants and a higher energy yield;
- reduce the volume of material for final disposal and therefore the use of landfills and incinerators;
- ensure the conditions of biological stability of the waste to minimise the formation of decomposition gases and leachate.

In an MBT plant, the unsorted MSW is mechanically sorted into three fractions, i.e. material organic, recyclables and waste. The recyclable fraction includes materials such as glass, metals, plastics, rubber, rags, papers etc. which can be differentiated by separation and sieving. The recyclable components (glass, metals etc.) can be sent for recycling, while the components non-recyclable partly contribute to the production of solid fuel to be sent to waste-to-energy plants and parts are sent to landfill.

The organic fraction is addressed to a biological stabilization process (aerobic digestion). The output of the aerobic digestion is called stabilized organic fraction (SOF), or off-specification compost, and it is codified by the European Waste Catalog (EWC) as EWC 19.05.03. This material is currently discarded and landfilled, with additional costs. According to the Urban Waste Report 2022 of ISPRA (ISPRA, 2022), in 2021 over 8.1 million tons of waste/materials were produced by mechanical biological treatment plants, which is about 560.000 tons of SOF. Furthermore, leachate is generated from the MSW landfilling. Landfill leachate (LL) is a tainted liquid arising from the bottom of solid waste disposal facilities that contain both soluble organic and inorganic compounds as well as suspended particles (Naveen et al., 2017).

In Italy, the regulation requires that it must be captured and appropriately treated on the same site of the landfill or transported in an ad hoc plant duly authorized for disposal in the sewers. Currently, physicochemical treatment methods such as reverse osmosis are widely used. Reverse osmosis membrane technology plants are employed for LL treatment, producing two fractions: the permeate (PF) (about 75%) and the concentrate (CF) (about 25%). Since the permeate might be directed to the sewers, the concentrate remains a burden. In this context, alternatives are needed to valorize the SOF, together with landfill waste reduction, as well as the landfill leachate and/or concentrate, leading the waste management business towards a circular economy perspective.

A valuable option is to use all these wastes as precursors in the production of carbon-based materials. This work arises from the project ECOPLASTER - Biostabilized for Ecosustainable Building -funded in 2022 by the Ministry of Environment and Energetic Security. The project intends to use the outputs of the municipal solid waste management chain, i.e. SOF, LL, and the CF as input for the hydrothermal carbonization (HTC) process. The HTC is a thermochemical valorization process during which the wet biomass remains heated at a low temperature range (150–350°C) over a few minutes to several hours under autogenic pressure (Villamil et al., 2020). Three types of products are resulting from the process. The main output is a carbon-rich solid material known as hydrochar, which accounts for approximately 45-70% of the product mass. A gas phase, approximately 1-3% of the raw material, consisting mainly of CO_2 (>90% of the gaseous products) with small amounts of CH_4, H_2, and CO. A liquid fraction (spent liquor), 5 and 25% of the mass of products, which is rich in bio-degradable soluble organic compounds (Magdziarz et al., 2021; Roman et al., 2021; Wilk et al., 2020). The HTC process has several advantages, including the ability to process heterogeneous wet biomasses without pre-drying or separation pre-treatment required by other thermochemical processes, since water acts as a reactant, solvent, and catalyst (Libra et al., 2011; Sharma et al., 2020). These advantages make the HTC process applicable to various wet residues, including agricultural and forestry residues (Başakçılardan Kabakcı and Baran, 2019), anaerobic digestate (Cavali et al., 2023), sewage sludge (Luo et al., 2020), algal biomass (Castro et al., 2021; Jabeen et al., 2023), olive mill sludge (Mendecka et al., 2020), pulp and paper mill sludge (Mohammadi et al., 2020) and off-specification compost (Basso et al., 2015). Nonetheless, within the HTC process, there are present some disadvantages. These include the use of complex and costly systems which use substantial amounts of water and further costs for the separation of the solid and liquid phases, as well as the discharge of significant quantities of wastewater (Ercan et al., 2023; Khan et al., 2019).

However, current research examining the possible valorization of the spent liquor derived from the biomass HTC process highlights the commercial rentability in a circular economy approach (Khan et al., 2019). Possible solutions cited include processes from which the resultant by-product represents a benefit such as anaerobic digestion, nutrient recovery, bioplastic production, wet oxidation, and liquid fertilizer (González-Arias et al., 2023; Ipiales et al., 2021; Langone and Basso, 2020; Tripathi et al., 2022; Zhang et al., 2023).

In the project ECOPLASTER, the hydrochar (solid fraction) of the HTC process will be used for the production of an eco-sustainable plaster to be used in the building sector, while the spent liquor (liquid fraction) will be employed for the growth of microorganisms aimed at the production of bioplastics. This study provides preliminary results on the application of the HTC process to the stabilized organic fraction of MSW for hydrochar production, by using both landfill leachate and the concentrate fraction as liquid substrate. Several studies have investigated the HTC as thermal pre-treatment for different types of MSWs, or streams obtained from it. (Ischia et al., 2021) performed the HTC to valorize municipal solid waste for biofuel production; the off-specification compost was used by (González-Arias et al., 2021) to be co-processed by HTC with olive tree pruning and obtaining a coal-like product with a high carbon content; Periyavaram et al. (2023) analyzed the thermal behavior of hydrochar derived from HTC of food waste using leachate as moisture source; likewise, Śliz et al. (2022) reported the technical feasibility of an industrial scale layout of an HTC plant by using the wet fraction mechanically separated from mixed MSW or under sieve fraction as solid substrate and water as moisture source.

Despite the many probable benefits, the potential application of LL or CF from reverse osmosis plants as liquid substrates for HTC remains less explored. This study aimed at comparatively evaluating the efficacy of landfill leachate and concentrate fraction as reaction media for the hydrothermal conversion of SOF derived from MSWs to hydrochar.

Product yield and proximate and ultimate analyses were taken into consideration to understand the basic physicochemical properties of the resulting hydrochars and optimize the process parameters (residence time and temperature) of the hydrothermal carbonization to be used in an industrial scale-up. Moreover, to further enhance the homogenization and viscosity of the solid and liquid substrate mixture before the HTC process, the application of hydrodynamic cavitation (HC) was investigated. HC is a promising physicochemical process consisting of the phenomenon of formation, growth, and rapid collapse of vapor cavities due to the reduced local pressure (Lanfranchi et al., 2022). The HTC was carried out at different process temperatures and residence times, while the solid-to-liquid ratio was maintained constant. Furthermore, HC was performed at a temperature set point of 60°C in order to investigate its influence on the hydrochar physical-chemical characteristics.

Central Composite Face-Centered Design (CCF-CD) and Response Surface Methodology (RSM) were used to examine any potential relationships of the hydrochar production parameters (temperature and residence time) on the fixed carbon content (FC), deashing (DE) and mass yield (MY) of the hydrochars. In detail, FC, DE and MY were selected as response variables in the optimization process in order to obtain the HTC conditions at which the hydrochar characteristics were maximized to improve the efficiency of the admixture material to be used as plaster in the building sector for carbon-capture (Gupta and Kua, 2017; Navaratnam et al., 2021), moisture absorption (Mrad and Chehab, 2019) and thermal and acoustic insulation (Kahandawa Arachchi et al., 2021; Srikanth et al., 2022). The results of the present work will be used to define the optimal mixture of mortar and hydrochar for the production of eco-sustainable plasters to be employed in the building sector.

2. Material and methods

2.1. Collection of SOF and liquid substrates

The stabilized organic fraction, the landfill leachate, and the concentrate fraction of the reverse osmosis of LL were obtained from the same MSWs management plant located in Viterbo, Italy. The SOF was collected from the MBT and locally sieved down to a particle size of approximately 2.5 mm before the laboratory experiments in order to remove any inorganic residues, e.g. glass, metal, plastic, paper, etc. The LL was spilled from the MSW landfill while the CF came from the reverse osmosis plant, both located in the same area as the MBT plant. The LL and CF were gathered in plastic containers and stored at a temperature of +4°C. The characteristics in terms of pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), conductivity, and total solids (TS) at 105°C of each liquid substrate are listed in Table 1.

Table 1. Characteristics of each liquid substrate

Liquid substrate	***LL***	***CF***
pH	7.9	6.8
BOD [mg/L]	2150	638
COD [mg/L]	8380	2490
Conductivity [mS/cm]	25.6	23.7
Total solids [%]	2.0	1.4

2.2. HTC experiment

A stainless-steel Parr 4560 mini-batch reactor with a volume of 600 ml was used for the hydrothermal carbonization treatment. The removable ceramic band heater was connected to the external control system (4848 reactor controller, Parr Instrument) which allowed the setting of both the temperature and the rotational speed of the stirrer. For each experimental run, the vessel was loaded with the solid and liquid substrate and purged with nitrogen to remove the air from the reactor. The reactor was heated up to the desired temperature with a heating rate of 3°C/min while the stirring rate was set to 200 rpm. The residence time is referred to the holding time of the reactor after reaching the temperature set point. Then, the internal cooling coil connected with an external chiller allowed for an immediate decrease in temperature by the coolant. Thus, the liquor was separated by using a Büchner funnel with a vacuum pump and filter paper (Whatman filter paper, 8 μm). While the hydrochar was washed with distilled water several times and oven-dried at 105°C for 24 h to remove residual moisture, the liquid fraction was collected and maintained at +4°C for further analyses. The mass yield (*MY*) of the HTC process was calculated as the ratio of the mass of hydrochar (M_f) to that of the initial feedstock (M_0) on a dry basis by using Eq. (1).

$$MY = \frac{M_f}{M_0} * 100\ [\%] \tag{1}$$

2.3. Hydrodynamic cavitation

When the HTC process is scaled up to industrial size, the homogenization and viscosity of the solid and liquid substrate mixture become essential parameters affecting its pumpability. The pumpability of the slurry is limited by the type of pump, which generally have an upper limit of about 10-15% solids (dry basis) loading (Nagarajan and Ranade, 2021). Thus, hydrodynamic cavitation was selected as a pre-treatment to enhance these characteristics.

The HC was performed by using single-step homogenization with a controlled cavitation approach patented by SOLDO Cavitators (Soldo Cavitators, 2023). The cavitation unit is composed of a feed tank and a 5.5 kW electric motor which provides power to a stainless steel rotor (cavitator) working at 20 L/min, 3 bar, and 3600 rpm. The solid and liquid substrates were mixed at the desired solid-to-liquid ratio and pumped inside the cavitator in a closed loop until the flow temperature reached the set point of 60 °C.

2.4. Chemical-physical analysis

Proximate analysis was carried out following the standards EN 14774-2 for the moisture content, EN 15148 for the volatile matter (VM), and EN 14775 for the ash content, by using a thermogravimetric analyzer (TGA-701, LECO Co., USA). Ultimate analysis was performed by using a LECO Truspec CHN analyzer, in compliance with UNI EN 15104 standard method. Fixed carbon (FC) and oxygen were computed by difference. Moreover, the deashing efficiency (DE) of the HTC process was evaluated according to Eq. (2):

$$DE = \frac{Ash_{SOF} - (Ash_{Hydrochar,i} * MY_i)}{Ash_{SOF}} * 100\ [\%] \tag{2}$$

where Ash_{SOF} is the ash content of the stabilized organic fraction before the HTC treatment, $Ash_{Hydrochar,i}$ is the ash content of the hydrochar obtained from the HTC process regarding the i-th test. All measurements were conducted in triplicate and a mean value was reported. Furthermore, the specific surface area of the samples was examined with a BET analyzer (ASAP2460, Micromeritics, USA).

2.5. Preliminary tests and experimental design

Firstly, preliminary tests of HTC were conducted to understand the influence of the liquid substrate (landfill leachate and concentrate fraction) on the chemical properties of the hydrochar. The HTC was performed at different process temperatures (200, 250, and 270 °C) and residence times (1, 3, and 6 h), while the solid-to-liquid ratio was maintained at 1/10. Then, the effect of the hydrodynamic cavitation on the chemical characteristics of the hydrochar was evaluated by considering a temperature set point of 60°C. Response Surface Methodology (RSM) and Central Composite Face-Centered Design (CCF-CD) were used to examine any potential relationships between the hydrochar production parameters (temperature and residence time) and the impacts on the fixed carbon content, deashing, and mass yield. A three-level, 2-factor CCF-CD was employed. HTC process temperature (X_1) and residence time (X_2) were assumed as independent variables and coded at three levels (−1, 0, and +1), corresponding to the minimum, medium and maximum levels. Each process factor level was carefully selected based on preliminary tests. For the hydrochars, the chosen responses were fixed carbon content (Y_1), deashing efficiency (Y_2), and mass yield (Y_3) of the HTC process. The software Minitab v17.1.0 (Minitab Ltd., Coventry, UK) was used to implement the statistical model. The statistical significance of the regression coefficients was examined by using analysis of variance (ANOVA) and regression analysis. This was accomplished by using the Fisher's F-test at a 95% confidence level, following the methodology outlined by Buratti et al. (2018). Multi-response analysis, based on Derringer's desirability function, was used to concurrently optimize the response variables (Derringer and Suich, 1980). The desired response of FC content, DE, and MY was the maximum of the target goal. The same importance was assumed for each response during the optimization analysis.

The method is described more exhaustively by Barbanera et al. (2018). Three replications of experiments under optimum conditions were conducted to validate the optimized models by comparing the experimental data to the expected values.

3. Results and discussion

3.1. Characterization of preliminary tests

The characteristics of biomass before and after the HTC process in terms of proximate and ultimate analysis, mass yield, and deashing efficiency are shown in Table 2.

Preliminary results indicate that tests performed at 250°C and a residence time of 3 h with LL rather than CF produce hydrochar with improved characteristics. Dehydration, decarboxylation, hydrolysis, and condensation are the main reactions that occur during the hydrothermal carbonization process (Nawaz and Kumar, 2023; Wang et al., 2022a). The balance between these different reactions determines the carbon content of the resulting hydrochar. At moderate temperatures (250 °C) and residence times (3 hours), the HTC process primarily involves dehydration and decarboxylation reactions, which lead to an increase in the carbon content (Djandja et al., 2023), resulting in about +22% and 23% by using LL and CF respectively. However, as the reaction temperature and residence time increase (270°C and 6 hours), hydrolysis and condensation reactions become more prevalent, leading to a decrease in the carbon content (Danso-Boateng et al., 2022) of about –5% and –21% by using LL and CF respectively. Thus, at lower temperatures and residence times, the increase in carbon content due to dehydration and decarboxylation reactions outweighs the decrease due to hydrolysis and condensation reactions. However, at higher temperatures and longer residence times, the decrease in carbon content due to hydrolysis and condensation reactions outperforms the increase due to dehydration and decarboxylation reactions, resulting in a net decrease in carbon content. Furthermore, for both the hydrochar obtained with LL and CF the ash content increased first and then lightly decreased as the temperature and residence time increased. A similar trend was found in literature (Chen et al., 2021). The reason might be attributed to the decrease of the organic compounds while the ash increased with the increment of the reaction temperature and residence time from 220 °C and 1 hour to 250 °C and 3 hours. However, with the further increase of the HTC process parameters (270 °C and 6 hours), the degradation of organic components promotes the decomposition of inorganics into the liquid fraction. Thus, despite a higher carbon content (+14.15%), the HTC of SOF with concentrate fraction promotes the formation of ashes (+7.19%) in comparison to using landfill leachate. Furthermore, by using the CF the deashing efficiency of the process resulted in a reduction of –51.69%. Higher ash content in hydrochar reduces its porosity as the inorganic materials can fill up the pore spaces. Additionally, ash could also coat the surface of hydrochar particles and reduce their specific area available for reactions or adsorption (Masoumi and Dalai, 2020). Thus, the reduction in porosity and specific area of the produced hydrochar might be unsuitable for the application as an admixture for plaster production. For this reason, the hydrodynamic cavitation was performed only on the mixture of SOF and LL. The mixture cavitated at a temperature set point of 60 °C was submitted to the HTC at a process temperature of 250 °C and a residence time of 3 hours to evaluate the effect of the HC on the hydrochar properties. The characteristics of the hydrochars from the HTC process of the mixture of SOF and LL before and after undergoing HC are reported in Table 3.

The hydrodynamic cavitation performed at a temperature set point of 60°C showed significant advantages in terms of hydrochar properties. In detail, HC as pre-treatment of HTC provided higher disintegration and homogenization of the solid/liquid mixture leading to higher carbon and fixed carbon content (+11.37% and +33.68% respectively), lower ash formation (–12.33%) and upgraded DE (+63.91%), lending support for producing hydrochar with raised porosity.

3.2. Central composite face-centered design and analysis

The CCF-CD experimental design was established from the results of the preliminary analysis. In detail, the HTC process was performed by using the mixture of SOF and LL cavitated at a temperature set point of 60°C. The factors and their coded values are shown in Table 4. A total number of 13 tests were carried out, including 4 runs of factorial points, 4 runs of face-centered points, and 5 replicates at the central point useful to evaluate the pure error.

3.2.1. Elemental analysis of hydrochars

Table 5 displays the results of the proximate analysis of hydrochars from the CCF-CD experimental design. The trials were performed in random order for minimising the effects of unexpected variability on the observed responses. The changes in the elemental composition of raw SOF and the obtained hydrochars are also given in the Van Krevelen diagram (Fig. 1), which is a plot of the atomic H/C ratio versus the atomic O/C ratio. The hydrochars had significantly lower H/C and O/C atomic ratios than the raw SOF. This mainly results from the dehydration and decar-boxylation reactions occurring during HTC (Si et al., 2023; Venna et al., 2021). The dehydration and decarboxylation reactions, which reduce the amount of H and O elements and increase the presence of C, were caused by the rise in HTC temperature (Budiman et al., 2022).

Table 2. Characteristics of raw SOF and hydrochars from preliminary tests

Liquid substrate		***LL***	***CF***	***LL***	***CF***	***LL***	***CF***
HTC temperature [°C]		200	200	250	250	270	270
Residence time [h]		1	1	3	3	6	6
Ultimate analysis [wt%$_{daf}$]							
	Raw SOF						
C	22.40	23.60	22.60	30.40	29.20	28.97	24.12
H	3.20	4.42	2.87	2.79	2.36	1.87	2.42
N	1.37	0.88	0.83	1.17	1.27	1.67	1.84
O	17.80	23.56	17.55	11.79	9.15	12.82	14.05
Proximate analysis [wt%$_{db}$]							
Ash	55.82	47.54	56.15	53.85	58.02	47.54	57.57
VM	41.79	46.77	36.73	41.72	36.82	46.77	39.38
FC	2.39	5.69	7.12	4.43	5.16	5.69	3.05
DE [%]	-	38.04	11.32	24.48	16.14	28.45	22.11
MY [%]	-	72.75	88.16	78.28	80.68	72.28	74.72

Note: db: dry basis; daf: dry and ash-free bases

Table 3. Proximate and ultimate analysis of hydrochars before and after HC

Mixture	***Not cavitated***	***Cavitated***
HTC temperature [°C]	250	250
Residence time [h]	3	3
Ultimate analysis [wt%$_{daf}$]		
C	30.40	34.3
H	2.79	3.77
N	1.17	1.44
O	11.79	12.55
Proximate analysis [wt%$_{db}$]		
Ash	53.85	47.94
VM	41.72	45.86
FC	4.43	6.68
DE [%]	24.48	67.86
MY [%]	78.28	37.45

Note: db: dry basis; daf: dry and ash-free bases

Table 4. Independent process variables, range values, and coded levels in experimental design

Independent variables	***Symbols***	***Coded levels***		
		–1	***0***	***1***
HTC temperature [°C]	X_1	220	250	280
Residence time [h]	X_2	1.5	3	4.5

Table 5. Ultimate analysis of hydrochars from CCF-CD experimental design

Run order	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***	***11***	***12***	***13***
X_1 [°C]	250	250	250	220	250	250	280	220	220	250	280	250	280
X_2 [h]	1.5	3	4.5	3	3	3	4.5	1.5	4.5	3	1.5	3	3
Ultimate analysis [wt%$_{daf}$]													
C	34.70	36.60	37.68	30.13	34.40	35.00	35.13	30.43	33.40	33.20	34.18	33.00	34.85
H	4.03	3.98	4.11	3.61	3.68	4.13	3.48	3.81	3.93	3.67	3.45	3.83	3.40
N	1.32	1.38	1.75	1.04	1.50	1.46	1.24	0.89	0.98	0.89	1.28	1.52	1.15
O	14.19	10.15	12.38	17.58	11.41	12.53	7.76	21.03	15.28	11.65	10.67	12.93	9.70

Note: db: dry basis; daf: dry and ash-free bases

Likewise, the increase in residence time only influenced the O/C ratios, which decreased. While dehydration and decarboxylation are the predominant reaction pathways, demethanation has a negligible influence on the HTC process.

3.2.2. BET analysis of hydrochars

As shown in Fig. 2, the specific surface area of all hydrochars was larger than that of the raw SOF. As the HTC temperature increased from 220 °C to 250 °C, the surface area gradually increased. This might be due to the release of gases from the decomposition of unstable components and the removal of VM during the hydrothermal process, resulting in the formation of open pores and cracks on the surface of the hydrochar (Fu et al., 2022; Wu et al., 2023; Yang et al., 2023).

However, at higher HTC temperatures and long residence times, the surface area decreased, which might be due to the secondary polymerization of soluble intermediates produced during the hydrolysis phase led to the blocking of pores (Magdziarz et al., 2021; Xu et al., 2013; Yang et al., 2023). Even though the values for the surface area were generally low for raw SOF and hydrochars produced at all conditions, ranging from around 7 to 12 m^2/g, they are consistent with previous studies on biomass-derived hydrochars. Low surface area values for hydrochars derived from municipal solid waste, sewage sludge, livestock manure, spent coffee grounds, and macroalgae, have been reported in the literature (Fu et al., 2022; Mlonka-Mędrala et al., 2022; Venkatesan et al., 2022; Wilk et al., 2023; Xu et al., 2013; Yang et al., 2023). Nevertheless, the combination of thermal and chemical or physical activation might explain the surface area increase (Jais et al., 2021; Ogungbenro et al., 2017; Zhang et al., 2021).

3.3. Effect of independent variables

The proximate analysis of hydrochars from the CCF-CD experimental design, together with their respective experimental responses are listed in Table 6. By applying multiple regression analysis to the experimental data, the relationship between the response variables, fixed carbon content (Y_1), deashing efficiency (Y_2), and mass yield (Y_3) of the HTC process, and the input variables, HTC process temperature (X_1) and residence time (X_2), was expressed by second-order polynomial equations with interaction terms. The final models generated in coded factors are shown as described by Eqs. (3-5).

$$Y_1 = -99.18 + 0.8427X_1 + 1.263X_2 - 0.001743X_1X_1 - 0.4149X_2X_2 + 0.00550X_1X_2 \tag{3}$$

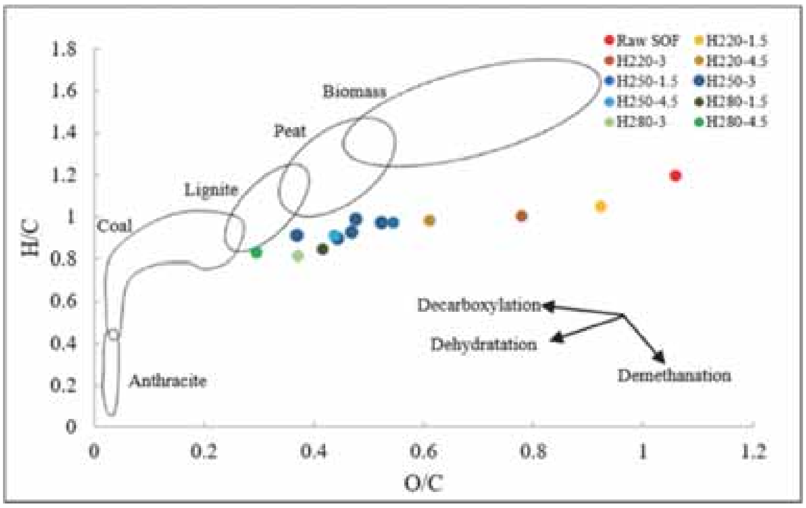


Fig. 1. Van Krevelen diagram for hydrochars under different conditions

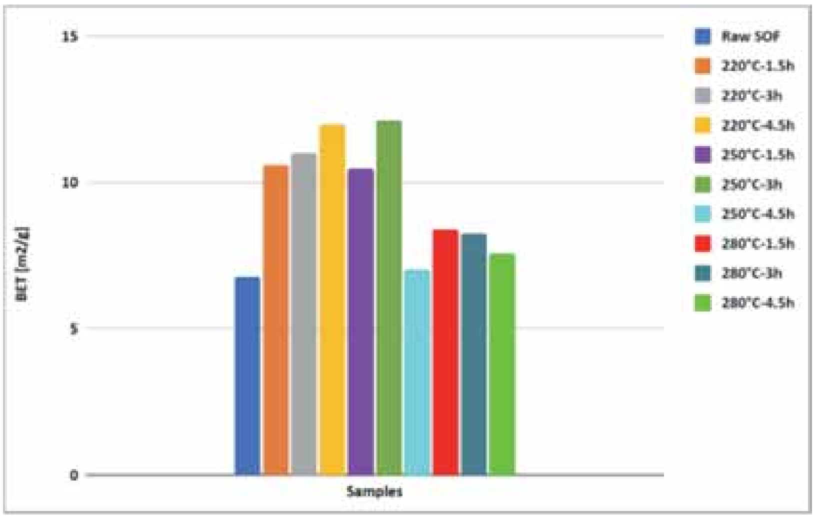


Fig. 2. BET surface area of the hydrochars from CCF-CD experimental design

$$Y_2 = -1635.0 + 13.376X_1 + 3.76\,X_2 - 0.026446X_1X_1 - 0.534X_2X_2 + 0.0058X_1X_2 \quad (4)$$

$$Y_3 = 1939.2 - 14.675X_1 - 15.60X_2 + 0.02866X_1X_1 + 1.723X_2X_2 + 0.0093X_1X_2 \quad (5)$$

Analysis of variance (ANOVA) was performed for the adequacy and fitness of predicted models and the results are presented in Table 7. The calculated F-values of 70.97, 197.38, and 182.08 for Y_1, Y_2, and Y_3 respectively, demonstrated that the regression models are highly significant ($p < 0.0001$).

There is only a 0.01% chance that these large F-values could occur due to noise, confirming the validity of the predicted model. Furthermore, the adequacy of the model was analyzed by the evaluation of the determination coefficient ($R^2 > 0.95$) and the lack of fit (LOF) test. An R^2 value of 0.9807, 0.9930, and 0.9924 for Y_1, Y_2, and Y_3 respectively, ensured that only 1.93%, 0.7%, and 0.76% of the total variations are not explained by the regression models, validating the precision of the deduced models. Moreover, the values of R^2_{adj} (0.9668, 0.9879, 0.9869) were very high and in reasonable agreement with the R^2 values, confirming that the regression models were highly significant.

The acceptability of the quadratic models was also verified by the lack of fit (LOF) test. A p-value higher than 0.05 means that LOF is insignificant due to relative pure error. Thus, the lack of fit p-values (0.265, 0.093, and 0.120 for each model) confirms that the models can be effectively employed for the prediction.

3.3.1. *Effect on fixed carbon content*

The influence of the independent variables on the responses and their interactions were evaluated by plotting response surface graphs and contour plots. Fig. 3 shows the effects of process temperature and residence time on fixed carbon content. The FC content increased with the increase in process temperature from 220 to 250°C and then decreased at the higher process temperature of 280°C.

Table 6. Proximate analysis of hydrochars from CCF-CD experimental design

Run order	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***	***11***	***12***	***13***
X_1 [°C]	250	250	250	220	250	250	280	220	220	250	280	250	280
X_2 [h]	1.5	3	4.5	3	3	3	4.5	1.5	4.5	3	1.5	3	3
Proximate analysis [wt%$_{db}$]													
Ash	45.76	47.89	44.09	47.64	49.01	46.88	52.39	43.84	46.41	50.58	50.44	48.71	50.90
VM	48.78	45.59	50.08	46.95	44.12	46.17	43.13	51.47	48.91	42.60	46.06	44.34	44.49
FC (Y_1)	5.46	6.52	5.83	5.41	6.87	6.95	4.48	4.69	4.68	6.82	3.50	6.95	4.61
DE (Y_2) [%]	60.45	67.51	70.17	37.86	65.63	67.98	49.78	35.10	38.77	67.68	45.06	66.88	47.56
MY (Y_3) [%]	47.73	37.47	37.37	72.04	38.73	37.72	52.94	81.76	72.87	35.29	60.16	37.55	56.90

Note: db: dry basis; daf: dry and ash-free bases

Table 7. ANOVA of response surface quadratic models

Source	***DF***	***F-Value***	***Prob > F***
Fixed carbon content			
Model	5	70.97	< 0.0001
X_1	1	18.06	0.004
X_2	1	6.76	0.035
X_1X_1	1	153.47	< 0.0001
X_2X_2	1	54.36	< 0.0001
X_1X_2	1	5.53	0.051
Lack-of-Fit	3	1.94	0.265
$R^2 = 0.9807$; $R^2_{adj} = 0.9668$			
Deashing efficiency			
Model	5	197.38	< 0.0001
X_1	1	73.08	< 0.0001
X_2	1	25.48	0.001
X_1X_1	1	729.38	< 0.0001
X_2X_2	1	1.86	0.215
X_1X_2	1	0.13	0.731
Lack-of-Fit	3	4.42	0.093
$R^2 = 0.9930$; $R^2_{adj} = 0.9879$			
Mass yield			
Model	5	182.08	< 0.0001
X_1	1	157.31	< 0.0001
X_2	1	34.32	0.001
X_1X_1	1	540.20	< 0.0001
X_2X_2	1	12.20	0.010
X_1X_2	1	0.20	0.664
Lack-of-Fit	3	3.68	0.120
$R^2 = 0.9924$; $R^2_{adj} = 0.9869$			

This result is in agreement with previous studies (Zhang et al., 2016). Moreover, according to the F-values and p-values of Table 7, it can be noted that for the FC content X_1, X_2, X_1X_1, and X_2X_2 are significant model terms because their p-values were higher than 0.05. From the F-values, the process temperature (X_1) had a slightly greater effect on the FC content rather than residence time (X_2). Therefore, the positive signs of X_1 and X_2 in the Eq. (3) indicate synergistic effects on the FC. However, the negative signs of X_1X_1 and X_2X_2 provide antagonistic effects on the response which make the FC increase up to a certain threshold with increasing HTC temperature and residence time after which it decreases.

3.3.2. Effect on dashing efficiency

A similar trend obtained for the FC was found for the deashing efficiency (Fig. 4). The proximate analysis of Table 6 shows that the DE increased from 35.10% up to 70.17% with the increase of process temperature and residence time from 220°C and 1.5h to 250°C and 4.5h and then decreasing up to 45.06% at 280°C and 1.5h. Similar findings were observed in literature studies (Mohammed et al., 2020; Nakason et al., 2018; Tahmid Islam et al., 2023). This was expected to be due to the fact that the ash can be leached into the liquid fraction during HTC and its increase may be caused by the condensation and reprecipitation of some inorganics on the hydrochar surface after a long residence time at high temperatures. Furthermore, the F-values and p-values of Table 7 highlighted how X_1, X_2, and X_1X_1 are significant model terms. Likewise, for FC content, the F-values of process temperature (X_1) had a slightly greater effect on the DE rather than residence time (X_2), while the quadratic effect of process temperature (X_1X_1) showed a higher impact. However, an important result from the ANOVA analysis is that the residence time had no significant quadratic and interactive effects on the dashing efficiency.

3.3.3. Effect on mass yield

The effect of the independent variables on hydrochars mass yield is shown in Fig. 5. By considering each process temperature, the increase in residence time determined a slight decrease in MY. On the other hand, the hydrochar yield decreased by a mean of 46% points from 220°C to 250°C and increased again by a mean of 40% points from 250°C to 280°C. The decrease in the yield as a function of temperature and residence time might be due to the higher carbonization degree, which led to a higher degree of material decomposition, fragmentation, and solubilization (Melo et al., 2017; Roslan et al., 2023; Wilk et al., 2023). Furthermore, by raising the HTC temperature from 250°C to 280°C the formation of secondary char by polymerization reactions of small molecules in the liquid phase and recondensation into the char phase made the mass yield increase (Surup et al., 2020).

The influence of the independent variables is confirmed by the ANOVA analysis, as reported in Table 7. All linear and quadratic terms were significant. In detail, having the highest F-value for both linear and quadratic coefficients, the process temperature affected most significantly the MY and might be considered the main controlling factor of the HTC process. Furthermore, the positive coefficients of the quadratic terms X_1X_1 and X_2X_2 denoted that there is a possible point of deflexion after which the independent variables have a negative or positive effect on the MY.

3.4. Determination and validation of optimum conditions

Since the aim of this work is the preliminary investigation of the possible use of hydrochar as an admixture for the production of a sustainable plaster as carbon-capture, thermal insulation, moisture absorption, and acoustic insulation material, the FC, DE, and MY were chosen as response variables to obtain the optimum HTC process conditions at which they are maximized. By using hydrochar as an admixture, plasters and other building materials might benefit from its low thermal conductivity, high surface area, and porous nature.

These properties work together to enhance the plaster thermal insulation by disrupting the thermal bridging, rendering the heat propagation routes multi-directional and hindering the effect of unidirectional heat propagation, thus reducing the propagation of heat flow (Cuthbertson et al., 2019; Zhang et al., 2022).

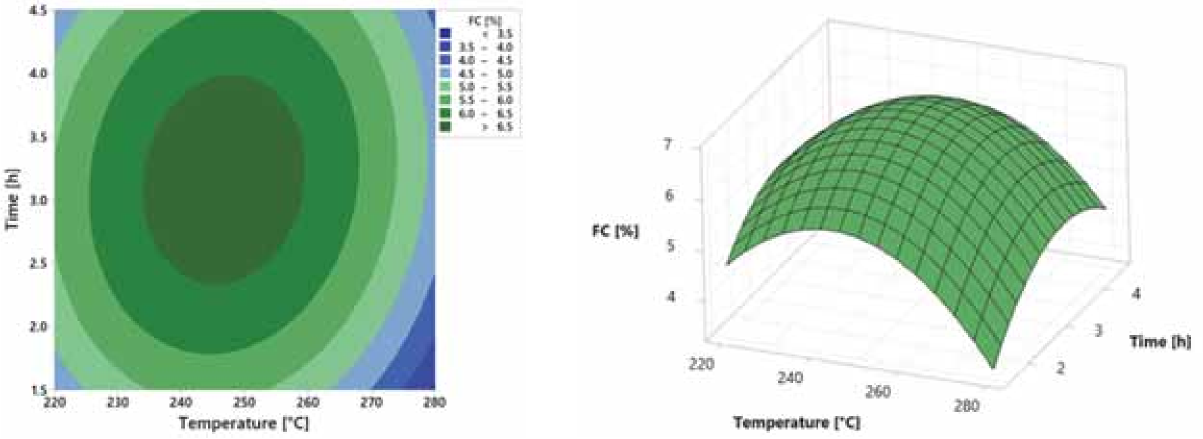


Fig. 3. Contour and surface plots of the fixed carbon content vs the independent variables (temperature and time)

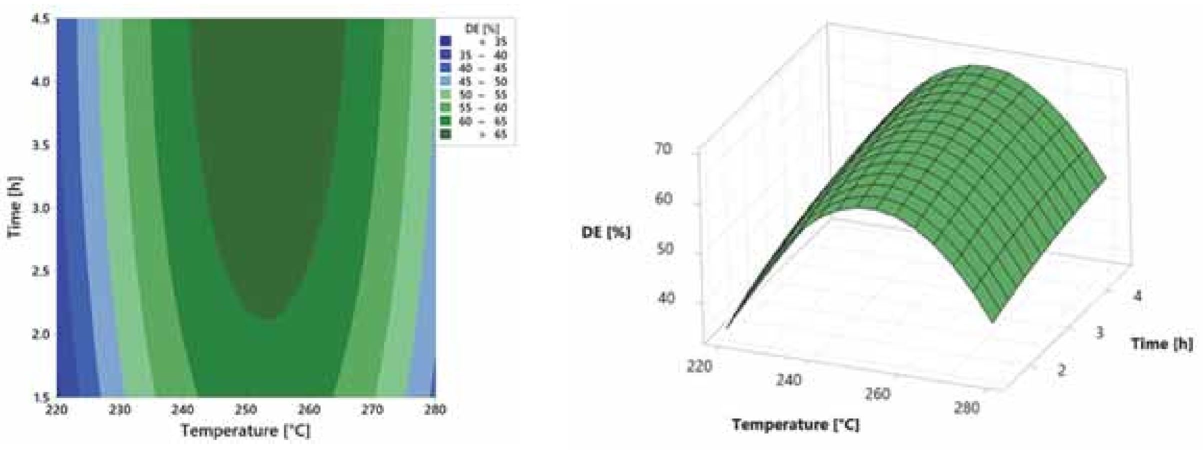


Fig. 4. Contour and surface plots of deashing efficiency vs the independent variables (temperature and time)

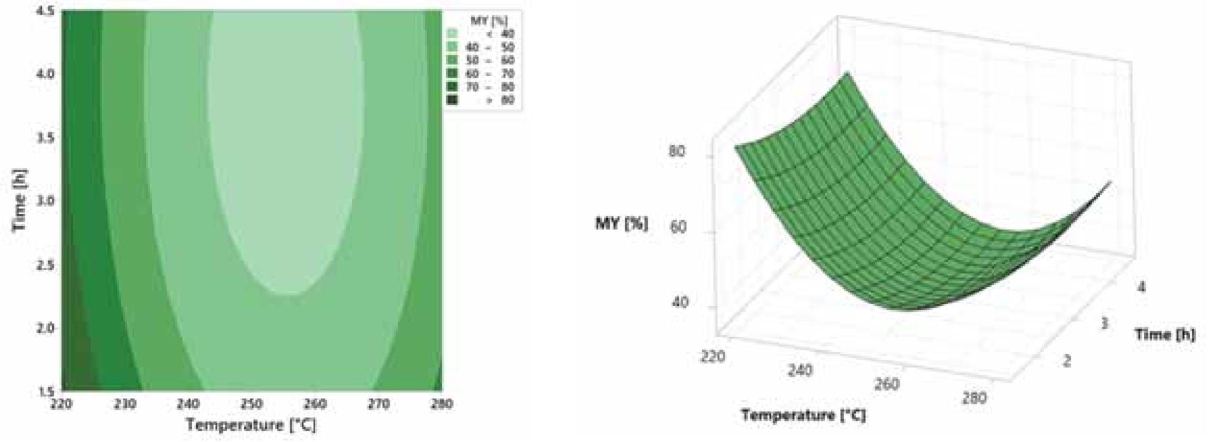


Fig. 5. Contour and surface plots of mass yield vs. the independent variables (temperature and time)

Additionally, hydrochar could increase the ability of the plaster to absorb sound, as sound waves would disperse and converted into heat through refraction within the increased porosity and interconnected pore networks of the admixture (Mota-Panizio et al., 2023; Rojas et al., 2019). Furthermore, a high surface area is favorable for the formation of a suitable pore structure for CO_2 uptake, which is subsequently mineralized into stable carbonates after being released into the plaster matrix, and moisture adsorption, which can help to regulate the relative humidity (Cuthbertson et al., 2019; Deepak et al., 2023; Gupta et al., 2022; Roychand et al., 2023; Zhang et al., 2022). These considerations are strictly related to the chosen response variables. The high ash content in the SOF may clog the pores, resulting in a decrease in specific surface area during the hydrothermal carbonization process (Gao et al., 2022). On the other hand, with the increase of FC the surface area of hydrochar generally shows a regular increase (Kahandawa Arachchi et al., 2021; Tu et al., 2021). This is because of the dehydration, decarboxylation, and devolatilization reactions, which increase the carbon content and open these clogged pores (Wang et al., 2022b). Furthermore, a higher MY could lead to greater efficiency in the production process, reducing production costs and increasing the economic viability of hydrochar in large-scale industrial production (Hussin et al., 2023; Yao et al., 2023). Thus, the deashing effect of the HTC process, the fixed carbon and the mass yield, should be maximised to enhance the characteristics of the plaster. However, the optimization of all responses under the same operative conditions is difficult because their intervals of variation are different. For this reason, the multi-response optimization was carried out by the desirability function approach. Composite desirability evaluates how the settings optimize a set of responses overall (Barbanera et al., 2021). In this study, equal weightage was given for all responses (FC, DE and MY) and an importance parameter equal to 1 were assumed. As can be noted in Fig. 6 the composite desirability (D) of the optimization was 56.87%, indicating that it is challenging to optimize all the response variables simultaneously. In particular, the maximum fixed carbon content, deashing efficiency and mass yield was found to be 6.34%, 54.73% and 53.81% respectively at an optimal parametric combination of a process temperature of 232°C and a residence time of 2.65h.

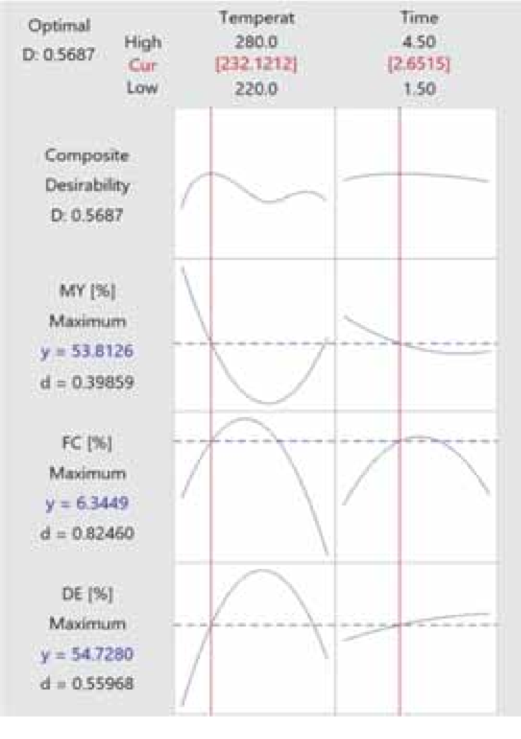


Fig. 6. Optimization plots of the operating variables

To consolidate the results of the model, a hydrothermal carbonization treatment of the cavitated mixture of SOF and LL was performed under the optimized conditions. Experiments were performed in triplicate and the values of the response variables are reported in Table 8. Results confirm the suitability of the developed quadratic models because the experimental findings are in close agreement with the predicted values within a < 3% error (Table 8).

Table 8. Physicochemical characterization of hydrochar and response variables at the optimal HTC conditions

Analysis	*Measured*	*Predicted*	*Deviation [%]*
FC (Y_1) [%]	6.17	6.34	–2.64
DE (Y_2) [%]	53.87	54.73	–1.58
MY (Y_3) [%]	54.26	53.81	0.84

Note: db: dry basis; daf: dry and ash-free bases

4. Conclusions

In this work, the hydrothermal carbonization of the stabilized organic fraction of municipal solid waste was performed at several process conditions by using landfill leachate as a liquid substrate. Also, the hydrodynamic cavitation was confirmed as a valid pretreatment to enhance both the homogenization of the slurry, avoiding incurring pumpability problems at an industrial scale, and the hydrochar characteristics. Furthermore, the Central Composite Face-Centered Design together with the Response Surface Model proved to be very useful in determining the influence of independent variables (process temperature and residence time) on the response variables (FC, DE, and MY), thus the optimal conditions for the HTC process of the cavitated mixture of SOF and LL. In detail, HTC temperature has the most influence on the physicochemical properties of hydrochar while the effects of residence time are less significant.

However, analysis of variance showed high R^2 values, indicating a good fit of the regression models to the experimental data. The optimum conditions for the HTC process found at 232°C and 2.65 h resulted in a fixed carbon content of 6.17%, a deashing efficiency of 53.87%, and a mass yield of 54.26%. Under the optimized conditions obtained from Derringer's desired function methodology, the experimental values are in close agreement with the predicted ones.

Acknowledgements

The authors would like to acknowledge the project ECOPLASTER (J83C22000290001)- Biostabilized for Ecosustainable Building - funded by the Ministry of Environment and Energetic Security. This research was supported by the project ECS00000024 "Ecosistemi dell'Innovazione" - Rome Technopole of the Italian Ministry of University and Research, public call n. 3277, PNRR—Mission 4, Component 2, Investment 1.5, financed by the European Union, Next GenerationEU.

References

Barbanera M., Cardarelli A., Carota E., Castellini M., Giannoni T., Ubertini S., (2021), Valorization of winery and distillery by-products by hydrothermal carbonization, *Scientific Reports*, **11**, 23973, https://doi.org/10.1038/s41598-021-03501-7.

Barbanera M., Pelosi C., Taddei A.R., Cotana F., (2018), Optimization of bio-oil production from solid digestate by microwave-assisted liquefaction, *Energy Conversion and Management*, **171**, 1263-1272.

Basso D., Weiss-Hortala E., Patuzzi F., Castello D., Baratieri M., Fiori L., (2015), Hydrothermal carbonization of off-specification compost: A byproduct of the organic municipal solid waste treatment, *Bioresource Technology*, **182**, 217-224.

Başakçılardan Kabakcı S., Baran S.S., (2019), Hydrothermal carbonization of various lignocellulosics: Fuel characteristics of hydrochars and surface characteristics of activated hydrochars, Waste Management, **100**, 259-268.

Budiman I., Subyakto Syafitri U.D., Widyaningrum B.A., Marlina R., Triastuti, Widodo E., (2022), Characteristics optimization of empty fruit bunches chars using central composite design, *Biomass Conversion and Biorefinery*, https://doi.org/10.1007/s13399-022-02892-5.

Buratti C., Barbanera M., Lascaro E., Cotana F., (2018), Optimization of torrefaction conditions of coffee industry residues using desirability function approach, *Waste Management*, **73**, 523-534.

Castro J.D.S., Assemany P.P., Carneiro A.C.D.O., Ferreira J., De Jesus Junior M.M., Rodrigues F.D.A., Calijuri M.L., (2021), Hydrothermal carbonization of microalgae biomass produced in agro-industrial effluent: Products, characterization and applications, *Science of The Total Environment*, **768**, 144480, https://doi.org/10.1016/j.scitotenv.2020.144480

Cavali M., Libardi Junior N., Mohedano R.D.A., Belli Filho P., Da Costa R.H.R., De Castilhos Junior A.B., (2022), Biochar and hydrochar in the context of anaerobic digestion for a circular approach: An overview, *Science of the Total Environment*, **822**, 153614, https://doi.org/10.1016/j.scitotenv.2022.153614

Chen C., Liang W., Fan F., Wang C., (2021), The effect of temperature on the properties of hydrochars obtained by hydrothermal carbonization of waste Camellia oleifera shells, *ACS Omega*, **6**, 16546–16552.

Cuthbertson D., Berardi U., Briens C., Berruti F., (2019), Biochar from residual biomass as a concrete filler for improved thermal and acoustic properties, *Biomass and Bioenergy*, **120**, 77–83.

Danso-Boateng E., Ross A.B., Mariner T., Hammerton J., Fitzsimmons M., (2022), Hydrochars produced by hydrothermal carbonisation of seaweed, coconut shell and oak: Effect of processing temperature on physicochemical adsorbent characteristics, *SN Applied Sciences*, **4**, 203, https://doi.org/10.1007/s42452-022-05085-x

Deepak K.R., Mohan S., Dinesha P., Balasubramanian R., (2023), CO_2 uptake by activated hydrochar derived from orange peel (Citrus reticulata): Influence of carbonization temperature, *Journal of Environmental Management*, **342**, 118350, https://doi.org/10.1016/j.jenvman.2023.118350

Derringer G., Suich R., (1980), Simultaneous Optimization of Several Response Variables, *Journal of Quality Technology*, **12**, 214-219.

Djandja O.S., Liew R.K., Liu C., Liang J., Yuan H., He W., Feng Y., Lougou B.G., Duan P.-G., Lu X., Kang S., (2023), Catalytic hydrothermal carbonization of wet organic solid waste: A review, *Science of the Total Environment*, **873**, 162119, https://doi.org/10.1016/j.scitotenv.2023.162119

Ercan B., Alper K., Ucar S., Karagoz S., (2023), Comparative studies of hydrochars and biochars produced from lignocellulosic biomass via hydrothermal carbonization, torrefaction and pyrolysis. *Journal of the Energy Institute*, **109**, 101298, https://doi.org/10.1016/j.joei.2023.101298

Eurostat, (2023), Overview – Waste - Eurostat, On line at: Https://ec.europa.eu/eurostat/web/waste

Fu H., Wang B., Wang H., Liu H., Xie H., Han L., Wang N., Sun X., Feng Y., Xue L., (2022), Assessment of livestock manure-derived hydrochar as cleaner products: Insights into basic properties, nutrient composition, and heavy metal content, *Journal of Cleaner Production*, **330**, 129820, https://doi.org/10.1016/j.jclepro.2021.129820

Gao Q., Ni L., He Y., Hou Y., Hu W., Liu Z., (2022), Effect of hydrothermal pretreatment on deashing and pyrolysis characteristics of bamboo shoot shells, *Energy*, 247, 123510, https://doi.org/10.1016/j.energy.2022.123510

González-Arias J., De La Rubia M.A., Sánchez M.E., Gómez X., Cara-Jiménez J., Martínez E.J., (2023), Treatment of hydrothermal carbonization process water by electrochemical oxidation: Assessment of process performance, *Environmental Research*, **216**, 114773, https://doi.org/10.1016/j.envres.2022.114773

Gupta S., Kua H.W., (2017), Factors determining the potential of biochar as a carbon capturing and sequestering construction material: critical review, *Journal of Materials in Civil Engineering*, **29**, 04017086, https://doi.org/10.1061/(ASCE)MT.1943-5533.0001924.

Gupta S., Kashani A., Mahmood A.H., (2022), Carbon sequestration in engineered lightweight foamed mortar – Effect on rheology, mechanical and durability properties, *Construction and Building Materials*, **322**, 126383, https://doi.org/10.1016/j.conbuildmat.2022.126383

Hussin F., Hazani N.N., Khalil M., Aroua M.K., (2023), Environmental life cycle assessment of biomass conversion using hydrothermal technology: A review, *Fuel Processing Technology*, **246**, 107747, https://doi.org/10.1016/j.fuproc.2023.107747

Ischia G., Fiori L., Gao L., Goldfarb J.L., (2021), Valorizing municipal solid waste via integrating hydrothermal carbonization and downstream extraction for biofuel production, *Journal of Cleaner Production*, **289**, 125781, https://doi.org/10.1016/j.jclepro.2021.125781.

Ipiales R.P., de la Rubia M.A., Diaz E., Mohedano A.F., Rodriguez J.J., (2021), Integration of hydrothermal carbonization and anaerobic digestion for energy recovery of biomass waste: An overview, *Energy Fuels*, **35**, 17032-17050.

ISPRA, (2022), Municipal Waste Report 2022 Edition (in Italian), On line at: Https://www.isprambiente.gov.it/it/pubblicazioni/rapporti/rapporto-rifiuti-urbani-edizione-2022

Jabeen S., Gao X., Hayashi J., Altarawneh M., Dlugogorski B.Z., (2023), Effects of product recovery methods on the yields and properties of hydrochars from hydrothermal carbonization of algal biomass, *Fuel*, **332**, 126029, https://doi.org/10.1016/j.fuel.2022.126029

Jais F.M., Chee C.Y., Ismail Z., Ibrahim S., (2021), Experimental design via NaOH activation process and statistical analysis for activated sugarcane bagasse hydrochar for removal of dye and antibiotic, *Journal of Environmental Chemical Engineering*, **9**, 104829, https://doi.org/10.1016/j.jece.2020.104829

Kahandawa Arachchi K.A.D.Y.T., Selvaratnam A., Gamage J.C.P.H., De Silva G.I.P., (2021), Green composite plaster with modified morphology for enhanced thermal comfort in buildings, *Case Studies in Construction Materials*, **15**, e00611, https://doi.org/10.1016/j.cscm.2021.e00611.

Khan T.A., Saud A.S., Jamari S.S., Rahim M.H.A., Park J.-W., Kim H.-J., (2019), Hydrothermal carbonization of lignocellulosic biomass for carbon rich material preparation: A review, *Biomass and Bioenergy*, **130**, 105384, https://doi.org/10.1016/j.biombioe.2019.105384

Lanfranchi A., Tassinato G., Valentino F., Martinez G.A., Jones E., Gioia C., Bertin L., Cavinato C., (2022), Hydrodynamic cavitation pre-treatment of urban waste: Integration with acidogenic fermentation, PHAs synthesis and anaerobic digestion processes, *Chemosphere*, **301**, 134624, https://doi.org/10.1016/j.chemosphere.2022.134624.

Langone M., Dasso D., (2020), Process waters from hydrothermal carbonization of sludge: characteristics and possible valorization pathways, International *Journal of Environmental Research and Public Health*, **17**, 6618, https://doi.org/10.3390/ijerph17186618

Libra J.A., Ro K.S., Kammann C., Funke A., Berge N.D., Neubauer Y., Titirici M.-M., Fühner C., Bens O., Kern J., Emmerich K.-H., (2011), Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis, *Biofuels*, **2**, 89-124.

Luo X., Huang Z., Lin J., Li X., Qiu J., Liu J., Mao X., (2020), Hydrothermal carbonization of sewage sludge and in-situ preparation of hydrochar/MgAl-layered double hydroxides composites for adsorption of Pb(II), *Journal of Cleaner Production*, **258**, 120991, https://doi.org/10.1016/j.jclepro.2020.120991

Magdziarz A., Mlonka-Mędrala A., Sieradzka M., Aragon-Briceño C., Pożarlik A., Bramer E.A., Brem G., Niedzwiecki L., Pawlak-Kruczek H., (2021), Multiphase analysis of hydrochars obtained by anaerobic digestion of municipal solid waste organic fraction, *Renewable Energy,* **175**, 108-118.

Masoumi S., Dalai A.K., (2020), Optimized production and characterization of highly porous activated carbon from algal-derived hydrochar, *Journal of Cleaner Production*, **263**, 121427, https://doi.org/10.1016/j.jclepro.2020.121427.

Melo C.A., Junior F.H.S., Bisinoti M.C., Moreira A.B., Ferreira O.P., (2017), Transforming sugarcane bagasse and vinasse wastes into hydrochar in the presence of phosphoric acid: an evaluation of nutrient contents and structural properties, *Waste and Biomass Valorization*, **8**, 1139-1151.

Mendecka B., Lombardi L., Micali F., De Risi A., (2020), Energy recovery from olive pomace by hydrothermal carbonization on hypothetical industrial scale: A LCA perspective, *Waste and Biomass Valorization*, **11**, 5503–5519.

Mlonka-Mędrala M., Sieradzka M., Magdziarz A., (2022), Thermal upgrading of hydrochar from anaerobic digestion of municipal solid waste organic fraction, *Fuel,* **324**, 124435, https://doi.org/10.1016/j.fuel.2022.124435

Mohammadi, A., Venkatesh, G., Sandberg, M., Eskandari, S., Joseph, S., & Granström, K. (2020). A comprehensive environmental Life Cycle Assessment of the use of hydrochar pellets in combined heat and power plants, *Sustainability*, **12**, 9026, https://doi.org/10.3390/su12219026

Mohammed I.S., Na R., Kushima K., Shimizu N., (2020), Investigating the effect of processing parameters on the products of hydrothermal carbonization of corn stover, *Sustainability*, **12**, 5100, https://doi.org/10.3390/su12125100.

Mota-Panizio R., Carmo-Calado L., Assis A.C., Matos V., Hermoso-Orzáez M.J., Romano P., Gonçalves M., Brito P., (2023), Properties and uses of biochars incorporated into mortars, *Environments*, **10**, 47, https://doi.org/10.3390/environments10030047

Mrad R., Chehab G., (2019), Mechanical and microstructure properties of biochar-based mortar: an internal curing agent for PCC, *Sustainability*, **11**, 2491, https://doi.org/10.3390/su11092491.

Nagarajan S., Ranade V.V., (2021), Valorizing Waste Biomass via Hydrodynamic Cavitation and Anaerobic Digestion, *Industrial and Engineering Chemistry Research*, **60**, 16577-16598.

Nakason K., Panyapinyopol B., Kanokkantapong V., Viriya-empikul N., Kraithong W., Pavasant P., (2018), Characteristics of hydrochar and liquid fraction from hydrothermal carbonization of cassava rhizome, *Journal of the Energy Institute*, **91**, 184-193.

Navaratnam S., Wijaya H., Rajeev P., Mendis P., Nguyen K., (2021), Residual stress-strain relationship for the biochar-based mortar after exposure to elevated temperature, *Case Studies in Construction Materials*, **14**, e00540, https://doi.org/10.1016/j.cscm.2021.e00540.

Nawaz A., Kumar P., (2023), Impact of temperature severity on hydrothermal carbonization: Fuel properties, kinetic and thermodynamic parameters, *Fuel*, 336, 127166, https://doi.org/10.1016/j.fuel.2022.127166

Naveen B.P., Mahapatra D.M., Sitharam T.G., Sivapullaiah P.V., Ramachandra T.V., (2017), Physico-chemical and biological characterization of urban municipal landfill leachate, *Environmental Pollution*, **220**, 1-12.

Ogungbenro A.E., Quang D.V., Al-Ali K., Abu-Zahra M.R.M., (2017), Activated carbon from date seeds for CO_2 capture applications, *Energy Procedia*, 114, 2313-2321.

Periyavaram S.R., Uppala L., Sivaprakash S., Reddy P.H.P., (2023), Thermal behaviour of hydrochar derived from hydrothermal carbonization of food waste using leachate as moisture source: Kinetic and thermodynamic analysis, *Bioresource Technology*, **373**, 128734, https://doi.org/10.1016/j.biortech.2023.128734.

Rojas C., Cea M., Iriarte A., Valdes G., Navia R., Cardenas-R, J.P., (2019), Thermal insulation materials based on agricultural residual wheat straw and corn husk biomass, for application in sustainable buildings, *Sustainable Materials and Technologies*, **20**, e00102, https://doi.org/10.1016/j.susmat.2019.e00102

Roman F.F., Diaz de Tuesta J.L., Praça P., Silva A.M.T., Faria J.L., Gomes H.T., (2021), Hydrochars from compost derived from municipal solid waste: Production process optimization and catalytic applications, *Journal of Environmental Chemical Engineering*, **9**, 104888, https://doi.org/10.1016/j.jece.2020.104888

Roslan S.Z., Zainudin S.F., Mohd Aris A., Chin K.B., Musa M., Mohamad Daud A.R., Syed Hassan S.S.A., (2023), Hydrothermal carbonization of sewage sludge into solid biofuel: influences of process conditions on the energetic properties of hydrochar, *Energies*, **16**, 2483, https://doi.org/10.3390/en16052483.

Roychand R., Li J., Kilmartin-Lynch S., Saberian M., Zhu J., Youssf O., Ngo T., (2023), Carbon sequestration from waste and carbon dioxide mineralisation in concrete – A stronger, sustainable and eco-friendly solution to support circular economy, *Construction and Building Materials*, **379**, 131221, https://doi.org/10.1016/j.conbuildmat.2023.131221

Sharma H.B., Sarmah A.K., Dubey B., (2020), Hydrothermal carbonization of renewable waste biomass for solid biofuel production: A discussion on process mechanism, the influence of process parameters, environmental performance and fuel properties of hydrochar, *Renewable and Sustainable Energy Reviews*, **123**, 109761, https://doi.org/10.1016/j.rser.2020.109761

Si H., Zhao C., Wang B., Liang X., Gao M., Jiang Z., Yu H., Yang Y., Gu Z., Ogino K., Chen X., (2023), Liquid-solid ratio during hydrothermal carbonization affects hydrochar application potential in soil: Based on characteristics comparison and economic benefit analysis, *Journal of Environmental Management,* **335**, 117567, https://doi.org/10.1016/j.jenvman.2023.117567

Śliz M., Tuci F., Czerwińska K., Fabrizi S., Lombardi L., Wilk M., (2022), Hydrothermal carbonization of the wet fraction from mixed municipal solid waste: Hydrochar characteristics and energy balance, *Waste Management*, **151**, 39-48.

Soldo Cavitators, (2023), Emulsification with Soldo Cavitators Technology, On line at: Https://soldocavitators.com/omogeneizzazione-industriale/#

Srikanth G., Fernando A., Selvaranjan K., Gamage J.C.P.H., Ekanayake L., (2022), Development of a plastering mortar using waste bagasse and rice husk ashes with sound mechanical and thermal properties, *Case Studies in Construction Materials*, **16**, e00956, https://doi.org/10.1016/j.cscm.2022.e00956.

Surup G.R., Leahy J.J., Timko M.T., Trubetskaya A., (2020), Hydrothermal carbonization of olive wastes to produce renewable, binder-free pellets for use as metallurgical reducing agents, *Renewable Energy*, **155**, 347-357.

Tahmid Islam M., Klinger J.L., Toufiq Reza M., (2023), Evaluating combustion characteristics and combustion kinetics of corn stover-derived hydrochars by cone calorimeter, *Chemical Engineering Journal*, **452**, 139419, https://doi.org/10.1016/j.cej.2022.139419.

Tripathi A.D., Mishra P.K., Darani K.K., Agarwal A., Paul V., (2022), Hydrothermal treatment of lignocellulose waste for the production of polyhydroxyalkanoates copolymer with potential application in food packaging, *Trends in Food Science & Technology*, **123**, 233–250.

Tu R., Sun Y., Wu Y., Fan X., Cheng S., Jiang E., Xu X., (2021), A new index for hydrochar based on fixed carbon content to predict its structural properties and thermal behaviour, *Energy*, **229**, 120572, https://doi.org/10.1016/j.energy.2021.120572

Venna S., Sharma H.B., Reddy P.H.P., Chowdhury S., Dubey B.K., (2021), Landfill leachate as an alternative moisture source for hydrothermal carbonization of municipal solid wastes to solid biofuels, *Bioresource Technology*, **320**, 124410, https://doi.org/10.1016/j.biortech.2020.124410.

Venkatesan S., Baloch H.A., Jamro I.A., Rafique R., (2022), Evaluation of the production of hydrochar from spent coffee grounds under different operating conditions, *Journal of Water Process Engineering*, **49**, 103037, https://doi.org/10.1016/j.jwpe.2022.103037

Villamil J.A., De La Rubia M.A., Diaz E., Mohedano A.F., (2020), *Technologies for Wastewater Sludge Utilization and Energy Production: Hydrothermal Carbonization of Lignocellulosic Biomass and Sewage Sludge*, In: *Wastewater Treatment Residues as Resources for Biorefinery Products and Biofuels*, Olivares J.A., Melero J.A., Puyol D., Dufour J. (Eds.), Elsevier, Amsterdam, 133–153.

Wang X., Li Z., Cheng Y., Yao H., Li H., You X., Zhang C., Li Y., (2022a), Wheat straw hydrochar induced negative priming effect on carbon decomposition in a coastal soil, *iMeta*, **2**, e134, https://doi.org/10.1002/imt2.134

Wang Q., Wu S., Cui D., Zhou H., Wu D., Pan S., Xu F., Wang Z., (2022b), Co-hydrothermal carbonization of organic solid wastes to hydrochar as potential fuel: A review, *Science of The Total Environment*, **850**, 158034, https://doi.org/10.1016/j.scitotenv.2022.158034

Wilk M., Magdziarz A., Kalemba-Rec I., Szymańska-Chargot M., (2020), Upgrading of green waste into carbon-rich solid biofuel by hydrothermal carbonization: The effect of process parameters on hydrochar derived from acacia, *Energy*, **202**, 117717, https://doi.org/10.1016/j.energy.2020.117717

Wilk M., Czerwińska K., Śliz M., Imbierowicz M., (2023), Hydrothermal carbonization of sewage sludge: Hydrochar properties and processing water treatment by distillation and wet oxidation, *Energy Reports*, **9**, 39–58, https://doi.org/10.1016/j.egyr.2023.03.092

Wu S., Wang Q., Cui D., Wu D., Bai J., Qin H., Xu F., Wang Z., (2023), Insights into the chemical structure evolution and carbonisation mechanism of biomass during hydrothermal treatment, *Journal of the Energy Institute*, 108, 101257, https://doi.org/10.1016/j.joei.2023.101257

Xu Q., Qian Q., Quek A., Ai N., Zeng G., Wang J., (2013), Hydrothermal carbonization of macroalgae and the effects of experimental parameters on the properties of hydrochars, *ACS Sustainable Chemical Engineering*, **1**, 1092-1101.

Yang X., Wang B., Guo Y., Yang F., Cheng F., (2023), Insights into the structure evolution of sewage sludge during hydrothermal carbonization under different temperatures, *Journal of Analytical and Applied Pyrolysis*, **169**, 105839, https://doi.org/10.1016/j.jaap.2022.105839

Yao F., Ye G., Peng W., Zhao G., Wang X., Wang Y., Zhu W., Jiao Y., Huang H., Ye D., (2023), Preparation of activated biochar with adjustable pore structure by hydrothermal carbonization for efficient adsorption of VOCs and its practical application prospects, *Journal of Environmental Chemical Engineering*, **11**, 109611, https://doi.org/10.1016/j.jece.2023.109611

Zhang S., Chen T., Li W., Dong Q., Xiong Y., (2016), Physicochemical properties and combustion behavior of duckweed during wet torrefaction, *Bioresource Technology*, **218**, 1157-1162.

Zhang Z., Li Y., Ding L., Yu J., Zhou Q., Kong Y., Ma J., (2021), Novel sodium bicarbonate activation of cassava ethanol sludge derived biochar for removing tetracycline from aqueous solution: Performance assessment and mechanism insight, *Bioresource Technology,* **330**, 124949, https://doi.org/10.1016/j.biortech.2021.124949

Zhang Y., He M., Wang L., Yan J., Ma B., Zhu X., Ok Y.S., Mechtcherine V., Tsang D.C.W., (2022), Biochar as construction materials for achieving carbon neutrality, *Biochar*, **4**, 59, https://doi.org/10.1007/s42773-022-00182-x

Zhang Q., Wang B., Feng Y., Feng Y., Li J., Ding S., He H., Xie H., (2023), Process water from hydrothermal carbonization: The impacts on the aquatic dissolved organic matter feature and microbial network at the soil-water interface, *Journal of Cleaner Production*, **397**, 136486, https://doi.org/10.1016/j.jclepro.2023.136486

Environmental Engineering and Management Journal
October 2023, Vol. 22, No. 10, 1703-1716
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

GREEN PUBLIC PROCUREMENT FOR A SUSTAINABLE PUBLIC ADMINISTRATION IN A RESILIENCE CONTEXT

Tiziana Crovella*, **Giovanni Lagioia**, **Annarita Paiano**

Department of Economics, Management and Business Law, University of Bari Aldo Moro, Italy

Abstract

Green Public Procurement is the approach adopted by Public Administration (PA) that integrate application of environmental criteria and technologies along entire life cycle of the ecological purchasing process. It is a voluntary instrument within the Europe but mandatory in Italy in accordance with article 34 of Law Decree 50/2016 and the new Public Contract Code. Subsequently, in the GPP was integrated the Action Plan for the environmental sustainability of public administration consumption in 2008 which defines national objectives, categories of goods and services, defines the Minimum Environmental Criteria (MEC) and provides guidelines for PA, with the aim of promoting the adoption of the GPP. Moreover, within European member state, the Italian Public Contract Code provides for compliance with public procedures only in the case that such contracts are strictly functional to the core business. The aim of this review is to analyze the difficulties that currently limit the application of GPP especially in Italy, strictly connected to the special sectors of the PA. The authors carried out an analysis of the evolution path of GPP and of the possible solutions that can be adopted to support the integration in the public administration. The result underlined that an important limitation concerns business of public administrations operating in special sectors such as gas, thermal energy, electricity, water, transport, postal services, exploitation of geographical area.

Key words: benefits, green public procurement, Italy, obstacles, public administration

Received: May, 2023; Revised final: July, 2023; Accepted: August, 2023; Published in final edited form: October, 2023

1. Introduction

Since the International Conference on Environment and Development hosted in Rio de Janeiro in 1992, the importance of Green Public Procurement (GPP) in supporting sustainable consumption and production models has been underlined. Nowadays, this awareness has greatly increased and disseminating through public authorities and public administrations (PAs), both as a political and technical tool in the planning of interventions and contracts (Testa et al., 2012a).

In the context of sustainability issues, PAs plays a crucial role: they have a high purchasing power, and the procurement market has enormous potential with positive repercussions on the economies of the countries. In 2018, EU PAs consumed around 670.31 billion euros, 22% more than in 2017 and about 29% more than in 2016 (European Commission, 2021). Additionally, in the same year, Italy invested 168 billion of euros, 36% more than 2016 (ANAC, 2022).

However, consumers and users play an important role by in public procurement context. Therefore, given that public procurement influences production and consumption trends, even a significant demand by public administrations for "greener" and environmentally friendly goods and services will expand the markets for such products and services (Li and Geiser, 2005).

Therefore, PAs must be ready to face the challenges of changes in consumption preferences and in parallel of climate change and socio-economic disparities (Rodriguez-Plesa et al., 2022). For this

---

* Author to whom all correspondence should be addressed: e-mail: tiziana.crovella@uniba.it; Phone: +39 3200188148

reason, local governments are slowly incorporating sustainability principles into their policies, as highlighted by Laurian and Crawford (2016). The approach towards the green and sustainability of the PAs has also been documented in the evolution of public procurement, translated into green public procurement (GPP) and sustainable (public procurement SPP), both public procurement practices (Alkadry et al. 2019).

Generally, the key role of GPPs in the economy and sustainable development is highlighted because the effects produced by their adoption fall on environment and companies that are identified in the procurement procedures and on PAs (Fig. 1).

Particularly, as shown in Fig. 1, in the basic framework the production and consumption patterns - in the public and private sectors - changed substantially over the past decades (Hermundsdottir and Aspelund, 2021), leading to social and environmental transformations and creating demands, constraints, new approaches and limitations for the companies. Furthermore, the key element driving this interconnected transformation is the management of innovation and sustainability (Annesi et al., 2023). Among these effects, the authors highlighted:

a) reduction of environmental impacts,

b) protection and improvement of the competitiveness of businesses, incentive for innovation, rationalization of public spending, diffusion of sustainable consumption and purchasing models, efficiency and saving of natural resources,

c) reduction of waste produced,

d) reduction in the use of hazardous substances,

e) integration of environmental considerations into the other policies of the institution, improvement of the image of the public administration,

f) enhancing the skills of public buyers.

Particularly, at national level, In Italy, GPP is playing a key role in public procurement considering the investment of the National Recovery and Resilience Plan (NRRP). As a matter of fact, this Plan provides that public administrations must adopt the DNSH (Do No Significant Harm) principle as a preparatory element for any funding from public or private entities, i.e. not causing significant damage to the environment. This procedure is accelerating and increasing GPP adoption procedures. Hence, the DNSH approach requires the mandatory adoption of Minimum Environmental Criteria (CAM). Furthermore, for 37% of the resources of the NRRP equal to approximately 200 billion euros, it will not be possible to limit oneself to *"not causing significant damage to the environment"* but must be shown to have contributed substantially to environmental improvement. Therefore, at the Italian level the implementation of NRR and GPP will be parallel (Falocco et al., 2022). Moreover, this direction in public procurement procedures has, however, led to some studies conducted over the years (Table 1). Amongst these studies, several empirical applications shown that public procurement can be a relevant innovation policy on the demand side (Castelnovo et al., 2023).

This review aims to analyze the difficulties that currently limit the application of GPP strictly connected to the public administration, in particularly in Italy, a European member state. The methodology consists in a review of the evolution path of GPP and of the possible solutions that can be adopted to support the integration in the public administration. Particularly, the novelty of this study relies in the analysis of the elements that facilitate or obstruct the adoption of the GPP under the NRRP which is involving Italy currently.

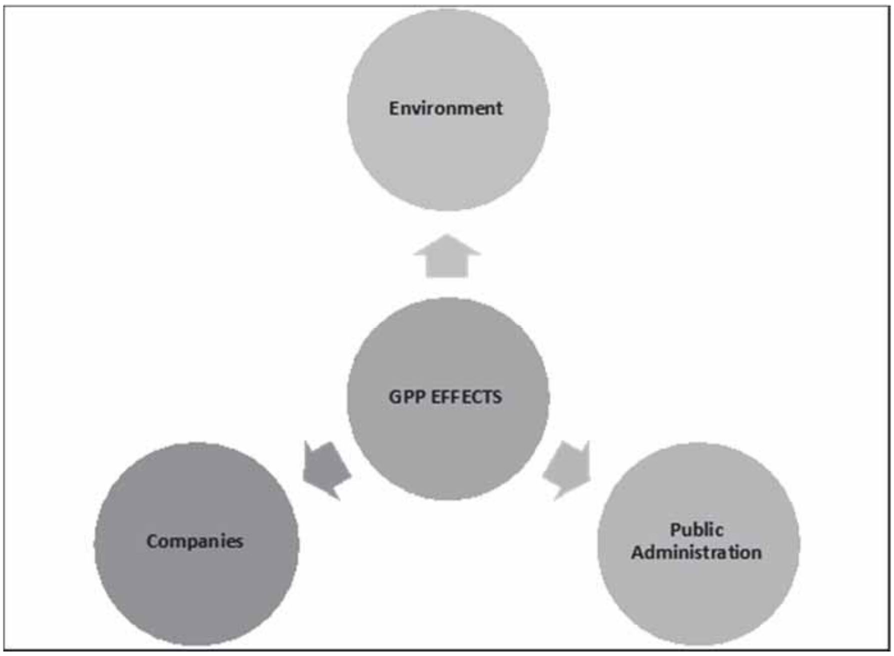


Fig. 1. Basic framework

Methodologically, this paper is based on a review but aims to identify some key issues related to GPP. Hence, this study not is a purely scientific interest analysis, but a reasoned discussion on the critical issues of GPP.

Lastly, this paper contains a critical analysis of the barriers that obstacle the GPP adoption in order to provide some solutions for overcoming and make the procurement procedure simple and sustainable, not only environmentally. Hence, the barriers exploration that constrain the adoption of GGP provides a better understanding of the adoption of GGP (Navarani et al., 2020).

2. Theoretical framework

With the aim to analyze the scientific interest about GPP, the authors performed a research on Scopus database. Using Green Public Procurement term in the "TITLE-ABS-KEY", the query revealed 536 scientific documents (Fig. 2) in which the term "GPP" was found at least in their title, summary or keywords. In 2021 it was recorded a pick with 81 articles, followed by 2022 with 60 publications. Subsequently, comparing the documents by country/region of publications, it emerged Italy as country in the top with 69 articles, equal of 12% of the total production.

The scholars that studied mainly GPP are Iraldo and Liu with 8 publications each, followed by Apolloni and Testa with 6. The articles represent 62.9% of production, 17.2% are conference papers, and other studies between book chapters (9.1%), reviews (5.4%), books (1.9%), conference review (1.7%) and other kinds with percentage less than 1% (note, editorial, erratum, short survey) (Table 1).

Only 20.9% are studies included in Environmental Sciences area, 15.0% in Social Sciences, 14.0% in Engineering, 12.8% in Business, Management and Accounting, 12.5% in Energy, 7.7% in Economy, Economics and Finance and other areas with less than 4% coverage.

Moreover, it has been stressed that 14 articles were elaborated under the sponsor of the European Commission: this event is explained by the European funding finalized with the adoption of the GPP in member countries, as Italy.

After this general analysis, the authors explored the scientific literature on Scopus platform using a composed string in "Green Public Procurement" AND "Public administration". The results quantified 35 scientific products. Moreover, adding a third element like "Europe", the results showed 3 papers. Then, considering the three results obtained and analyzing abstract, keywords and introduction the unique article published in line with our study was a documental analysis of European Practices processed by Litardi et al. (2020). The authors presented a study on the state of the art of GPP in the new trends promoted by the United Nations Agenda 2030. They mapped the main practices and their environmental impact, using a qualitative research methodology such as the documentary analysis of the most important GPP practices, divided into 129 documents and separated for each sector. Subsequently, analyzing the scientific production on Italian adoption of GPP, using "Green Public Procurement" AND "Public administration" AND "Italy" the unique study in line with this topic was elaborated in Spanish by Fuentes Bargues et al. (2021), and focused of Piedmont Region, in Northwest Italy.

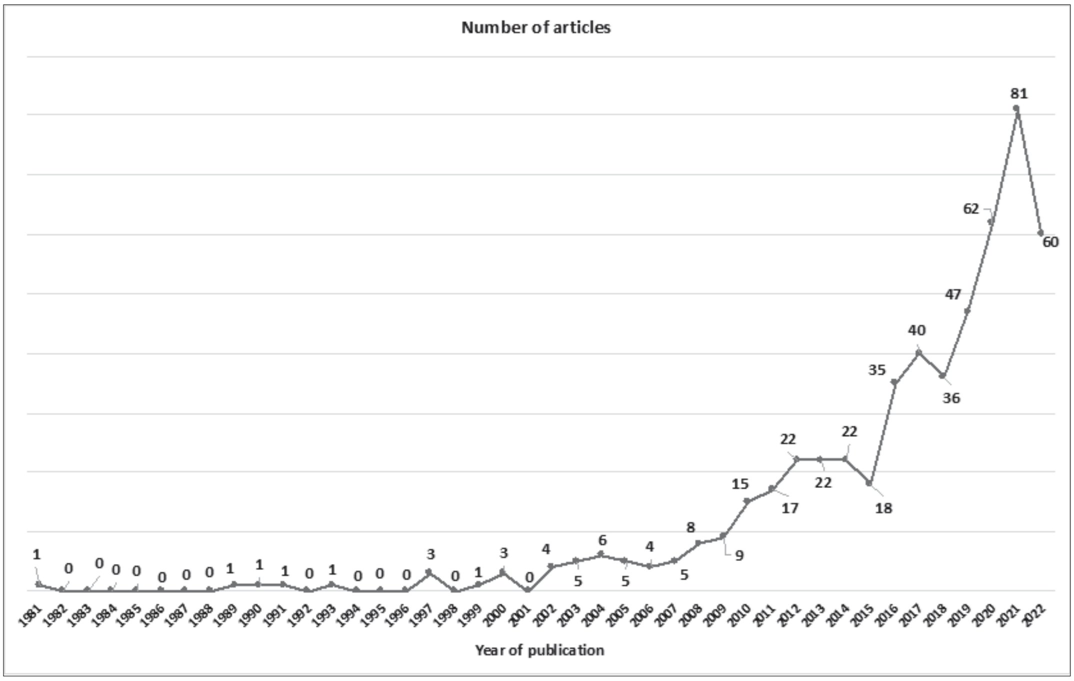


Fig. 2. Documents per year

Table 1. Most representative publications

Authors	*Year*	*Title*	*Journal*
Apolloni et al.	2013	Is public procurement going green?: Experiences and open issues	*Experience and Open Issue*
Apolloni et al.	2014	Green Procurement in the private sector: A state of the art review between 1996 and 2013	*Journal of Cleaner Production*
Bartolozzi et al.	2018	The application of life cycle assessment (LCA) in municipal solid waste management: A comparative study on street sweeping services	*Journal of Cleaner Production*
Cheng et al.	2018	Green Public Procurement, missing concepts and future trends – A critical review	*Journal of Cleaner Production*
De Giacomo et al.	2019	Does Green Public Procurement lead to Life Cycle Costing (LCC) adoption?	*Journal of Purchasing and Supply Management*
Liu et al.	2021	How external stakeholders drive the green public procurement practice? An organizational learning perspective	*Journal of Public Procurement*
Liu et al.	2019a	Improving the green public procurement performance of Chinese local governments: From the perspective of officials' knowledge	*Journal of Purchasing and Supply Management*
Liu et al.	2019b	Enhancing green public procurement practices in local governments: Chinese evidence based on a new research framework	*Journal of Cleaner Production*
Ma et al.	2021	Does green public procurement encourage firm's environmental certification practice? The mediation role of top management support	*Corporate Social Responsibility and Environmental Management*
Marucci et al.	2021	Investigating the management challenges of the EU Ecolabel through multi-stakeholder surveys	*The International Journal of Life Cycle Assessment*
Marucci et al.	2019	The integration of circular economy with sustainable consumption and production tools: Systematic review and future research agenda	*Journal of Cleaner Production*
Nucci et al.	2016	The relevance of life cycle costing in green public procurement	*Economics and Policy of Energy and the Environment*
Rizzi et al.	2014	Environmental value chain in green SME networks: The threat of the Abilene paradox	*Journal of Cleaner Production*
Testa et al.	2016a	Examining green public procurement using content analysis: existing difficulties for procurers and useful recommendations	*Environment, Development and Sustainability*
Testa et al.	2016b	Drawbacks and opportunities of green public procurement: An effective tool for sustainable production	*Journal of Cleaner Production*
Testa et al.	2012b	What factors influence the uptake of GPP (green public procurement) practices? New evidence from an Italian survey	*Ecological Economics*
Wang et al.	2020	Price/time/intellectual efficiency of procurement: Uncovering the related factors in Chinese public authorities	*Journal of Purchasing and Supply Management*
Wang et al.	2021	Green public procurement as a promoter for green consumption: From the perspective of individual's knowledge	*Cleaner and Responsible Consumption*
Ye et al.	2022	Why do public sectors perform high-level green public procurement practice? A new insight with fsQCA approach	*Journal of Environmental Planning and Management*

Particularly, the scholars investigated how procurement is green, recognizing public purchasing authorities a leadership position in promoting greening of operations (Apolloni et al., 2011; Apolloni et al., 2014), focused on the role of Life Cycle Approaches useful to analyze the impact of particularly products and goods involved in procurement (Bartolozzi et al. 2018; De Giacomo et al., 2019; Nucci et al., 2016), examined the integration of circular economy with sustainable consumption and production (Testa et al., 2016).

This shortage in the scientific publication (Table 1) led the authors to carry out this study to enrich the production and provide an overview to the stakeholders involved in the sector. The structure of the papers contains a section of introduction, presenting the essential elements of the GPP, a theoretical framework in second section and material and methods used for the analysis presented in section 3. Moreover, section 4 presents the results obtained analyzing different element associated to GPP, first of all the technical/economic/social obstacles to apply

GPP in public procurement, subsequently the role of GPP in Circular Economy Action Plan, an examination of the differences between Green Public Procurement and Sustainable Public Procurement, the importance of LCC (Life Cycle Costing) in GPP implementation, GPP in Italian Analysis. In this section authors presented the GPP in Italian National Ecological Transition and the numbers of the GPP in Italy. Subsequently, authors presented a best practice about GPP in energy sector. Therefore, the general question who drove this article is "what are the barriers that obstacle the implementation of GGP at national level?".

3. Materials and methods

This section has been elaborated through a structured analysis, starting from the scientific literature, regulations, laws and technical reports published in recent years. Considering that GPP has been presented for the first time in Rio de Janeiro in 1992 at the UN Conference on Environment and Development, this analysis carried out at Italian level with the aim of making a critical analysis within the Next Generation EU program, which involves different European member countries, including Italy.

Contemplating that European public authorities and member states as Italy are large consumers of goods and services produced and supplied by small and medium-sized enterprises and large companies, corrective measures for producing and procurement need to be taken. These products, if not accurately identified, generate significant impacts on the environment, such as emissions of carbon dioxide, waste and hazardous waste, consumption of natural resources and impacts on urban areas and populations. At European level, the first analysis is based on European regulation on GPP and are worth drawing attention to:

a) For Defining the requirements of a contract: "Defining technical specifications is guided through Article 42 and Annex VII of Directive 2014/24/EU; and Article 60 and Annex VIII of Directive 2014/25/EU",

b) For Use of labels: "Conditions for using labels are laid out in Article 43 of Directive 2014/24/EU; and Article 61 of Directive 2014/25/EU",

c) For Lowest price award and life-cycle costing (LCC): "Awarding public contracts on the basis of the most economically advantageous tender is provided as part of Article 67 of Directive 2014/24/EU; and Article 82 of Directive 2014/25/EU",

d) For Innovation partnerships: "The procedure for establishing an innovation partnership is set out in Article 31 of Directive 2014/24/EU",

e) For Consulting the market: "The procurement directives specifically allow for preliminary market consultation with suppliers in order to get advice, which may be used in the preparation of the procedure. Article 40 of Directive 2014/24/EU (European Commission, 2014)".

The EU also required to define clearly the concept of GPP: it must be a verifiable and justifiable environmental criterion, based on a life cycle approach and scientific evidence (COM (2008) 400) by recommending the creation of a process for the definition of common criteria for GPP.

Therefore, since 2008 the Commission has developed more than 20 common GPP criteria through a multi-criteria analysis including: scope of environmental improvement; public spending; potential impact on suppliers; potential to lead by example for private/corporate consumers; political sensitivity; existence of relevant and user-friendly criteria; market availability and economic efficiency. Table 2 shows these criteria that has been updated regularly.

Table 2. European GPP Criteria*

Developed criteria	***Under development criteria***
copying and graphic paper	food and catering
computer and monitors	cleaning services
transport	imaging equipment
electricity	transport
textiles	street lighting
cleaning products and services	data centers
office buildings	public space management
furniture	
food & catering services	
gardening products and services	
water based heaters	
waste water infrastructures	
flushing toilets & urinals	
imaging equipment	
roads	
road lighting and traffic signals	
sanitary tapware	
health care sector	
paints and varnishes	

*Authors' elaboration on European Commission and Lombardia Region, 2022; *GPP criteria for products are largely based on standard Type I ecolabels*

Particularly, recently EU has updated several criteria (Table 2) for cleaning products and services, computers, monitors, tablets and smartphones, data centers, server rooms and cloud services, electricity, food and catering services and vending machines, furniture, imaging equipment, consumables, print services, office building design, construction and management, paints, varnishes and road markings, public space maintenance, road design, construction and maintenance, road lighting and traffic signals, road transport, textiles. Hence, considering that Italy is a European member state, these criteria must also be applied in Italian public procurement.

More generally, conducting an analysis of the Italian level of adoption, GPP was introduced in Italy in 2008 with the National GPP Action Plan which provided for the adoption, with subsequent ministerial decrees, of the Minimum Environmental Criteria (MEC) for each category of products, services and works purchased or entrusted by the Public administration.

In Italy, the application of the MEC has been ensured by art. 18 of Law 221/2015 and by article 34 containing "Criteria for energy and environmental sustainability" (Table 3) of Legislative Decree 50/2016 "Procurement Code", which made it mandatory for all contracting authorities to apply it.

Table 3. Italian MEC criteria

Developed criteria	***Under adoption criteria***	***Under development criteria***
Interior furnishings	Design services and works for the new construction and maintenance of roads	Cultural events
Street furniture	Supply and rental of textile products	Food and beverage sales services (indoor bars and vending machines)
Supports for incontinence		Urban furniture
Work shoes and leather accessories		PC and server
Paper		Public transport service
Building		Energy services for buildings
Public lighting (service)		
Lighting, heating / cooling for buildings		
Industrial washing and rental of textiles and mattresses		
Urban waste and street sweeping		
Collective catering		
Disinfection		
Printers		
Public green		
Cartridges		
Public lighting (supply and design)		
Textiles		
Vehicles		

Authors' elaboration on MITE, 2022

Table 3 shows the evolution in MEC Italian Criteria, highlighting how Italy is steadily operating towards a complete green transition of public procurement. Moreover, recently, a directorial decree established the planning of activities aimed at defining the minimum environmental criteria preliminary to the adoption of the related ministerial decrees, for the year 2023 (MITE, 2023).

As highlighted by the European Commission, the criteria used by the Member States (e.g. MEC in Italy, see Table 3) must be similar to the general criteria of the GPP (Table 2) and suitable to avoid distortion of the single European market and the consequent reduction of competition. Therefore, choosing common criteria across member countries and at European level, this significantly reduces the administrative burden for economic operators and public administrations implementing GPP. Therefore, having common GPP criteria is an advantage for companies operating in more than one Member State and for SMEs and public administrations managing public procurement.

Then in order to carrying out a structured study, the authors envisaged some research questions developed after analyzing some reports and some scientific articles.

3.1. Research questions

RQ1. The GPP implementation is obstructed by some technical, social and economic limits that cannot be overcome.

RQ2. The terminological confusion of the approaches does not support the stakeholders.

RQ3. The absence of technical standards and holistic approaches does not convince public administrations to use GPP.

RQ4. Italy is a country lagging behind in adopting the GPP.

RQ5. At the European level, there are no funding programs to favor GPP in the energy sector.

4. Results and discussion

In this section the authors presented the obstacles to implementation of GPP, the role of GPP in the Circular Economy Action Plan, the differences between two approaches, the Green Public Procurement (GPP) and the Sustainable Public Procurement (SPP), the innovative LCC approach for GPP, the GPP in Italian public administration and a case study with the aim of addressing the themes proposed in the research questions.

4.1. Obstacles to GPP

A survey conducted by the European Commission on "Green Public Procurement in Europe" revealed numerous barriers for the implementation of GPPs at European level. In Table 4 authors inserted in the first column the barriers that restrict the adoption of GPP followed by a synthetic description. Moreover, in third column authors proposed a possible solution in order to overcome the obstacles. Then, the hypothesis of RQ1 is not verified because there are many barriers but they can be overcome through systematic activities and behaviors starting from correct communication and training.

4.2. Green Public procurement in circular economy action plan

An evolution to GPP is the *"circular procurement"* that defines an approach to green public procurement with particular attention "to the purchase of works, goods or services that seek to contribute to the closure of energy and material circuits within supply chains, reducing to a minimum and, in the best of cases, avoiding environmental impacts and the creation of waste along the entire life cycle".

These kinds of procurement:

a) allow buyers to focus on meeting needs,

b) consider life cycle costs with potential savings,

c) provide a framework for a more holistic consideration of environmental impacts and creation of waste along the entire life cycle of goods and services (European Commission, 2022).

For this reason, in order to support public buyers to leverage support for a transition to a circular economy, the European Commission published the "Public Procurement for a Circular Economy" manual in 2017.

Table 4. Barriers and possible solution for GPP implementation at European level

Barriers to adoption GPP	***Description***	***Solutions***
Lack of political support	Many public authorities complained about the lack of support in the implementation of the GPP. The reason for this difficulty is associated with a lack of awareness of the importance of the GPP agenda of European civil servants and purchasing staff	1) train senior officials and GPP practitioners 2) provide tools and indications necessary to implement the approach 3) update with new regulations and technical evolutions
Green products are perceived to cost more	Using the purchase price alone to decide between offers, rather than the cost of the entire life cycle of the product or service, can affect the adoption of ecological products and services and not justify a difference in price between product/service traditional and green product/service	1) use a life cycle costing (LCC) approach to calculate the financial impact of GPP 2) do not use only the purchase price of the product/service 3) the average financial impact of GPP is lower because maintenance and disposal costs decrease
Lack of legal expertise in applying environmental criteria	Many senior public purchasing officials do not and cannot be aware of all the environmental and social impacts of purchasing certain products or services In some cases, senior officials and buyers still struggle to define what an "environmentally and/or socially preferable" product or service is and how to include appropriate criteria to identify them in the procurement process	Provide technical data sheets of the products with the indications of: a) the environmental criteria b) the reduced impacts c) the production and disposal procedures
Lack of practical tools and information	Continuous lack of practical tools and information both in the purchase phase and in the use and disposal phase	Overcoming this gap by publishing information on international, community and national digital platforms
The need for systematic implementation and integration into management systems	Decentralized organizations require effective management systems to ensure the consistent application of environmental and social initiatives – and this applies equally to GPP.	Joint procurement/contracting and public/private partnerships are possible approaches to overcome these types of obstacles
Lack of training	The staff responsible for carrying out specific tasks (from the preparation of contracts, to execution and control) does not always have the appropriate skills and training	Optimize the training required of contractors and subcontracted stations on the legal and technical aspects of GPP implementation, on the concept of life cycle cost and for end users on the sustainable use of products
Lack of co-operation between authorities	Systematic implementation of GPP between different public authorities is still completely absent and is an obstacle to implementation	1) Need to push for informal and formal cooperation between public authorities to improve GPP 2) Promote a coordinated exchange of good practices and networks between authorities.
Limited established environmental criteria for products/services	Lack of clear and accurate information for many product and service groups and difficulty in accessing clear and verifiable criteria that allow them to incorporate environmental considerations into tenders	Provide a clear and organized communication of the criteria to be considered in the procurement, use, disposal phase

Source: Authors' elaboration on European Commission (2020)

This publication contains a series of good practice case studies and a guide on integrating circular economy principles into procurement.

Therefore, recognized the key role of the Circular Economy, this new approach:

a) placed particular emphasis on aspects of the circular economy in terms of setting criteria,

b) supported greater dissemination of GPP criteria by public authorities,

c) has required training and ongoing assistance,

d) has guaranteed the accompaniment of the Commission and an increase in funding.

4.3. Differences between Green Public Procurement and Sustainable Public Procurement

Generally, sustainable public procurement (SPP) supports the organization's sustainability goals and optimizes environmental, social, and economic impacts throughout the product or service life cycle. Therefore, it does not only consider purely environmental aspects. Hence, SPP includes complying with environmental laws and objectives, removing hazardous/prohibited materials and wastes in the supply chain, thoroughly auditing suppliers for fair labor practices, operating for the long term (CIPS, 2023). According to a definition by Rodriguez-Plesa et al. (2022) the "*Sustainable Public Procurement (SPP)"* consists of a mechanism for governments to address problems strategically using government funds efficiently and effectively, promoting the well-being of the environment, economy and society.

Conversely, according to a definition by the Commission of the European Parliament (2008), the "Green public procurement" is a process by which authorities seek to purchase goods [...], with reduced environmental impact throughout their life cycle compared to goods […] with the same primary function that would otherwise be purchased".

Analyzing the main characteristics between GPP and SPP, it emerged that:

1) GPP approach is characterized by the presence of two types of criteria for each covered sector:

a) "core criteria, which can be used by any contracting authority in the Member States, address key environmental impacts and are designed to be used with minimal additional verification effort or increased costs",

b) "comprehensive criteria, suitable for those who wish to purchase the best environmental products available on the market, and may require additional verification effort or a slight cost increase compared to other products with the same functionality".

2) Sustainable Public Procurement (SPP) is an interconnected and interdependent system consisting of the environmental, social and economic dimensions (Rodriguez-Plesa et al., 2022):

a) above all the environmental dimension was included in the existing literature (Grandia and Kruyen, 2020),

b) the economic dimension focused on the material well-being of all people (Fiorino, 2010),

c) the social dimension emphasizes an "effective, stable and democratic government" (Fiorino, 2010).

However, the social and economic dimensions have overlapping elements because they are focused on people.

At the government level, many public authorities in the EU are implementing GPP as part of a broader approach to sustainability in their purchasing, which also addresses economic and social aspects. Instead, the United Nations developed a detailed guide on SPPs to address all three aspects of sustainability (economic, social and environmental) and summarize the operation as *"Buying for a Better World"*.

Then, when discussing sustainability in public procurement public administration are operating according economic, social and environmental sustainability, towards the three levels of sustainability that do not only concern the environment. Conversely, green public procurement only refers to environment. In conclusion, RQ2 is verified. These two approaches can confuse public administrations in the approach to be adopted because they often do not know the difference.

4.4. Life Cycle Costing (LCC)

The use of GPP supports various environmental policy tools, in line with the logic of the Integrated Product Policy promoted at European level, such as the improvement programs prepared as part of EMAS or ISO 14001 processes or the action plans of the Agenda 21 or simply the political will of the institution to improve its environmental impacts and demonstrate the results internally and externally, as highlighted in MITE (2007).

Therefore, the criteria indicated in Tables 3-4, to be functional to the purpose of the GPP, must be evaluated on the basis of methodology proposed in the National Plan on GPP (for the Italian case) with reference to market analysis. Therefore, these can also be accompanied, where appropriate, by cost-benefit analyzes or by LCC analyzes, bearing in mind, in general, the concept of sustainability.

In scientific literature, Querol et al. (2020) analyzed life cycle cost (LCC) as a useful tool for green public procurement (GPP). The cost savings obtained during the life of the product are negatively offset by the price premiums linked to the impact on the environment. Therefore, through the environmental component of the LCC the authors included not only the "internal" costs but also the "external". The LCC internalizes externalities to consider environmental aspects in addition to the usual elements of operating, maintenance and end-of-life costs. Hence, this option consists in defining stringent environmental technical specifications to ensure an ecological result and using this approach as an award criterion when selecting among alternatives already considered ecological.

Unfortunately, despite its usefulness, LCC is little used in public procurement because PAS have not yet understood its potential and effectiveness. However, at the EU level the new directive on public procurement has been issued which recognizes the LCC as a key role in operations conducted for sustainable procurement (De Giacomo et al., 2019).

Therefore, this kind of operation is regulated by the technical standard, the ISO 15686-5:2017, "which provides requirements and guidelines for performing life cycle costing (LCC) analyzes of buildings and constructed assets and their parts, new or existing". Therefore, RQ3 is not verified because there isn't a lack of technical standards and holistic approaches to coexist public administrations in using GPP. Indeed, it is enough to consider the LCC or the various certifications regulated by technical standards.

4.5. GPP in Italian analysis

Among the EU member states, the authors analyzed the GPP implementation in Italy. For this reason, they present two subsections, the first about the national program of the ecological transition and the second dealt with the diffusion of this approach among public administrations.

4.5.1. GPP in Italian national ecological transition

At national level, starting from the indication contained in the Communication of the European Commission "Integrated product policy, develop the concept of the environmental life cycle" (COM (2003) 302), the Ministry of Ecological Transition has developed the "action for the environmental sustainability of public administration consumption" (PAN GPP). This tool provided a general framework on GPP, defined national objectives, identified the categories of goods, services and priority intervention works for environmental impacts and the volumes of expenditure on which to define the Minimum Environmental Criteria (MEC) (MITE, 2017).

Moreover, the PAN GPP also orders specific requirements for public bodies, which are called to carry out an analysis of their needs with the aim of rationalizing consumption and favoring decoupling (the dissociation between economic development and environmental degradation), identifying the functions responsible for the implementation of the GPP involved in the purchasing process, draw up a specific internal program to implement the actions in the GPP area. In particular, it invites Provinces and Municipalities to promote energy efficiency measures in the school buildings of competence. Finally, the PAN GPP provides for annual monitoring to verify its application, with relative analysis of the environmental benefits obtained and the training and dissemination actions to be carried out on the national territory (MITE, 2017).

4.5.2. The numbers of the GPP in Italy

There are 18 Italian municipalities that declared that always apply MEC: Belluno, Bolzano, Brescia, Chieti, Cuneo, Ferrara, Forlì, Imperia, Latina, Mantua, Modena, Monza, Padua, Pavia, Pordenone, Rimini, Savona and Trento. Furthermore, the cities that have an application rate between 99% and 99.99% compared to the 17 monitored MECs are 9: Bari, Bologna, Gorizia, Livorno, Ravenna, Turin, Treviso, Venice and Verona (Table 5).

As shown in Table 5, other 8 municipalities shown percentages between 88% and 99% such as Brindisi, Cremona, Oristano, Perugia, Pistoia, Reggio Emilia, Syracuse and Teramo. It emerged that the highest rates of adoption of MEC are medium-sized cities, with a population between 50,000 and 200,000 inhabitants, such as Trento (Table 5).

Technically, the synthetic indicator of GPP expresses the systematic commitment of an administration in the implementation of this policy: it is higher than 0.90 in provincial capitals such as Bolzano, Modena, Monza, Padua, Rimini, Teramo, Turin. On the other hand, the administrations that do not adopt the MECs do not even adopt the GPP policy. Moreover, GPP process indicators and MEC adoption indicators are two indexes elaborated with the aim to indicate, respectively, the level of application of GPP criteria and MEC criteria. The sum of these two indicators reveals the synthetic GPP Indicator. Generally, these indicators quantity the performance on the GPP implementation in Italy.

Practically, amongst the factors that facilitate the adoption of MEC and GPP, the authors highlighted knowledge of GPP (almost 90%), training on GPP, monitoring, social criteria, gender equality, the adoption of plastic-free policies. As shown in the Fig. 3, the MEC most used by the municipalities are those relating to the purchase of paper and cleaning services (over 70%), followed by printers, toner cartridges and paper graphics (between 60% and 70%). These are activities prevalent in all public administrations. Conversely, the least used MECs, with values between 30% and 40%, are related to vehicles, energy services, textiles and footwear.

Particularly, considering that some sectors presented the same level of influence in the environmental impact generated by public administration activities, the percentage of application of MEC by these areas is equal (e.g. printers and cartridges, energy services and road vehicles).

Notwithstanding, from the data analyzed and presented at a general level, Italy is not a country lagging behind in the adoption of the GPP, indeed many regions and countries have achieved a full application of it. So, RQ4 is not true.

Table 5. Statistics on GPP and MEC adoption in Italy (2021)*

Municipalities capital of the Region	*Inhabitants (in millions)*	*GPP Process Indicators*	*MEC adoption indicators*	*% MEC adoption*	*Synthetic GPP Indicator*
Roma	2.864	0.23	0.18	n.d.	0.40
Milano	1.372	0.25	0.45	64.3	0.70
Napoli	0.962	0.30	0.00	0.00	0.30
Torino	0.878	0.30	0.65	92.3	0.95
Palermo	0.666	0.30	0.35	50.0	0.65
Genova	0.578	0.12	0.45	64.3	0.57
Bologna	0.390	0.20	0.65	92.9	0.85
Firenze	0.381	0.30	0.44	62.5	0.74
Bari	0.322	0.12	0.65	93.3	0.77
Venezia	0.261	0.25	0.64	91.7	0.89
Trieste	0.204	n.d.	n.d.	n.d.	n.d.
Perugia	0.166	0.23	0.59	84.6	0.82
Cagliari	0.154	0.20	0.43	61.5	0.63
Trento	0.118	0.15	0.70	100.0	0.85
Ancona	0.101	0.10	0.26	37.5	0.36
Catanzaro	0.089	0.08	0.35	50.0	0.43
L'Aquila	0.678	0.30	0.31	43.8	0.61
Potenza	0.670	0.30	0.00	0.00	0.30
Campobasso	0.492	0.05	0.19	26.7	0.24
Aosta	0.339	0.15	0.32	46.2	0.47

**Trieste did not reply to the OAV 2022 questionnaire on GPP; Source: Authors' elaboration on Falocco et al. (2022)*

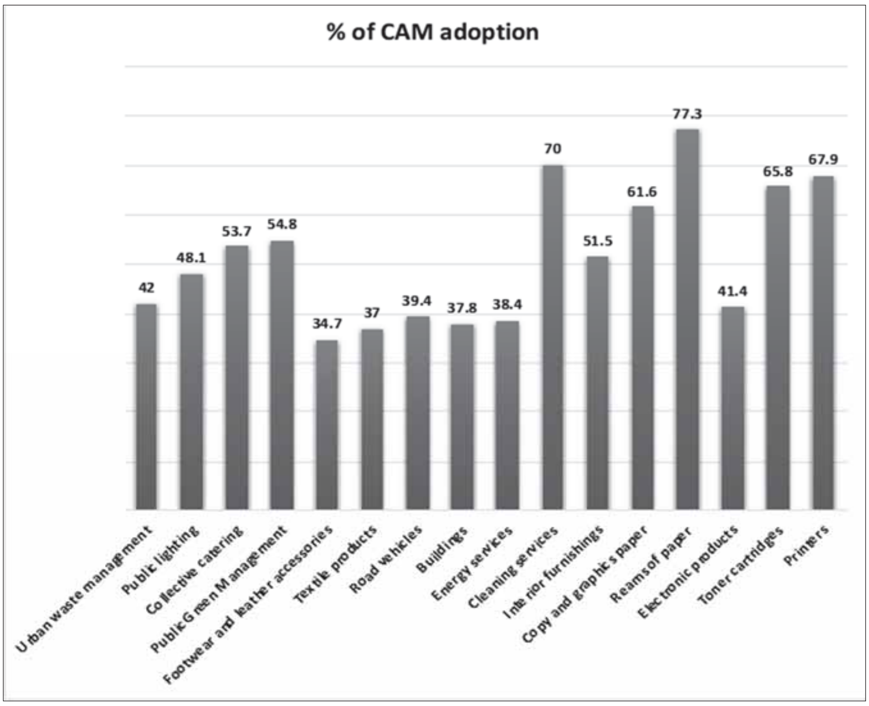


Fig. 3. MEC adoption rate in the Italian capital municipalities, 2021 (in%)
Source: Authors' elaboration on data Falocco et al. (2022)

4.6. GPP in energy industry – The XPRESS Project case study

With the aim to implement a close cooperation between public and private sector and for creating a useful partnership that facilitate the implementation of the GPP, European Union launched various tools. Particularly, in the renewable energy sector, for example, an important project, the XPRESS, has been planned. This project, funded by the Horizon Europe 2020 program for research and innovation of the Union program, aims to facilitate introduction technologies of Renewable Energy Sources and increasing their share in final energy consumption along two dimensions:

1) through the use of Smart Green Public Procurement (SGPP), to create the new market and strengthen the performance of innovators in Renewable Energy Sources (RES) technologies,

2) with the development of innovative financing tools and the sharing of best practices with the aim of supporting the innovation of SMEs (Small

and Medium Enterprises) and producing new RES technologies.

The XPRESS program initially focused on cities and municipalities in Italy, the United Kingdom, Norway, Germany, Sweden, Spain, Denmark, Slovakia, Portugal and Belgium with the aim of extending the analysis and involvement to wider regions of all European countries. Nevertheless, the general aim is to facilitate the adoption of GPP in the energy sector. This program allows you to operate on several levels: understanding the problem, finding the solution, preparing a financial analysis with constraints on RES innovations, analyze barriers and innovative challenges in GPP for both stakeholders involved, public authorities and SMEs, analyze the environmental impact of RES Innovations carried out through GPP.

Furthermore, with this project, public authorities and SMEs can be supported in minimizing any financial and regulatory constraints that affect their collaboration, organizing GPP co-creation workshops, coffee moments between stakeholders (SMEs and policy makers), collection of eco-design and examples of good practices, recommendations for the use of RES solutions (XPRESS, 2022).

Italy, through EURADA, the European Association of Development Agencies, has created a moment to bring together Italian PAs and SMEs gathered in Venice for the XPRESS Co-creation Policy Workshop on the development of GPP in the renewable energy sector. Moreover, the need to overcome the bureaucratic, financial and technical barriers that hinder the full involvement of public administrations and innovative companies in the development of Green Public Procurement (GPP) in the renewable energy sector was discussed. Through this partnership, between Italy, the Express Program and EURADA, the need to acquire responsible behaviors for the reduction of CO_2 emissions in the area of the Po river basin, for example, an area critical for air quality, was highlighted. and pollution (EURADA, 2022). For this reason, there are several financing programs to support the implementation of the GPP in the energy sectors (RQ5).

4.7. Possible actions to adopt GPPs in the future

Firstly, as Navarani et al. (2020) underlined, among the major obstacles emerged: not providing for the obligation in some sectors (Ahsan and Rahman, 2017), difficulties in carrying out the procedures (Hall et al., 2015), not specifying the method of transport of the product and the frequency of deliveries to predict more sustainable hypotheses (Thomson and Jackson, 2007), non-indication of the achievable level of sustainability (Adjei-Bamfo and Maloreh-Nyamekye, 2019). For this reason, the problems related to obstacles to GPP implementation can be solved in various modes. Among these stand out above all (Fig. 4):

a) Modify calls for tenders and communications to businesses,

b) Implement adequate internal staff training,

Initiate specific monitoring activities.

Figure 4 includes the results of a survey carried out by Legambiente (2021) in Italy for analyzing the adjustment actions due to the GPP. The answers highlighted as the first area of intervention consists of a change in the process of preparing and communicating with companies (first column), which is followed by the internal training of personnel (second column), subsequently moving on to the activity of monitoring or updating internal information systems such as networking and external support. Finally, to a lesser extent there is interest in hiring new personnel.

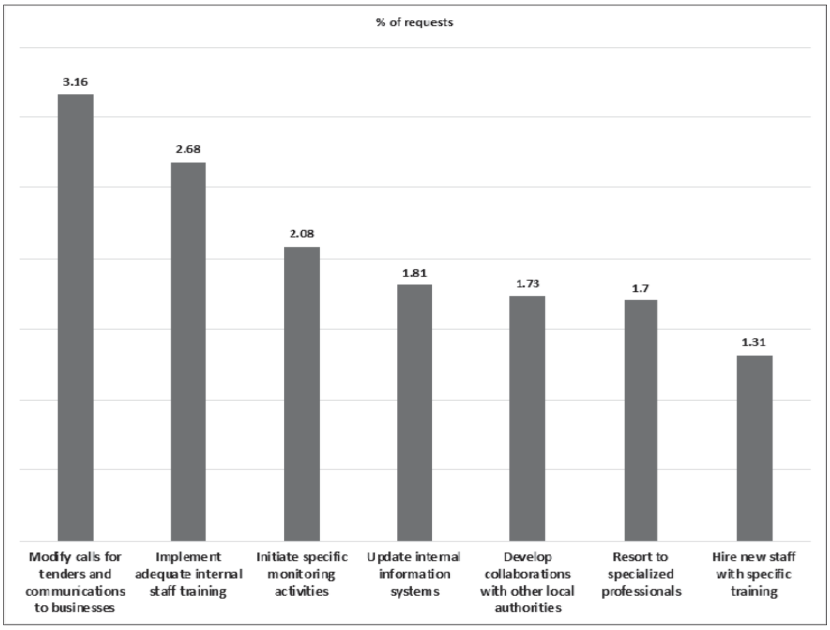


Fig. 4. Possible solution to increase MEC adoption rate in the Italy (in %)
(authors' elaboration on data Falocco et al., 2022)

Of minor importance, the authors emphasized the hiring of new staff with specific training. Therefore, by adopting the GPP and the MEC in Italy, as well as in other countries, important benefits can be achieved: Therefore, by adopting the GPP and the MEC in Italy, as well as in other countries, important benefits can be achieved:

a) 35% of the fallout are positive territorial impact from the point of environmental and / or social view,

b) 25% improvement of the image towards citizens and users,

c) 15% reduction of environmental management costs (e.g. waste, energy),

d) 12.5% rationalization of public spending,

e) 11% better access to Community funding (criterion reward) (Falocco et al., 2022).

Furthermore, considering that sustainability innovation is an integrated and interdependent process between PA and Companies, through the collaboration of stakeholders, as Cillo et al. (2019) underlined, a public service company can be a strategic player in the improvement of local policies towards sustainability (Annesi et al., 2023).

4. Conclusions, limitations and future implications

GPP represent 14% of GDP (Gross Domestic Product) and include environmental, economic, social and political benefits. Particularly, in environmental field this approach allows to decrease GHG and hazardous substances, increase resource and energy efficiency. From the economic point of view, the GPP approach supports the achievement of environmental obligations, shows commitment to the protection of the environment, sustainable consumption and production. Furthermore, politically, it supports the growing diffusion of green technologies and products, supporting innovation. Finally, it also supports the social issue by improving health and well-being of populations with less impacting products and services.

Among the major obstacles, it emerged the lack of knowledge and awareness. However, the financial constraint is not the main obstacle for GGP implementation, as previously perceived, because especially in Italy it is favored by funding from the NRRP. However, widespread barriers can be considered: limited budget, precise legislation, involvement of people such as customers and suppliers, lack of knowledge and awareness, decentralization of purchasing, GGP policy and strategies, size of the organization, political and top management commitment, lack of monitoring evaluation and lack of incentives.

Therefore, for the future authorities must carry out the control of the appropriate execution of the contracts and set up a legislative observatory GPP and MEC, for verifying that each local authority operates on the basis of a regional action plan and that a bank is planned "green" procurement data. Moreover, a positive note that could accelerate the adoption of GPPs is the introduction of the DNSH (Do no significant harm) approach at European level, a principle according to which the interventions envisaged by the Italian NRPP must not cause significant damage to the environment. Therefore, GPP can be considered an important operational and evaluation tools for the sustainable management of materials and energy in a public administration that moves towards the Circular Economy. Moreover, GPP supports public administrations to achieve the environmental sustainability of their countries earlier.

This review mainly investigated the barriers for GPP adoption, conducting a comparative and qualitative research, focusing on the Italian case. For the future, more investigations are needed at different levels and for different sectors to understand in quantitative terms also the nature of barriers. In this first study, it was not possible to quantify the criticality of the barriers as it was decided to observe the phenomenon in order to build a quantitative analysis model for a future application.

In conclusion, future research should explore a shift from green procurement to sustainable procurement, contemplating environmental, economic and social sustainability aspects, also favoring the application of life cycle costing approaches. In this way public administrations can benefit and not damage the environment and humanity.

Acknowledgements

This research was carried out thanks to PNRR M4C2-Investment 1.3 Enlarged Partnership GRINS - Growing Resilient, INclusive and Sustainable by University of Bari Aldo Moro, Department of Economics, Management and Business Law and to address the objectives of Spoke 1. CUP: H93C22000650001, Code PNRR_PE_71, Identified Code PE0000018, Thematic: Building of datasets for the circular economy of the main Italian production systems.

References

Adjei-Bamfo P., Maloreh-Nyamekye T., Ahenkan A., (2019), The role of e-government in sustainable public procurement in developing countries: a systematic literature review, *Resources, Conservation and Recycling*, **142**, 189-203.

Ahsan K., Rahman S., (2017), Green public procurement implementation challenges in Australian public healthcare sector, *Journal of Cleaner Production*, **152**, 181-197.

Alkadry M. Trammell E., Dimand A.M., (2019), The power of public procurement: social equity and sustainability and externalities and as deliberate policy tools, *International Journal of Procurement Management*, **12**, 336-362.

ANAC, (2022), Report to Parliament on the activity carried out by ANAC in 2021, (in Italian), On line at: https://www.anticorruzione.it/documents/91439/39459199/2.ANAC+-+Relazione+annuale+2022+-+Mercato+appalti.pdf/7c528e73-285a-3735-c813-c717e7a2ce73?t=1655914102317

Annesi N., Battaglia M., Sganzetta L., (2023), Mutual benefits of sustainability integration in the value chain: Responsible innovation by public utilities, *Utilities*

Policy, **82**, 101564, https://doi.org/10.1016/j.jup.2023.101564.

Apolloni A., Sun H., Jia F., Li X., (2014), Green Procurement in the private sector: A state of the art review between 1996 and 2013, *Journal of Cleaner Production*, **85**, 122-133.

Appolloni A., D'Amato A., Cheng W., (2011), Is public procurement going green? *Experiences and Open Issues*, http://dx.doi.org/10.2139/ssrn.1970583.

Bartolozzi I., Baldereschi E., Daddi T., Iraldo F., (2018), The application of life cycle assessment (LCA) in municipal solid waste management: A comparative study on street sweeping services, *Journal of Cleaner Production*, **182**, 455-465.

Castelnovo P., Clò S., Florio M., (2023), A quasi-experimental design to assess the innovative impact of public procurement: An application to the Italian space industry, *Technovation,* **121**, 102683, https://doi.org/10.1016/j.technovation.2022.102683.

Cheng W., Apolloni A., D'Amato A., Zhu Q., (2018), Green Public Procurement, missing concepts and future trends – A critical review, *Journal of Cleaner Production*, **176**, 770-784.

Cillo V., Petruzzelli A.M., Ardito L., Del Giudice M., (2019), Understanding sustainable innovation: a systematic literature review, *Corporate Social Responsibility and Environmental Manag*ement, **26**, 1012-1025.

CIPS, (2023), Why sustainable procurement continues to be important?, On line at: https://www.cips.org/intelligence-hub/sustainability/sustainable-procurement

Commission of the European Parliament, (2008), Public Procurement for a Better Environment. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, On line at: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52008DC0400&from=EN

De Giacomo M.R., Testa F., Iraldo F., Formentini M., (2019), Does Green Public Procurement lead to Life Cycle Costing (LCC) adoption?, *Journal of Purchasing and Supply Management*, **25**, 100500, https://doi.org/10.1016/j.pursup.2018.05.001.

De Giacomo M.R., Testa F., Iraldo F., Formentini M., (2019), Does Green Public Procurement lead to Life Cycle Costing (LCC) adoption?, *Journal of Purchasing and Supply Management*, **25**, 100500, https://doi.org/10.1016/j.pursup.2018.05.001.

EC, (2008), Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the sustainable consumption and production and sustainable industrial policy action plan, COM (2008) 397/3, Brussels, On line at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A52008DC0397.

EURADA, (2022), Italian PAs and SMEs gathered in Venice for the XPRESS Co-creation Policy Workshop about the development of GPP in Renewable Energy Sector, On line at: https://www.eurada.org/news/detail/italian-pas-and-smes-gathered-in-venice-for-the-xpress-co-creation-policy-workshop-about-the-development-of-gpp-in-renewable-energy-sector

European Commission and Lombardia Region, (2022), EU Green Public Procurement (GPP) – Policy, On line at: https://www.regione.lombardia.it/wps/wcm/connect/c217f834-1be3-45da-a87e-1a2d9705576d/02_INFODAY+GPP_Commissione+Europea_De+Giorgis.pdf?MOD=AJPERES&CACHEID=ROOTWORKSPACE-c217f834-1be3-45da-a87e-1a2d9705576d-mKupQW0

European Commission, (2014), EU public procurement directives, On line at: https://ec.europa.eu/environment/gpp/eu_public_directives_en.htm

European Commission, (2020), EU Green Public Procurement (GPP) Policy, On line at: https://noharm-europe.org/sites/default/files/documents-files/4441/1%20Robert%20Kaukewitsch.pdf

European Commission, (2021), Public Procurement Indicators 2018, On line at: https://ec.europa.eu/docsroom/documents/48156

European Commission, (2022), Circular Procurement, On line at: https://ec.europa.eu/environment/gpp/circular_procurement_en.htm

Falocco S, Le Donne G., Minutolo A., Mancini M., (2022), The Numbers of Green Public Procurement in Italy - 2022 Report, (in Italian), 44, On line at: https://www.legambiente.it/wp-content/uploads/2021/11/Green-Public-Procurement_report2022.pdf

Fiorino D.J., (2010), Sustainability as a conceptual focus for public administration, *Public Administration Review*, **70**, 78-88.

Fuentes Bargues J.L., Piccirillo E., Rebaudengo M., (2021), *Green Public Procurement of building works in the Piedmont Region of Italy*, 25th International Congress on Project Management and Engineering Alcoi, 6-9 July, Spain.

Grandia J.J., Kruyen P.M., (2020), Assessing the implementation of sustainable public procurement using quantitative text-analysis tools: a large-scale analysis of Belgian public procurement notices, *Journal of Purchase and Supply Management*, **26**, 100627, https://doi.org/10.1016/j.pursup.2020.100627.

Hall P., Lofgren K., Peters G., (2015), Greening the street-level procurer: challenges in the strongly decentralized Swedish system, *Journal of Consumer Policy*, **39**, 467-483.

Hermundsdottir F., Aspelund A., (2021), Sustainability innovations and firm competitiveness: a review, *Journal of Cleaner Production*, **280**, 124715, https://doi.org/10.1016/j.jclepro.2020.124715.

ISO 15686-5:2017, (2017), ISO 15686-5:2017 Buildings and constructed assets — Service life planning — Part 5: Life-cycle costing, On line at: https://www.iso.org/standard/61148.html

Laurian L., Crawford J., (2016), Sustainability in the USA and New Zealand: explaining and addressing the implementation gap in local government, *Journal of Environmental Planning Management,* **59**, 2124-2144.

Legambiente (2021), City Climate Report 2021 - "the climate has already changed" (in Italian: Rapporto Citta' Clima 2021 - "il clima e' gia' cambiato"), https://www.legambiente.it/rapporti/rapporto-cittaclima/.

Li L., Geiser K., (2005), Environmentally responsible public procurement (ERPP) and its implications for integrated product policy (IPP), *Journal of Cleaner Production*, **13**, 705-715.

Litardi I., Fiorani G., Alimonti D., (2020), *The State of the Art of Green Public Procurement in Europe: Documental Analysis of European Practices*. In: *Accountability, Ethics and Sustainability of*

Organizations. New Theories, Strategies and Tools for Survival and Growth, Brunelli S., Di Carlo E. (Eds.), Springer, Cham, 175-192.

Liu J., Ma Y., Apolloni A., Cheng W., (2021), How external stakeholders drive the green public procurement practice? An organizational learning perspective, *Journal of Public Procurement*, **21**, http://dx.doi.org/10.1108/JOPP-04-2020-0035.

Liu J., Shi B., Xue J. Wang Q., (2019a), Improving the green public procurement performance of Chinese local governments: From the perspective of officials' knowledge, *Journal of Purchasing and Supply Management*, **25**, 100501, https://doi.org/10.1016/j.pursup.2018.05.002.

Liu J., Xue J., Yang L., Shi B., (2019b), Enhancing green public procurement practices in local governments: Chinese evidence based on a new research framework, *Journal of Cleaner Production*, 211, 842-854.

Ma Y., Liu Y., Apolloni A., Liu J., (2021), Does green public procurement encourage firm's environmental certification practice? The mediation role of top management support, *Corporate Social Responsibility and Environmental Management*, **28**, 1002-1017.

Marucci L., Iraldo F., Daddi T., (2021), Investigating the management challenges of the EU Ecolabel through multi-stakeholder surveys, *International Journal of Life Cycle Assessment*, **26**, 575-590.

Marucci L., Daddi T., Iraldo F., (2019), The integration of circular economy with sustainable consumption and production tools: Systematic review and future research agenda, *Journal of Cleaner Production*, **240**, 118268, https://doi.org/10.1016/j.jclepro.2019.118268.

MITE, (2007), Action Plan for Environmental Sustainability of Consumption in the Public Administration Sector, (in Italian), On line at: https://www.mite.gov.it/sites/default/files/archivio/allegati/GPP/all.to_19_PAN_GPP_definitivo__21_12_2007.pdf

MITE, (2017), National Action Plan on GPP, (in Italian), On line at: https://gpp.mite.gov.it/Home/PianoAzioneNazionaleGPP

MITE, (2022), CAM - Minimum Environmental Criteria, (in Italian), On line at: https://gpp.mite.gov.it/Home/Cam#3

MITE, (2023), Definition of minimum environmental criteria prior to the adoption of the relevant ministerial decrees, for the year 2023, (in Italian), On line at: https://gpp.mite.gov.it/sites/default/files/2023-04/DD_CAM_protocollato_MASE_EC_REGISTRO_DECRETI%28R%29_0000015.31-03-2023.pdf

Navarani V., Zeeda F.M., Santha C., (2020), A systematic review of barriers impeding the implementation of government green procurement, *Journal of Public Procurement*, **20**, 451-471.

Nucci B., Iraldo F., De Giacomo M.R., (2016), The relevance of life cycle costing in green public procurement, *Economics and Policy of Energy and the Environment*, **2016**, 91-109.

Querol A.A., Schaefer B., Esquerrà i Roig J., (2020), *LCC and GPP - Competing or complementary approaches?* In: *The Challenges of Public Procurement Reforms*, 1st Edition, Routledge, 16.

Rizzi F., Frey M., Testa F., Apolloni A., (2014), Environmental value chain in green SME networks: The threat of the Abilene paradox, *Journal of Cleaner Production*, **85**, 265-275.

Rodriguez-Plesa E., Dimand A.M., Alkadry M.G., (2022), Community social capital, political values, or organizational capacity? Indicators of engagement in sustainable public procurement at the local level, *Journal of Cleaner Production*, **338**, 130556, https://doi.org/10.1016/j.jclepro.2022.130556.

Testa F., Iraldo F., Frey M., Daddi T., (2012a), What factors influence the uptake of GPP (green public procurement) practices? New evidence from an Italian survey, *Ecological Economics*, **82**, 88-96.

Testa F., Iraldo F., Frey M., Daddi T., (2012b), What factors influence the uptake of GPP (green public procurement) practices? New evidence from an Italian survey, *Ecological Economics*, **82**, 88-96.

Testa F., Eleonora A., Iraldo F., Fray M., (2016a), Drawbacks and opportunities of green public procurement: An effective tool for sustainable production, *Journal of Cleaner Production*, **112**, 1893-1900.

Testa F., Grappio P., Gusmerotti N.M., Iraldo F., Fray M., (2016b), Examining green public procurement using content analysis: existing difficulties for procurers and useful recommendations, *Environmental Development and Sustainaibility*, **18**, 197-219.

Thomson J., Jackson T., (2007), Sustainable procurement in practice: lessons from local government, *Journal of Environmental Planning and Management*, **50**, 421-444.

Wang Q., Wang S., Zhang M., Bu Z., Liu J., (2021), Green public procurement as a promoter for green consumption: From the perspective of individual's knowledge, *Cleaner and Responsible Consumption*, **3**, 100035, https://doi.org/10.1016/j.clrc.2021.100035.

Wang Q., Zhang R., Liu J., (2020), Price/time/intellectual efficiency of procurement: Uncovering the related factors in Chinese public authorities, *Journal of Purchasing and Supply Management*, **26**, 100622, https://doi.org/10.1016/j.pursup.2020.100622.

XPRESS, (2022), Facilitating green public procurement in the energy sector, On line at: https://www.xpress-h2020.eu/digital-brochure-of-xpress-project.pdf

Ye M., Ma Y., Liu J., (2022), Why do public sectors perform high-level green public procurement practice? A new insight with fsQCA approach, *Journal of Environmental Planning and Management*, **65**, 2719-2747.

Environmental Engineering and Management Journal

October 2023, Vol. 22, No. 10, 1717-1727
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2023.146

"Gheorghe Asachi" Technical University of Iasi, Romania

POTENTIAL OF AEROBIC STABILIZATION IN DRASTIC SLUDGE REDUCTION: A FULL-SCALE EXPERIMENT

Marta Domini[*], Andrea Volpi, Giorgio Bertanza

Department of Civil, Environmental, Architectural Engineering and Mathematics (DICATAM), University of Brescia, 25123 Brescia, Italy

---

Abstract

The management of sewage sludge is a recognized and pressing issue. Traditional and innovative sludge minimization processes are applied at full-scale or are at the research stage. However, the processes traditionally applied in wastewater treatment plants (WWTP), at times, have a not fully exploited potential due to a lack of process optimization. Therefore, careful monitoring, coupled with functionality checks and experimental tests, can provide useful indications for maximizing the performance of the treatment units already in place. In this work a full-scale experimental campaign was set up in a recently renewed WWTP, to investigate the potential of aerobic sludge stabilization in reducing the volume of sludge produced and, consequently, the management costs. Operating data were collected and analysed. Two tests were conducted in a stabilization tank, varying the dissolved oxygen (DO) concentration (1 mg/L and > 3 mg/L). The energy consumption was monitored. A model of the volatile suspended solids removal was built, and results were ultimately compared after homogenization. The reduction of volatile suspended solids was 60% and 44%, respectively. The reduction of the quantity of sludge obtained in the two tests was 38% and 29%, respectively. Improved sludge stabilisation rather than sludge reduction was achieved by pushing aerobic stabilisation. The modelled sludge reduction after 2 weeks of treatment would have been 12% and 15% under the tested conditions, respectively. It resulted that, for contact times up to 2 weeks, the DO concentration had not a relevant influence on the sludge stabilization, while consuming more energy.

Key words: aerobic stabilisation, dewaterability, dissolved oxygen, optimization, sludge minimization

Received: May, 2023; Revised final: July, 2023; Accepted: August, 2023; Published in final edited form: October, 2023

---

1. Introduction

Sewage sludge management is a key challenge and topical issue in water cycle management. The sludge produced by wastewater treatment plants (WWTPs) has to be recovered in terms of material and energy (Morello et al., 2022; Salisu et al., 2023), or it has to be disposed of. The annual sludge production in the European Union (EU 27) could be estimated in the range of 7 -8 million tons in 2018 (EU, 2022). In Italy, wastewater treatment produced about 3.4 million tons of sludge in 2020, and of the over 3 million tons managed, 53.5% was disposed of and 44.1% was recovered (ISPRA, 2022). Sludge management, regardless of its production process, can account for about 25-65% of the operating costs in a sewage treatment plant (Scrinzi et al., 2022), with recovery/disposal costs ranging between 120 and 200 €/t in 2021 in Italy (Campo et al., 2021; Domini et al., 2022a). Despite the sludge production trend has been stabilizing in recent years, a slight increase is expected, due i.e., to the extension of the service, estimated as 10% in Lombardy, North of Italy (Domini et al., 2022b). Therefore, great interest and many efforts are directed to sludge minimization, to respect the European Directive 2018/851 on waste that prioritizes prevention over recovery and, ultimately disposal, and to reduce management costs.

Sludge minimization can be obtained through the adoption of consolidated processes reducing the

---

[*] Author to whom all correspondence should be addressed: e-mail: marta.domini@unibs.it; Phone: +39 303711301

production of sludge, and/or the water content (dewatering, drying) and /or the fraction of volatile solids (stabilization) (Collivignarelli et al., 2019; Øegaard, 2004). Moreover, various innovative sludge minimization options could be coupled or implemented in addition to traditional ones (Pérez-Elvira et al., 2006). Sludge reduction mechanical methods include, i.e., stirred ball-mill and ultrasonic disintegrator (Atay and Akbal, 2016; Shrestha et al., 2020; Yao et al. 2021); chemical methods include i.e., ozonization and wet oxidation (Bertanza et al., 2015a; Semblante et al., 2017); physical methods include, i.e., thermal and thermal/chemical hydrolysis (Hii et al., 2014); biological methods include. i.e. enzymatic processes, microbial metabolism, membrane bioreactor, granular sludge systems (De Oliveira et al., 2018; Guo et al 2020; Øegaard, 2004). Finally, other processes have been studied such as the oxic-settling-anaerobic (OSA) process, and electroosmosis (Collivignarelli et al., 2019; Morello et al., 2022).

However, the implementation of a new process or the installation of a new technology in an existing plant would be expensive, and not always possible. WWTPs often work less optimally when it comes to resource management, and there is space for further optimization of the process to achieve better performances, maximizing the sludge stabilization and dewaterability, through attentive monitoring, coupled with functionality checks and experimental tests, on existing facilities (Bertanza and Collivignarelli, 2012; Silva and Rosa, 2020). These activities provide valuable information for maximizing the performances of existing units, and, in principle, they should always precede the design of upgrades involving complex and costly renovations.

The aerobic stabilization of sewage sludge is a solid technology for volatile suspended solids (VSS) abatement, and its efficiency depends on factors such as temperature, sludge retention time, dissolved oxygen (DO) concentration, and on the characteristics of the sludge entering the process (De Feo et al., 2012). In particular, DO is a critical parameter which can affect the biological activities, but there is scarce information on its effects on the performance of aerobic sludge stabilisation (Arunachalam et al., 2004; Ji et al., 2016).

This work aims at studying the potential for sludge minimization of the aerobic stabilization of a WWTP at full-scale by improving its performance acting on the aeration. We studied the degree of stabilization in the tank, in terms of VSS abatement, the degree of dry solids, in terms of reduction of the water content in the sludge (by mechanical dewatering), and the energetic consumption of the system.

2. Materials and methods

2.1. Investigation site

Experimental tests were carried out, full-scale, in an activated WWTP treating municipal wastewater located in the Province of Brescia Lombardy, in the North of Italy. The plant was recently revamped to reach the current nominal capacity of 90.000 population equivalent (PE). It entered into operation in its current configuration, after commissioning, in April 2021. The water line counts 6 biological lines; the sludge line is composed of a gravity sludge pre-thickener, two aerobic stabilization tanks (A and B) in parallel, a post-thickener, and mechanical dewatering, supplied by an external company (truck-mounted POLAT S570 centrifuge). Tests were carried out in the aerobic stabilization thank A, dimensions 15 x 11 x 5.3 m (usable depth), with a net capacity of 874 m^3. The tank is served by a fine bubble aeration system, powered by 2 blowers (type Kaeser FBS 660 M SFC), insufflating the air through an aeration duct with a manual gate valve, and by 2 mixers.

2.2. Operational and management data

2.2.1 Data collection

Operational and management data for the years 2021-2022 were retrieved from the plant database. The inlet flow rate, and the sludge level in the aerobic stabilization tanks, were measured by probes in the field and collected through the Programmable Logic Controller (PLC) of the plant.

Data on the pollutants' inlet and outlet concentrations resulted from weekly laboratory analyses on wastewater and sludge samples: ammoniacal nitrogen ($N\text{-}NH_4$), total nitrogen (TN), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total phosphorus (TP), sludge volume index (SVI), sedimentable solids (SS), total and volatile suspended solids (TSS and VSS).

2.2.2 Data analysis

All data were elaborated in Excel (Microsoft, 2010). The operational data of the plant were summarized graphically over time, and normed parameters were compared to national and regional regulatory limits. The average and median values of the inlet flow were calculated. Pollutant removal yields η (%) were calculated considering the average loads of the pollutants in input and output to the plant in the reference period.

To estimate the pollutant loads incoming from the sewer, excluding the contribution of the recirculated flows, BOD_5 and COD loads were reduced by 7%, while that of TN by 10%. Values were estimated based on literature (Bertanza et al. 2015b; Bertanza et al., 2018; Mininni et al., 2015). To calculate the sludge load C_f (kgBOD/(kgSST·d), the average seasonal value for the BOD_5 load in the i-th oxidation tank ($BOD_{5in,i}$) and the biomass concentration in terms of TSS in the i-th oxidation tank (X_i) were used.

To calculate the sludge age θ(d), the average seasonal values for the daily excess flow rate extracted from the i-th oxidation tank ($q_{s,i}$), the TSS concentration in the recirculation sludge of the i-th oxidation tank ($X_{r,i}$) and X_i were used.

2.3. Experimental campaign

2.3.1. Data collection and analysis

An experimental campaign was carried out from April to July 2022. Two tests were performed in the aerobic stabilization tank A (Fig. 1), in batch, with continuous aeration, varying the DO concentration: the first test (P1) had a DO target concentration of 1 mg/L; the second test (P2), had a DO target concentration of > 3 mg/L.

The same procedure was followed for both tests. The tank, previously emptied, was filled with sewage sludge from the pre-thickener to a level of 5.3 m, with mixers on and aeration off (2 days). Sludge thickening followed for 1 day, with supernatant removal (1 day), and the tank was re-filled back to the 5.3 m level (1 day). Then, the aeration started, and the test began, to continue till the stabilization of the VSS/TSS ratio (or other operational time constraints of the plant).

Part of the sewage sludge (2 containers, equivalent to about 250 m^3), was dewatered at the start, middle, and end of each test, with sampling of the liquid and solid fractions. Measurements of sewage sludge temperature and DO concentrations in the tank were taken with a portable probe and multimeter (Hach HQ40D), during weekdays, at 5 different points at a depth of 4 meters, 3 measures for each point, twice per day (Fig. 1). Depending on DO measurements, the aeration was controlled by the regulation of the gate valve and of the blowers' frequency, manually. During the tests, tank B was operated as usual in continuous.

Sewage sludge was sampled in the tanks during weekdays (Fig. 1). An internal laboratory determined analytically TSS and VSS concentrations on sewage sludge and dewatered sludge samples; and, it determined N-NH$_4$, TN, BOD$_5$, COD, TSS and VSS on the liquid fraction of dewatered sludge. SVI tests in cylinder were carried out (CNR-IRSA, 2003).

Data on air temperature were derived from the online regional database at https://www.arpalombardia.it/. Data on blowers' frequency and intensity were recorded through the PLC. The voltage was assumed equal to 398 volts, and the power factor (PF) equal to 0.9. All data were elaborated in Excel (Microsoft, 2010).

2.3.2. VSS abatement model

To study the stabilization kinetics in more detail, a numerical model of VSS abatement was constructed. The reaction was assumed to be a first-order reaction, as follows (Eq. 1):

$$[VSS]_t = [VSS]_0^{-k*t} \tag{1}$$

where *[VSS]$_t$* and *[VSS]$_0$* denote the concentration of *VSS* [g/L] at time t and time $t = 0$, t is the elapsed time [d] and k is the kinetic constant [d^{-1}]. The kinetic constants were normalized under standard homogeneous temperature conditions using the following simplified Van't Hoff - Arrhenius equation (Eq. 2):

$$k_{20°C} = k_P * \theta^{(20°\mathrm{C}-\mathrm{TP})} \tag{2}$$

where $k_{(20°C)}$ is the kinetic constant at the standard temperature of 20°C and k_P is the kinetic constant at the average test temperature T_P. The value of θ was assumed equal to 1.04 (Anderson and Mavinic, 1992).

2.3.3. Simulation of performance under homogeneous conditions

To perform a relevant comparison, having the sewage sludge different characteristics in the two tests, a simulation of the stabilization performance was performed considering the following homogenous initial sludge conditions: TSS concentration of 19 g/L; VSS$_i$ concentration of 15 g/L; 20% dewaterability of TSS on the total dewatered sludge; VSS/TSS of 78.9%.

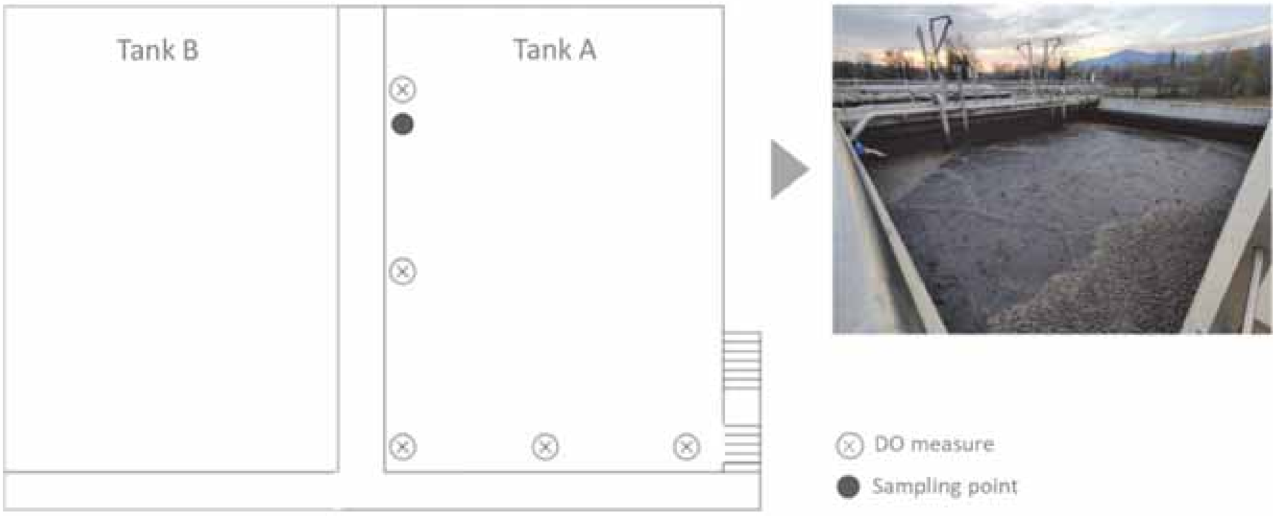


Fig. 1. Investigation site: schema and picture of aerobic stabilization tanks A and B, with indication of the sampling point and DO measure points

For each test, the following parameters were calculated after 7, 14, 21, 30 and 45 days of stabilization:

- quantity of VSS and TSS in the dewatered sludge produced from 1 m^3 of stabilisation sludge (batch);
- quantity of VSS and TSS in the dewatered sludge produced from 1 m^3 of stabilisation sludge (continuous sludge feeding);
- quantity of water in the dewatered sludge produced from 1 m^3 of stabilisation sludge;
- total quantity of dewatered sludge produced from 1 m^3 of stabilisation sludge;
- VSS/TSS ratio of the stabilisation sludge;
- energy consumption per 1 m^3 of stabilisation sludge treated.

VSS abatement was calculated by Eq. (1), and k calculated under real conditions were used. VSS_u leaving the tanks concentration under continuous feeding conditions was calculated as (Eq. 3):

$$VSS_u = \frac{VSS_i}{(\theta_H * k+1)} \tag{3}$$

where θ_H is the hydraulic retention time of the sludge in the stabilization tank [d]; values of θ_H equal to 7, 14, 21, 30 and 45 days were considered.

The TSS concentration was calculated as the difference between TSS_i and the VSS removed. The quantities of TSS and VSS in the dewatered sludge produced from 1 m^3 of stabilization sludge, were derived as the product of the calculated TSS and VSS concentrations for the volume considered. The percentage of TSS in the dewatered sludge over time was calculated using the following equation (Eq. 4):

$$TSS_t = TSS_0 + m_{TSS} * t \tag{4}$$

where TSS_0 is the initial percentage of TSS in the dewatered sludge set to 20%, m_{TSS} is the slope of the interpolation line of the TSS percentage values measured for the dewatered samples in P1 and P2.

The total amount of dewatered sludge remaining from 1 m^3 of stabilization sludge was calculated by dividing the amount of TSS in the dewatered sludge by the percentage of dry part provided by laboratory analysis. The amount of water in the dewatered sludge was calculated by the difference between the total dewatered sludge and the dry part. The concentration of TN(t) [mg/L], in the liquid fraction obtained from dewatering, over time, was calculated by the following relationship (Eq. 5):

$$TN(t) = TN_0 + m_N * t \tag{5}$$

where TN_0 indicates the initial concentration of TN set equal to 100 mg/L, t indicates the time elapsed from the stabilisation start [d], m_N is the slope of the trend line obtained from the linear interpolation of the TN concentration values in P1 and P2.

The percentage of TN load recirculated in the plant, defined N_r, was calculated by Eq. (6):

$$N_r = \frac{N_{TOT}(t) * 200m^3}{N_{in,average}} \tag{6}$$

where $N_{in,average}$ indicates the average input of the TN load [kg/d], and 200 m^3 is assumed as the average volume of supernatant recirculated.

3. Results and discussion

3.1. Operational and management data

The inlet flow to the WWTP, in 2021 - 2022, presented an average value of 30,501 m^3/d, a median of 26.248 m^3/d, a minimum of a 5.300 m^3/d and a maximum of 67.933 m^3/d. Table 1 summarizes the main results on the concentrations of pollutants at the input and output of the plant. We observed that regulatory limits were always respected in the period of reference for TN, N-NH_4 and TSS. The BOD_5 and COD presented concentration values in the outlet exceeding limits only once, in the period of reference. The TP exceeded limits in some samples, especially in the first months of 2021. Overall, the plant performed well in respecting regulatory limits. With the exception of the first months of 2021 (before the commissioning), the removal yelds of the plant were elevated (Table 2), with values ≥ 93% for BOD_5 and COD, and ≥ 82% for TN and TP.

Calculated sludge loading values C_f were relatively low (Collivignarelli and Bertanza, 2012), close to 0.1 kgBOD_5/(kgTSS*d) with lower values at the beginning of 2021, probably due to the fact that after the revamping, the full plant operation had not yet been restored (Table 2). Calculated sludge ages θ_c exceeded one week (Table 2). The values of SVI, SS and TSS in oxidation tanks showed great variability in 2021 and 2022 in all lines.

3.2. Experimental campaign

The average DO concentration, sludge temperature in the tank and air temperature measured for tests P1 and P2, are summarized in Table 3. In test P1, after the first week in which the biomass requirement of DO was elevated, the DO concentration stabilized around 1 mg/L, with an average value of 1.2 mg/L (min 0.24 mg/L; max 2.6 mg/L). The temperature of the sewage sludge in the tank was on average 31°C (min 29.9°C; max 32.8°C). The air temperature was on average 22°C (min 13.5°C; max 28.7°C). In test P2, the DO concentration was kept over 3 mg/L, and after a few days, it stabilized around an average value of 6.8 mg/L (min 5.7 mg/L; max 7.8 mg/L). The temperature of the sewage sludge was on average 32°C (min 31.5°C; max 32.6°C). The air temperature was on average 27°C (min 22.6°C; max 30.7°C).

It has to be noted that the temperature in the tank reached similar values in both tests, whilst the air temperature varied, being warmer in June/July (during test P2). The variability of measured DO concentrations depended on the manual regulation of the airflow, and on the fact that the blowers and aeration duct served both stabilization tanks (A and B), and that tank B was in operation serving the plant during tests. The two blowers feeding the air supply for aerobic stabilisation operate on a single pipeline, which only splits in two near the inlet to stabilisation tanks A and B. Due to this configuration, the flow of the supplied air is influenced by the sludge level in the two stabilisation tanks: as the difference in sludge head between the two tanks increases, the air tends to flow with greater inertia towards the tank with the lower level. It is possible to partially control the flow of the supplied air and the DO concentration by adjusting the blowers' frequency and the opening of the gate valves.

However, these adjustments only result in constant DO concentrations over time if the sludge level does not vary in either tank. In the experimental tests, the sludge level was only kept constant in tank A, while in tank B it varied according to the plant's operational needs. For these reasons, it was not possible to conduct a precise regulation of the DO in the stabilization sludge.

Table 1. Concentrations of pollutants in input and output at the plant (period of reference 2021 - 2022)

	Inlet (mg/L)				***Outlet (mg/L)***			
Parameter	***Average***	***Median***	***Min***	***Max***	***Average***	***Median***	***Min***	***Max***
BOD_5	145	149	22	490	6	5	3	36
COD	323	307	66	1,000	21	19	5	104
TSS	144	131	17	680	4	3	3	14
TN	37	38	8	90	4	4	1	10
$N\text{-}NH_4$	30	32	6	49	1	0.5	0.3	3.5
TP	4	4	1	17	0.7	0.6	0.1	3.7

Table 2. Removal yields for main parameters, average sludge temperatures in biological lines, sludge load and age, on a seasonal basis

Period	***T [°C]***	***BOD_5 (%)***	***COD (%)***	***TN (%)***	***TP (%)***	***Cf [$kgBOD_5/(kgTSS \cdot d)$]***	***θ_c [d]***
01/21/2021-02/28/2021	-	89.6	86.7	62.9	71.7	0.04	16.1
03/01/2021-05/31/2021	-	91.9	86.2	80.8	64.3	0.05	9.6
06/01/2021-08/31/2021	23.8	96.0	93.0	89.1	81.9	0.09	9.0
09/01/2021-11/30/2021	19.5	95.7	93.3	91.3	87.4	0.09	12.5
12/01/2021-02/28/2022	12.4	95.3	93.4	88.6	91.2	0.10	8.2
03/01/2022-05/31/2022	16.6	95.5	92.9	90.4	86.5	0.07	7.5
06/01/2022-08/31/2022	25.1	98.1	95.7	84.6	84.0	0.10	7.0
09/01/2022-11/30/2022	20.8	98.0	96.5	86.3	82.3	0.08	9.1
12/01/2021-12/31/2022	13.8	95.7	93.3	83.2	77.5	0.06	11.4

Table 3. Summary of results on DO concentration, sludge temperature and air temperature measured for tests P1 and P2

Description	***Test P1***	***Test P2***
DO target concentration	1 mg/L	>3 mg/L
Start and end date	04/12/2022 - 05/30/2022	06/21/2022 – 07/25/2022
Duration	49 days	35 days
DO average concentration	1.2 mg/L	6.8 mg/L
Average sludge temperature in the tank	31°C	32°C
Average air temperature	22°C	27°C

The total duration of the tests differed, the first (P1) lasting 49 days and the second (P2) 35 days. This was due to the fact that during P2, a foaming problem occurred: the aeration was stopped, and the test was concluded earlier to avoid the overflow of the sludge from the tank and other operational problems. It was determined by microscopical observations that the foam consisted of floating sludge flakes due to the proliferation of a filamentous bacterium Type 0092. The presence and proliferation of this filamentous bacterium are favoured by the high temperatures and the presence in the sludge of rapidly biodegradable substrates (Burger et al., 2017; Madoni et al., 2000; Sam et al, 2022). It is suspected that, during the filling phase of test P2, the bacterium was already present in the biological reactor sludge, whose temperature was higher than in P1. The stabilization tank offered ideal conditions for the proliferation, with the temperature rising over 32°C. It was hypothesized that the foaming was possibly due to the increased airflow leading to the flotation of the mud flakes with the filamentous bacteria, rather than to the DO concentration.

During the test P1, the sludge characteristics varied as follows: the TSS decreased from 19.0 g/L to 10.1 g/L (47% reduction); the VSS decreased from 15.2 g/L to 6.1 g/L (60% reduction); the VSS/TSS ratio passed from 81% to 60% (Fig. 2). The dewaterability of the sludge, in terms of the percentage of dry matter in the dewatered sludge resulted: 20.8% TSS and 16.7% VSS at the beginning of the test; 20.0% TSS and 14.3% VSS at mid-test; 18.6% TSS and 12.4% VSS at the end of the test (Fig. 2). The settleability showed a slight deterioration: the SVI varied from 114 mL/g to 137 mL/g.

During the test P2, the sludge characteristics varied as follows: the TSS decreased from 18.0 g/L to 11.6 g/L (36% reduction); the VSS decreased from 12.2 g/L to 6.7 g/L (45% reduction); the VSS/TSS ratio passed from 68% to 58% (Fig. 3). The dewaterability of the sludge, in terms of the percentage of dry matter in the dewatered sludge resulted: 23.6% TSS and 16.0% VSS at the beginning of the test; 21.8% TSS and 15.6% VSS after about 2 weeks; 21.7% TSS and 13.0% VSS at the end of the test (Fig. 3). The settleability of the sludge remained stable, with SVI varying from 102 mL/g to 96 mL/g.

The concentration of TN in the liquid fraction separated during dewatering increased from about 170 mg/L to over 700 mg/L in P1, and from about 170 mg/L to about 500 mg/L in P2. The concentration of N-NH_4 in the liquid fraction separated during dewatering, increased from about 138 mg/L to about 270 mg/L in P1, and decreased from about 260 mg/L to about 80 mg/L in P2.

Table 4 summarizes the results of energy consumption observed and calculated for tests P1 and P2, that are in line with literature (Foladori et al., 2010). The test P2, characterized by the largest aeration, had the highest energy specific consumption (1.75 kWh/(m^3*d)), despite lasting less than P1, considering the specific energetic consumption per unit of volume per day.

The main identified factors influencing the outcomes of experimental tests on the stabilization were: the DO concentration in the stabilization sludge; the duration of the tests; the characteristics of the sludge entering stabilization; the process temperature. The DO concentration and duration were controllable factors, while the characteristics of the sludge in input and the process temperature were non-controllable factors. Therefore, the results of tests were processed to draw general conclusions untethered from occasional factors.

3.3. Degree of stabilization

Since the sludge entering the stabilization tank in the two tests had different characteristics, results were compared at a common value of the VSS/TSS ratio, equal to 67%, set at day 28 of P1 (Fig. 4). VSS had a reduction respectively of 60% (P1) and 44% (P2) that are respectively higher and in line with what expected: VSS abatement is generally expected to be in the range of 20%-50% (Arunachalam et al., 2004; Bertanza et al., 2015b; Minnini et al., 2015). Tas (2010) reported a 31% VSS removal in 18 days of aerobic stabilization, in line with what was observed in P1. Sanchez et al. (2006) reported a VSS/TSS ratio of 0.56 after 46 days of aerobic stabilization with a DO concentration of 0.5 - 1.4 mg/L. A high VSS abatement (60%) was reported after 31 days by Zupančič and Roš (2008) under thermophilic conditions (50-58°C), which are more favorable than the temperature reached in the tank in our study (31 - 32°C).

The trends of VSS/TSS ratios and VSS concentrations in P1 and P2 thus compared were similar, suggesting that the different DO concentrations adopted did not substantially affect the sludge stabilization process. Differently, Ji et al. (2016), observed an amelioration of VSS abatement by anaerobic stabilization when increasing the DO concentration from 3 to 7 mg/L after 15 d. It should be noticed that the experiment was conducted at lab scale, while this study was conducted on a full-scale plant under real operating conditions.

The model developed supported the modelling of the VSS abatement as a function of the sludge characteristics (VSS concentration) and time. The reaction rates for the VSS abatement resulted equal to 0.0152 d^{-1} in test P1, and equal to 0,0191 d^{-1} in test P2. The normalized rates calculated at 20°C resulted equal to 0.0099 d^{-1} in test P1 and 0.0118 d^{-1} in test P2 (Table 5).

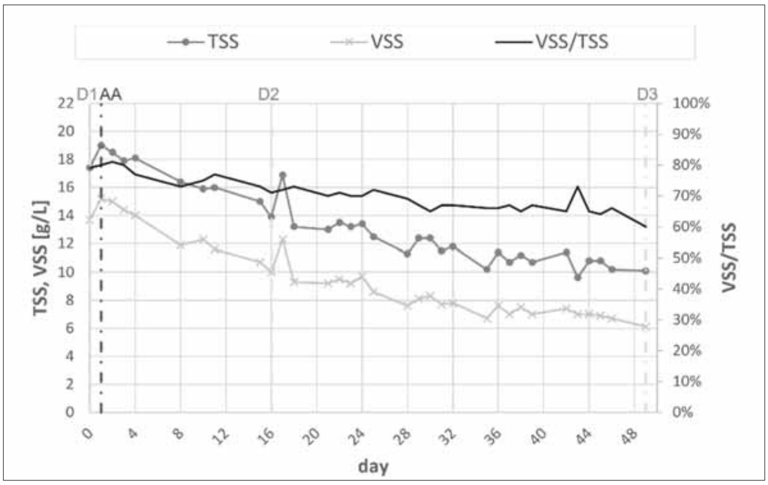


Fig. 2. Variation of the concentration of VSS and TSS in test P1. Note that D = dewatering, AA = test start

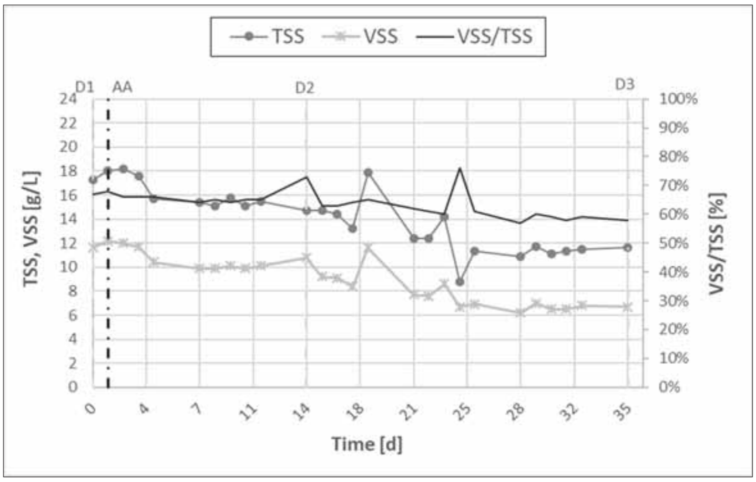


Fig. 3. Variation of the concentration of VSS and TSS in test P2. Note that D = dewatering, AA = test start

Table 4. Energetic consumption of tests P1 and P2

	Energy consumption				
Test	***kWh***	***kWh/kg$_{TSS\ removed}$***	***kWh/kg$_{VSS\ removed}$***	***kWh/m^3***	***kWh/(m^3*d)***
P1	27,428	8.63	8.41	33.35	1.16
P2	31,534	10.31	13.82	32.05	1.75

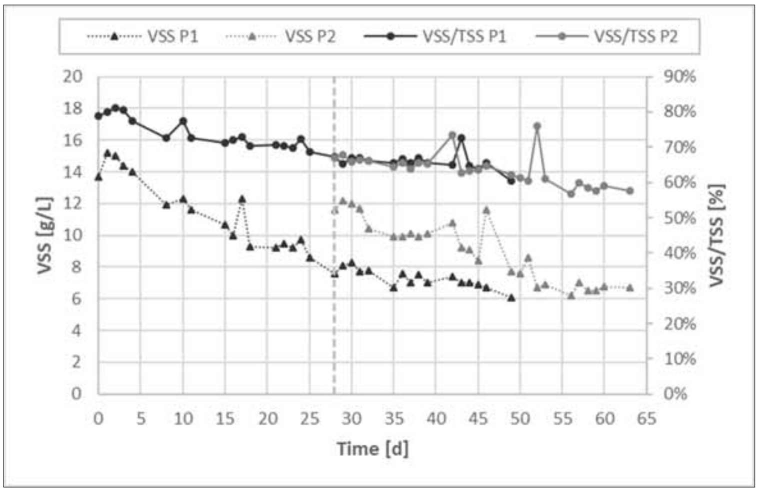


Fig. 4. Comparison between VSS concentration and VSS/TSS ratio in P1 and P2, at the same value of VSS/TSS ratio

Table 5. Reaction rate of VSS abatement at the temperature of the test T_P and at the standard temperature T=20°C

Test	***T_P [°C]***	***$K_{(Tp)}$ [d^{-1}]***	***$K_{(20°C)}$ [d^{-1}]***
P1	31.0	0.0152	0.0099
P2	32.3	0.0191	0.0118

Under real conditions, the highest reaction rate is that of P2, characterized by the highest temperature and aeration. However, the reaction rate values at the homogeneous temperature of 20°C, were more similar to each other than under real conditions, thus suggesting that the process temperature had a greater influence on the reaction kinetics than the DO concentration, according to literature (Anjum et al., 2016; Arunachalam et al., 2004). Arunachalam et al. (2004), comparing aerobic digestion in batch at high (3-4 mg/L) and low (0.2-1 mg/L) DO concentrations, and observed slower VSS digestion at low DO concentrations. It should be noted that the experiment was conducted at lab scale under controlled conditions, while our work was conducted at in a plant at full-scale under operating conditions. It can be hypothesized that, while higher aeration could favour faster VSS abatement under optimal conditions, real conditions might mitigate this effect.

3.4. Dewaterability

To compare results, the quantities of dewatered sludge obtained in each dewatering phase were calculated starting from 1 m^3 of stabilization sludge, and divided as dry and liquid fractions. During the test P1, it was produced 87.5 kg of dewatered sludge, of which 18.2 kg (20.8%) was dry fraction and 69.3 kg was aqueous fraction, at the first dewatering; 77.1 kg of dewatered sludge, of which 15.4 kg (20.0%) was dry fraction and 61.7 kg was aqueous fraction, at the second dewatering; 54.3 kg of dewatered sludge, of which 10.1 kg (18.6%) was dry fraction and 44.2 kg was aqueous fraction, at the third dewatering. Between the first and third dewatering there was a 38% reduction of the dewatered sludge produced.

During the test P2, starting from 1 m^3 of stabilization sludge, it was produced: 75.6 kg of dewatered sludge, of which 17.8 kg (23.6%) was dry part and 57.8 kg was aqueous part, during the first dewatering; 67.4 kg of dewatered sludge, of which 14.7 kg (21.8%) was dry part and 52.7 kg was aqueous part, during the second dewatering; 53.6 kg of dewatered sludge, of which 11.6 kg (21.7%) was dry part and 42.0 kg was aqueous part, during the third dewatering. Between the first and third dewatering there was a 29% reduction of the dewatered sludge produced. The comparison between the two tests was started in correspondence with similar values of TSS: on the third day of test P1, with a value of TSS of 18.0 g/L (Fig. 5).

It is possible to observe that the higher reduction was in P1 (38%). On the other hand, final TSS values obtained were 18.6% in P1 and 21.7% in P2: in P2, a higher quantity of dry fraction and a lower quantity of liquid fraction, in percentage, were obtained indicating a meliorate dewaterability. These results suggested that, when the aerobic stabilization process was pushed, as in P1 where we had a longer duration to reach a better stability of the VSS/TSS ratio values, it did not result in a higher sludge reduction, but rather in an improved sludge stabilization. In P1, a 60% VSS abatement was achieved, which corresponds to a high quality sludge in terms of characteristics for reuse in agriculture.

In the liquid fraction from dewatering, both TN and N-NH$_4$ concentrations increased in P1, suggesting that the low DO concentration prevented anaerobic conditions for denitrification but was insufficient to induce aerobic conditions for nitrification. In P2, the TN concentration increased, as shown in (Ji *et al.*, 2016), while decreasing that of N-NH$_4$: it is hypothesized that the greater aeration triggered spontaneous nitrification.

3.5. Simulation of performance under homogeneous conditions

Table 6 and Fig. 6 report the results of the simulation of performances of the stabilization under homogeneous conditions, for tests P1 and P2, carried out in batch, and also simulating the tests performed with continuous sludge feeding.

The simulation showed that, for test P1, in 45 days of stabilization in batch, the total amount of dewatered sludge produced from 1 m^3 of stabilization sludge would decrease from 95.0 kg (at 20% TSS), to 64.2 kg (at 18% TSS). The VSS/TSS ratio would decrease from about 79% to 65%, with an estimated energy consumption of 52 kWh per unit of volume of sludge treated. The 90% VSS removal yields would have been obtained after 151 days (in batch), and after 590 days (in continuous). For the test P2, in 45 days of stabilization in batch, the total amount of dewatered sludge produced from 1 m^3 of stabilization sludge would decrease from 95 kg (at 20.0% TSS), to 59 kg, (at 17.7% TSS). The VSS/TSS ratio would decrease from 79% to 61%, with an estimated energy consumption of 79 kWh per unit volume of sludge treated. The VSS removal yields of 90% would have been obtained after 120 days (in batch), and after 470 days (in continuous).

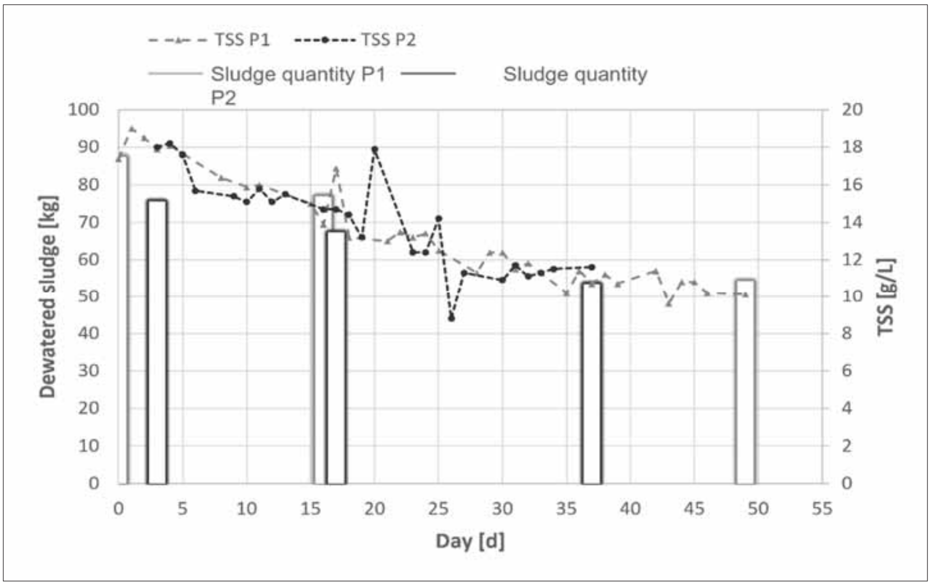


Fig. 5. Comparison of dewatered sludge quantities produced from 1 m^3 of stabilization sludge

Table 6. Results of the simulation of the stabilization performance on 1 m^3 of sludge under homogeneous initial conditions (P1, and P2), in batch and in continuous, in terms of energy consumption, VSS/TSS ratio and amount of dewatered sludge produced from 1 m^3 of stabilization sludge

Time [d]	***VSS [kg]***		***VSS$_{cont}$ [kg]***		***TSS [kg]***		***TSS [%]***		***H$_2$O [kg]***		***TOT [kg]***		***VSS/TSS [%]***		***Energy consumption [kWh]***	
	P1	***P2***	***P1***	***P2***	***P1***	***P2***	***P1***	***P2***	***P1***	***P2***	***P1***	***P2***	***P1***	***P2***	***P1***	***P2***
0	15.0	15.0	15.0	15.0	19.0	19.0	20.0	20.0	76.0	76.0	95.0	95.0	78.9%	78.9%	0.0	0.0
7	13.5	13.1	13.6	13.2	17.5	17.1	19.7	19.6	71.3	70.0	88.8	87.2	77.1%	76.6%	8.2	12.3
14	12.1	11.5	12.4	11.8	16.1	15.5	19.4	19.3	67.1	64.8	83.2	80.3	75.2%	74.2%	16.3	24.5
21	10.9	10.0	11.4	10.7	14.9	14.0	19.1	18.9	63.2	60.1	78.1	74.2	73.1%	71.5%	24.4	36.8
30	9.5	8.5	10.3	9.5	13.5	12.5	18.7	18.5	58.8	55.0	72.3	67.4	70.4%	67.9%	34.9	52.6
45	7.6	6.4	8.9	8.1	11.6	10.4	18.0	17.7	52.7	48.1	64.2	58.5	65.4%	61.3%	52.4	78.9

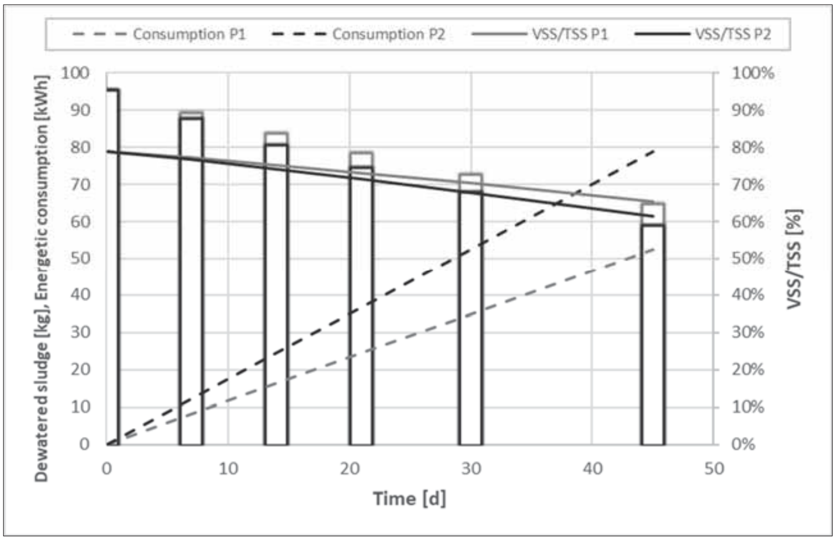


Fig. 6. Stabilization performance on 1 m^3 of sludge under homogeneous initial conditions in terms of energy consumption, VSS/TSS ratio and amount of dewatered sludge produced from 1 m^3 of stabilization sludge (represented by the vertical bars) , in test P1(light grey lines) and P2 (dark grey lines)

The VSS/TSS ratios would have similar trends, which diverge as the retention times considered increase (Fig. 6). Sludge is stabilized more rapidly in P2. The amounts of dewatered sludge produced from 1 m^3 of stabilization sludge would be similar in tests P1 and P2, with the difference increasing with time. Differences would be noticed after about 20 days of treatment (Fig. 6). The energy consumption is higher in P2, characterized by higher aeration, with the divergence increasing with time (Fig. 6).

In general, for VSS/TSS ratio and dewatered sludge production, clear differences are noted only for high retention times, while for more realistic duration, as of less than two weeks, there are no substantial differences. On the contrary, higher energy consumption could be noticed in P2 since the shorter duration of a few days. For a 7-day sludge treatment time, the simulated removal of VSS was approximately 10% in P1 and 12% in P2; it was 19% in P1 and 23% in P2 for a 14-days treatment time. The difference in VSS removal for batch and continuous sludge feed stabilisation is minimal for low retention times. If, on the other hand, high retention times are considered, batch treatment is much faster than continuous feeding in achieving removal yields of 90%.

The simulation model of stabilization performance was built on data from only two tests and it was based on several approximations. For this reason, the numerical results obtained are not intended as exact values, but rather as a likely prediction of actual performance.

Based on the results obtained, aerobic stabilization would need high retention times to reach VSS reduction compared to other sludge minimization processes. As an example, the MBR thermophilic process with intermittent aeration, showed, at a pilot scale, a VSS removal efficiency > 80%, for a retention time < 15 d (Collivignarelli et al., 2017). Ozonation was reported to achieve a reduction in TSS from 30% to 99% (water line) and from 10% to 60% (sludge line), for a treatment duration of up to 2 weeks at lab or pilot scale, the great variability in the performance being influenced by the dosage of the oxidizing agent (Collivignarelli et al., 2019). An experimental full-scale test reported 39% sludge reduction by applying ozonization and mechanical dewatering, for an average treatment time of 14 days (Peroni et al 2022).

Among study limitations, the results of experimental tests were carried out exclusively in batch mode on a single full-scale plant, but they represent the starting point for further research. Future studies should focus on verifying the effectiveness of continuous and alternating-cycle stabilization under real conditions with continuous sludge feeding; on researching other possible influencing factors on stabilization performance; and, on repeating the same experimental tests on other existing plants to identify conclusions of general validity.

4. Conclusions

The study permitted to investigate the potential of the aerobic stabilisation compartment of a real plant to provide operating indications. The performance of the aerobic sludge stabilization was studied in two experimental tests comparing different DO concentrations (1 mg/L and >3 mg/L). A VSS abatement of 60% and 44% was reached in the two tests respectively. The aerobic stabilization coupled with the mechanical dewatering had the potential to reduce the TSS up to about 40% for retention times longer than 1 month.

The simulation of performance carried out under homogeneous conditions, showed a VSS abatement of about 10% in P1 and 12% in P2, for a sludge treatment time of 7 days, and also a VSS abatement of about 19% in P1 and 23% in P2 for a treatment time of 14 days.

Therefore, the study showed that, for sludge treatment times of up to 14 days, which can be realistically replicated in management practice, the removal of VSS, as well as the reduction of dewatered sludge produced, did not differ substantially by varying the DO concentration in continuous aeration in the aerobic stabilization. Targeting a lower DO concentration, on the other hand, required lower aeration, and consequently implied a lower energetic consumption.

Acknowledgements

The Authors acknowledge the staff of Acque Bresciane (AB) Srl, and students Silvia Minelli and Paolo Ariotti, for their support and contribution to data collection and field activities. Authors acknowledge Roberta Pedrazzani for the microscopical determination of bacteria in the sludge during foaming.

Funding

This research was supported by the funding PON Ricerca e Innovazione Green D.M. 1062/21, from the Italian Ministry of University (MUR), contracts number 4/2022 of 11/01/2022 and 0225788 of 08/08/2022.

References

Anderson B.C., Mavinic D.S., (1992), Assessment and application of kinetic reaction rates in pilot-scale semi-continuous aerobic sludge digestion, *Environmental Technology*, **13**, 115-128.

Anjum M., Al-Makishah N.H., Barakat M.A., (2016), Wastewater sludge stabilization using pre-treatment methods, *Process Safety and Environmental Protection*, **102**, 615-632.

Arunachalam R., Shah H.K., Ju L.K., (2004), Aerobic sludge digestion under low dissolved oxygen concentrations, *Water Environment Reserach*, **76**, 453-462.

Atay Ş., Akbal F., (2016), Classification and effects of sludge disintegration technologies integrated into sludge handling units: an overview, *CLEAN–Soil, Air, Water*, **44**, 1198-1213.

Bertanza G., Canato M., Heimersson S., Laera G., Salvetti R., Slavik E., Svanström M., (2015a), Techno-economic and environmental assessment of sewage sludge wet oxidation, *Environmental Science and Pollution Research*, **22**, 7327-7338.

Bertanza G., Canato M., Laera G., (2018), Towards energy self-sufficiency and integral material recovery in wastewater treatment plants: assessment of upgrading options, *Journal of Cleaner Production*, **170**, 1206-1218.

Bertanza G., Canato M., Laera G., Tomei MC., (2015b), Methodology for technical and economic assessment of advanced routes for sludge processing and disposal, *Environmental Science and Pollution Research*, **22**, 7190-7202.

Bertanza G., Collivignarelli C., (2012), *Water treatment plants: operational control and functional testing*, (in Italian), Hoepli Editore, Milan, Italy.

Burger W., Krysiak-Baltyn K., Scales P.J., Martin G.J., Stickland A.D., Gras S.L., (2017), The influence of protruding filamentous bacteria on floc stability and solid-liquid separation in the activated sludge process, *Water Research*, **123**, 578-585.

Campo G., Cerutti A., Lastella C., Leo A., Panepinto D., Zanetti M., Ruffino B., (2021), Production and destination of sewage sludge in the Piemonte Region (Italy): the results of a survey for a future sustainable management, *International Journal of Environmental Research and Public Health*, **18**, 3556, https://doi.org/10.3390/ijerph18073556.

CNR-IRSA, (2003), Papers of the Water Research Institute, 64, Analytical Methods for Sludge. Vol. 2. Technological parameters , (in Italian), National Research Council - Water Research Institute, Rome, Italy.

Collivignarelli C., Bertanza G., (2012), *Wastewater treatment plants*, In: *Sanitary and environmental enigineering*, (in Italian), CittàStudi, Turin, Italy, 207-269.

Collivignarelli M.C., Abbà A., Carnevale Miino M., Torretta V., (2019), What advanced treatments can be used to minimize the production of sewage sludge in WWTPs?, *Applied Sciences*, **9**, 2650, https://doi.org/10.3390/app9132650.

Collivignarelli M.C., Abbà A., Castagnola F., Bertanza G., (2017), Minimization of municipal sewage sludge by means of a thermophilic membrane bioreactor with intermittent aeration, *Journal of Cleaner Production*, **143**, 369-376.

De Feo G., De Gisi S., Galasso M., (2012), *Wastewater. Design and management of wastewater treatment plants*, (in Italian), Dario Flaccovio Editore, Palermo, Italy.

De Oliveira T.S., Corsino S.F., Di Trapani D., Torregrossa M., Viviani G., (2018), Biological minimization of excess sludge in a membrane bioreactor: effect of plant configuration on sludge production, nutrient removal efficiency and membrane fouling tendency, *Bioresource Technology*, **259**, 146-155.

Domini M., Abbà A., Bertanza G., (2022a), Analysis of the variation of costs for sewage sludge transport, recovery and disposal in Northern Italy: a recent survey (2015-2021), *Water Science and Technology*, **85**, 1167-1175.

Domini M., Bertanza G., Vahidzadeh R., Pedrazzani R., (2022b), Sewage sludge quality and management for circular economy opportunities in Lombardy, *Applied Sciences*, **12**, 10391, https://doi.org/10.3390/app122010391.

EU, (2022), Support to the evaluation of the Sewage Sludge Directive Final study report. Commission staff working document evaluation. Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture Publications Office of the European Union, On line at: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52023SC0157

Foladori P., Andreottola G., Ziglio G., (2010), *Sludge Reduction Technologies in Wastewater Treatment Plants*, IWA Publishing, London, UK.

Guo J.S., Fang F., Yan P., Chen Y.P., (2020), Sludge reduction based on microbial metabolism for sustainable wastewater treatment, *Bioresource Technology*, **297**, 122506, https://doi.org/10.1016/j.biortech.2019.122506.

Hii K., Baroutian S., Parthasarathy R., Gapes D.J., Eshtiaghi N., (2014), A review of wet air oxidation and thermal hydrolysis technologies in sludge treatment, *Bioresource Technology*, **155**, 289-299.

ISPRA, (2022), Sustainability in the recovery of biological sludge in agriculture, Italian Institute for Environmental Protection and Research, On line at: https://www.isprambiente.gov.it/en/archive/news-and-other-events/ispra-news/2022/09/sustainability-in-the-recovery-of-biological-sludge-in-agriculture

Ji B., Yang K., Chen W., Wang J., Zhu L., (2016), Impacts of Dissolved Oxygen and Initial Sludge Concentrations on Aerobic Stabilization of Sewage Sludge, *Polish Journal of Environmental Studies*, **25**, 153-157.

Madoni P., Davoli D., Gibin G., (2000), Survey of filamentous microorganisms from bulking and foaming activated-sludge plants in Italy, *Water Research*, **34**, 1767-1772.

Mininni G., Laera G., Bertanza G., Canato M., Sbrilli A., (2015), Mass and energy balances of sludge processing in reference and upgraded wastewater treatment plants, *Environmental Science and Pollution Research*, **22**, 7203-7215.

Morello R., Di Capua F., Esposito G., Pirozzi F., Fratino U., Spasiano D., (2022), Sludge minimization in mainstream wastewater treatment: Mechanisms, strategies, technologies, and current development, *Journal of Environmental Management*, **319**, 115756, https://doi.org/10.1016/j.jenvman.2022.115756.

Øegaard H., (2004), Sludge minimization technologies-an overview, *Water Science and Technology*, **49**, 31-40.

Pérez-Elvira S.I., Nieto Diez P., Fdz-Polanco F., (2006), Sludge minimization technologies, *Reviews in Environmental Science and Bio/Technology*, **5**, 375-398.

Peroni M., Pasinetti E., Soderino D., Cascio M., Preda D., Catenacci A., Canziani R., Bernardi M., Oliva D., (2022), Ozonolysis in biological oxidation: a full-scale case study (in Italian), *Ingegneria dell'Ambiente*, **9**, 248-264.

Salisu S., Gao N., Quan C., Yanik J., Artioli N., (2023), Co-gasification of rice husk and plastic in the presence of CaO using a novel ANN model-incorporated Aspen plus simulation, *Journal of the Energy Institute*, **108**, 101239, https://doi.org/10.1016/j.joei.2023.101239.

Sam T., Le Roes-Hill M., Hoosain N., Welz P.J., (2022), Strategies for controlling filamentous bulking in activated sludge wastewater treatment plants: the old and the new, *Water*, **14**, 3223, https://doi.org/10.3390/w14203223.

Sanchez J.B., Alonso J.M.Q., Oviedo M.D.C., (2006), Use of microbial activity parameters for determination of a biosolid stability index, *Bioresource Technology*, **97**, 562-568.

Scrinzi D., Ferrentino R., Baù E., Fiori L., Andreottola G., (2022), Sewage Sludge Management at District Level: Reduction and Nutrients Recovery via Hydrothermal Carbonization, *Waste and Biomass Valorization*, **14**, 2505-2517.

Semblante G.U., Hai F.I., Dionysiou D.D., Fukushi K., Price W.E., Nghiem L.D., (2017), Holistic sludge management through ozonation: a critical review, *Journal of Environmental Management*, **185**, 79-95.

Shrestha B., Hernandez R., Fortela D.L.B., Sharp W., Chistoserdov A., Gang D., Revellame E., Holmes W., Zappi M.E., (2020), A review of pretreatment methods to enhance solids reduction during anaerobic digestion of municipal wastewater sludges and the resulting digester performance: implications to future urban biorefineries, *Applied Science*, **10**, 9141, https://doi.org/10.3390/app10249141.

Silva C., Rosa M.J., (2020), Performance assessment of 23 wastewater treatment plants-a case study, *Urban Water Journal*, **17**, 78-85.

Tas D.O., (2010), Respirometric assessment of aerobic sludge stabilization, *Bioresource Technology*, **101**, 2592-2599.

Yao S., Ma F., Liang B., Wang Y., Xie Y., Hao L., Zhu T., (2021), Mechanism investigation of excess sludge disintegration by stirred ball mill-utilized transmission electron microscope observation and peptidoglycan concentration determination, *Waste and Biomass Valorization*, **12**, 6543-6554.

Zupančič G.D., Roš M., (2008), Aerobic and two-stage anaerobic–aerobic sludge digestion with pure oxygen and air aeration, *Bioresource Technology*, **99**, 100-109.

Environmental Engineering and Management Journal
October 2023, Vol. 22, No. 10, 1729-1734
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2023.147

"Gheorghe Asachi" Technical University of Iasi, Romania

HORIZONTAL SUBSURFACE FLOW PHYTOTREATMENT FOR DOMESTIC WASTEWATER TREATMENT: NITRIFICATION-DENITRIFICATION EFFICIENCY TESTED ON BERTALIA-UNIBO PILOT PLANT

Carmine Fiorentino*, Maurizio Mancini

Department of Civil, Chemical, Environmental and Materials Engineering – DICAM, University of Bologna, Viale Risorgimento, 2 - 40136, Bologna Italy

Abstract

Climate change and environmental crises have a very big impact on water cycle in terms of water availability. The scarcity of water impacts agricultural production, while its quality influences the safety of agricultural products and consequently public health. A sustainable way to supplement agricultural production and industrial water needs stands in the reuse of wastewater. Moreover, it is so necessary to develop smart, sustainable and efficient wastewater treatment technologies in terms of construction and management cost for small communities. Natural wastewater treatment systems represent a cost-effective treatment, already tested and implemented all around the world.

In this context, this study focuses on horizontal sub-surface flow phytotreatment systems implementation with the aim to understand the processes and features involved to optimize both design and technical management phases. This work is a continuation and extension of previous studies conducted by the authors and focuses on nitrification and denitrification processes.

To this aim, a pilot plant located on Bertalia-UNIBO campus in Bologna was monitored to evaluate the nitrification-denitrification efficiencies related to seasonal variation of Temperature, dissolved oxygen at different hydraulic retention time. The pilot plant was charged with a domestic wastewater and the emergent macrophytes were *Phragmites australis*. The tests show good nitrification efficiencies in summer (from 78% to 91%) at HRT more than 12 h and the resulting data were stable at 30h. Winter nitrification efficiencies are lower than summer (44%, 66%) at HRT more than 12 h. As expected, dissolved oxygen was greater in winter than summer. Denitrification efficiency were in the range 40% - 75%, increasing with HRT. Results also show that full scale implementations need HRT equal 30h in order to reach significant nitrification rates.

Key words: denitrification, nitrification, small plants, SFS-H phytotreatment, wastewater reuse

Received: May, 2023; Revised final: October, 2023; Accepted: October, 2023; Published in final edited form: October, 2023

1. Introduction

Climate change together with population growth and urbanization have a huge impact on water cycle in terms of water quality and availability. In the last years, many countries suffer from drought. Indeed, the number and duration of droughts have increased by 29% since 2000, as compared to the two previous decades (UNDRR, 2021). Hence, more than 2.3 billion people already face water stress, especially in developing countries. The scarcity of water impacts agricultural production, while its quality influences the safety of agricultural products such as fresh fruits or vegetables and consequently public health (FAO, 2017).

A sustainable way to supplement agricultural production and industrial water needs stands in the reuse of wastewater. Thus, on the one hand, research

---

* Author to whom all correspondence should be addressed: e-mail: carmine.fiorentino2@unibo.it; Phone: +39 051 2093751

and development in wastewater treatment must focus on the improvement of water quality in water bodies, where treated sewage is discharged, to reach adequate sanitary quality standards. On the other hand, it is necessary to develop smart, sustainable and efficient wastewater treatment technologies in terms of construction and management cost, with a direct impact on the treatment processes adopted. Natural wastewater treatment systems represent a cost-effective treatment, thoroughly tested and implemented all around the world (Barjoveanu et. Al., 2010; Kadlec and Wallace, 2009) which interest is still very high (Jiang and May Chui, 2022).

Processes involved in those systems are related to several natural parameters: plant growth, soil substrate and atmospheric parameters (such as Temperature, solar irradiation, wind). Consequently, it is a low-cost technology in terms of construction and maintenance (very low or even zero energy consumption), minimal hands-on maintenance (Kadlec et al., 2000; Vymazal, 2014). In the last years many studies have been conducted on efficiency of those systems mainly related on the HRT under different process conditions: influent sewage, previous treatments, soil media, plants and obviously different climatic zones and countries.

Ghosh and Gopal (2010) studied the efficiency of a subsurface flow constructed wetlands (CWs) used as tertiary treatment showing a good removal efficiency at 4 days HRT. The study also showed removal efficiency at lower HRT even if the system was not as stable. In subtropical climate Merino-Solís et al. (2015) set al studied the performance of a pilot plant for urban wastewater treatment consisting of anaerobic filter followed by a horizontal subsurface constructed wetland showing the real possibility to implement those systems in subtropical climate zones. According to the Italian environmental law, natural wastewater treatment systems are suitable and recommended for urban discharges of towns under 2000 population equivalent (PE) (DLGS, 2006). In wider terms, natural wastewater treatment plants are well suitable for small communities, less than 10000 PE (García et al., 2001; Garfí et al., 2017). In larger agglomeration, it would be arduous to achieve the legal discharge thresholds as the plant design and technical management is much complicated. Design difficulties are mainly related to the Nitrogen removal from wastewater while technical management difficulties are related to transient inlet loading, high wet weather flows due to runoff, primary treatment adequate management. Instead, the implementation of natural wastewater treatment plants for water reuse is a smart solution especially in small communities (like farmhouses, holiday parks) as reused water needs are close-range from the treatment facilities.

In this context, it is necessary to deepen the hydraulic behavior and the efficiency of natural treatment systems implemented in the specific climatic conditions of Northern Italy. To this aim this study focuses on Horizontal Sub-Surface flow (SFS-H) phytotreatment systems implementation with the aim to understand the processes and features involved to optimize both design and technical management phases.

This work is a continuation and extension of previous studies conducted by the authors Fiorentino and Mancini, (2020) and Mancini (2004), and focuses on nitrification and denitrification processes in Horizontal Sub-Surface flow (SFS-H). A pilot plant located on Bertalia-UNIBO campus in Bologna was monitored to measure and evaluate the nitrification-denitrification efficiency related to seasonal variation due to Temperature, Dissolved Oxygen (DO) at different Hydraulic Retention Time (HRT), from 1.5 to 30 hours. Seasonal monitoring also considers the vegetation state of plants (*Phragmites australis*). The pilot plant was charged with a domestic wastewater coming from bathrooms and bar activities of the Bertalia Engineering Campus. The measurement campaigns were performed over twelve months, to compare summer and winter conditions, considering the following parameters that affect the nitrification-denitrification processes such as: pH, Dissolved Oxygen (DO), Ammonia (NH_4^+-N) and Total Nitrogen (TN) concentrations.

2. Materials and methods

For this study, experimentations were conducted on the existing pilot plant scale located in Bertalia campus of the University of Bologna (School of Engineering) (Fig. 1a).

The experimental unit of the pilot plant consisting in a sedimentation tank followed by the Horizontal Sub-Surface flow tank called “SFS H-1” containing sand (diameter = 2-4 mm) in which were planted *Phragmites australis* (Fig. 1b). The pilot plant is fed by the raw sewage from the campus sewage system coming from toilets, canteen service and bar.

The sedimentation tank aims to avoid that suspended solids could clog the following SFS-H tank gravel bed, as often happens in biofiltering beds when the path from discharge point is short (Fig. 2). Eight monitoring campaigns were conducted in one year, in different seasonal conditions (five in summer and three in winter) setting three Hydraulic Retention times (HRT): 1.5, 12 and 30 hours. After an acclimatization time of the bed, the tests were done at HRT equal to 1.5 and 12 hours in order to have a complete and exhaustive timeline and to see the hydraulic steady state conditions (Fiorentino and Mancini, 2020). HRT equal to 30 hours, after the acclimatization time, is the minimum limit above which the system starts to be interesting in efficiency terms. During each monitoring campaign were measured: Ammonium Nitrogen (NH_4^+-N); Total Nitrogen (TN); Dissolved Oxygen (DO), Temperature (T). Ammonium nitrogen, dissolved oxygen, pH and temperature were measured on site using the Ion Selective Electrod Crison 9663C (NH_4^+-N) and the multiparameter system YSI 556 (DO, pH and T) in probe tubes specifically positioned at the beginning and the end of the SFS H-1 tank.

Fig. 1. (a) Bertalia campus of the University of Bologna (School of Engineering) - pilot plant location marked with black circle (44°30'50.4''N – 11°19'16.5''E); (b) pilot plant front view

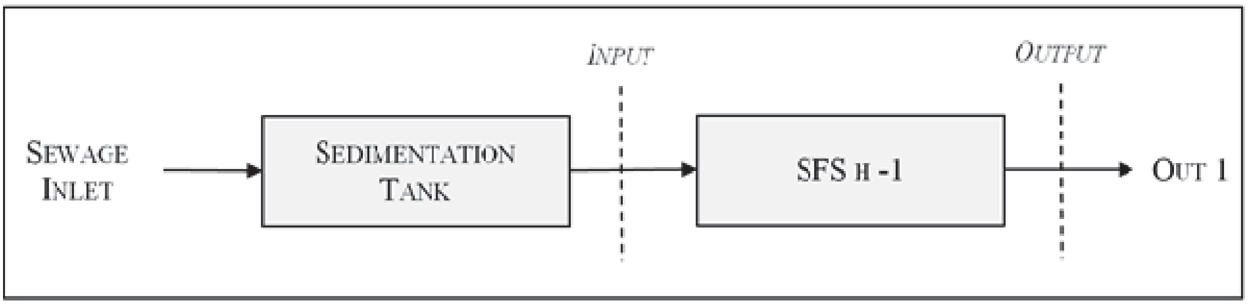


Fig. 2. Pilot plant flow scheme with sampling sections (Input and Output)

Simultaneously, samples were collected in the same tubes for TN analysis. TN was determined according to the 4500-N C. Persulphate Method from APHA Methods for water and wastewater (APHA, 1998). According to this method, TN concentration is determined by alkaline oxidation of all nitrogen compounds to nitrate at 100 to 110°C. The digestion reagent is potassium persulfate ($K_2S_2O_8$). Spectrophotometric measurement permits to obtain the Nitrate concentration, resulting from the oxidation, reading the absorbance against distilled water at the wavelength of 220 nm.

However, organic matter may also absorb at 220 nm and a second measure must be done at the wavelength of 275 nm to correct the nitrate value, as it does not absorb at this wavelength. The implementation of this method is more appropriate than Kjeldahl method in our case, because it hasbeen shown more precision and accuracy to determine TN in aqueous samples (Smart et al., 1981).

3. Results and discussion

Table 1 shows the results of experimentation in terms of Ammonium nitrogen (NH_4^+-N) and Total Nitrogen (TN), Dissolved Oxygen (DO) and Temperature (T) at different HRT in summer and winter. Nitrification and denitrification efficiency have been calculated from NH_4^+-N and TN monitoring results and reported in columns five and eight. During the monitoring campaigns M6-M7-M8 was not possible to measure TN and consequently the denitrification efficiency ("-" in Table 1). Each measurement campaign has been called "M" with progressive number from 1 to 8 followed by "Summer" or "Winter", depending on the monitoring season. DO and T is reported in the last two columns of Table 1 and discussed to understand the process conditions in each monitoring campaign.

We observe that nitrification efficiency increase with HRT in winter, from 16% to 66% with similar NH_4^+-N inlet concentrations. Summer nitrification efficiency in M2, M3 (HRT=12h) M4 and M5 (HRT = 30h) is higher than M1 (HRT=1.5h), in accordance with winter results but we don't observe a marked increase with higher HRT even if the value is very similar. This could be due to the NH_4^+-N inlet concentrations variation, from 22.12 mgN/L to 57.66 mgN/L, and in particular in M4 we observe a good removal efficiency (81%) with input concentration very high (57.66 mgN/L) showing that nitrification process is stable and efficient at this HRT.

The consideration made above is even more clearer in Fig. 3 where we reported the NH_4^+-N results for each measurement campaign and we observe that vertical line corresponding to M4 is the biggest meaning that is the biggest NH_4^+-N decrease.

Concerning the denitrification process, the data shown a TN removal efficiency increase with HRT, from 40% to 75% with Input form 26.54 mgN/L to 69.19 mgN/L. Also in this case in M4 we observe (Fig.

4) the best removal efficiency (75%) with the higher Input concentration (69.19 mgN/L).

DO concentration measured in the tank gravel bed is greater than 2 mg/L, lower limit below which oxi-nitrification process may not operate. In general terms, Oxygen inlet in the system occurs both in winter and summer but, as expected, DO concentrations are higher in winter than summer due to due to the higher oxygen saturation concentration at lower temperatures. Temperature measures follows seasonal variation and directly affects the degradation kinetics: lower. Temperature correspond to lower nitrification efficiencies. The nitrification efficiency variations between summer and winter also depends on the photosynthetic activity of the plants, *Phragmites australis* in this case, which is responsible of the oxygen concentration near the roots. Oxigen supply near the roots is maximum in summer when the plants are in the vegetative stage (Wang et al., 2019).

4. Conclusions

The study focuses Horizontal Sub-Surface flow (SFS-H) implementation for small communities and wastewater reuse. To this aim, the efficiency of nitrification and denitrification processes in SFS-H have been tested in Bertalia-UNIBO pilot plant conducting eight monitoring campaigns at different Hydraulic Retention Rates, in summer and winter. The tests show good nitrification efficiencies at HRT more than 12 h even if the data start to be stable at HRT equal to 30h.

It is possible to consider that HRT more than 30h, realist for full scale implementations, this process is even more stable. In any case, it is important to point out that, removal efficiency is strictly connected to treated sewage and in this it comes case from the Bertalia Campus facilities (toilets, canteen service and bar) that was already oxygenated.

Table 1. NH_4^+-N, TN, DO and T monitoring data in INPUT and OUTPUT sections, in summer and winter measurement campaigns in different Hydraulic Retention Time (HRT)

Measurement Campaign	*HRT (h)*	*NH_4^+-N (mgN/L)*	*NH_4^+-N (mgN/L)*	*Nitrification efficiency (%)*	*TN (mgN/L)*	*TN (mgN/L)*	*Denitrification efficiency (%)*	*DO (mg/L)*	*T (°C)*
		Input	*Output*		*Input*	*Output*			
M1 - Summer	1.5	30.11	19.48	35	36.13	21.79	40	1.56	20.2
M2 - Summer	12	24.60	2.30	91	29.52	10.88	63	2.92	19.5
M3 - Summer	12	22.12	2.95	87	26.54	13.38	50	2.44	21.5
M4 - Summer	30	57.66	11.18	81	69.19	17.18	75	2.39	28.2
M5 - Summer	30	29.18	6.36	78	35.02	12.70	64	1.99	22.0
M6 - Winter	1.5	35.39	29.72	16	-	-	-	4.03	6.5
M7 - Winter	12	33.45	18.86	44	-	-	-	4.24	3.9
M8 - Winter	30	32.21	11.02	66	-	-	-	4.14	6.1

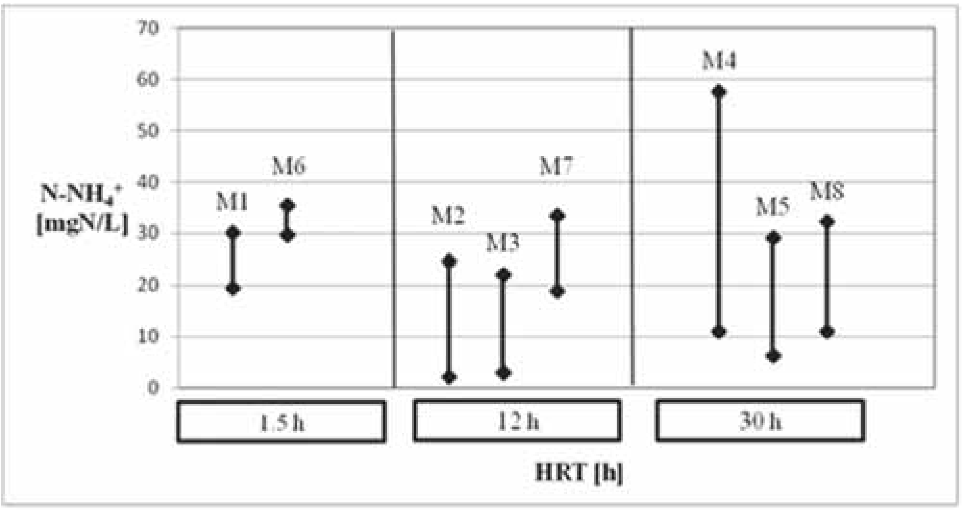


Fig. 3. Ammonium concentration in INPUT and OUTPUT sampling points in summer (M1, M2, M3, M4 and M5) and winter (M6, M7 and M8) related to each HRT

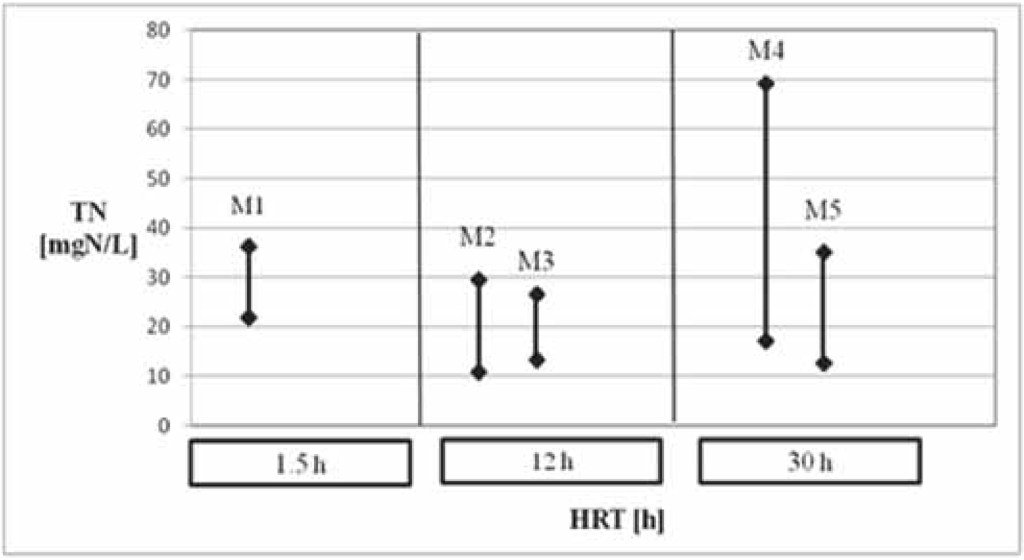


Fig. 4. Total Nitrogen concentration in INPUT and OUTPUT sampling points in summer (M1, M2, M3, M4 and M5) and winter (M6, M7 and M8) related to each HRT

Denitrification efficiency was evaluated only in summer and the values were in the range 40% - 75%, increasing with HRT. Hence, the data shown that denitrification process in those systems may have good efficiencies due to the presence of anoxic areas in the gravel bed. Denitrification efficiency also depends on nitrification in terms of ammonia concentration as well as organic matter.

As expected, Dissolved Oxygen values, measured in the tank gravel bed, are greater in winter than summer but they show the proper functioning of the system in terms of oxi-nitrification as all values are greater than 2 mg/L.

It has been confirmed that full scale implementations need HRT equal 30h in order to reach significant and reasonable nitrification rates. HRT more than 30 h should be tested in future.

References

APHA, (1998), *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, American Water Works Association, W.E.F., 20th Edition, Standard Methods, https://www.standardmethods.org/

Barjoveanu G., Cojocariu C., Robu B., Teodosiu C., (2010), Integrated assessment of wastewater treatment plants for sustainable river basin management, *Environmental Engineering and Management Journal*, **9**, 1251-1258.

DLGS, (2006), Legislative Decree Number 152/2003 (in Italian), Official Gazzette Number 88, 14-04-2006 – Suppl. Ord. Number 96, Rome, Italy, On line at: https://www.normattiva.it/uri-res/N2Ls?urn:nir:stato:decreto.legislativo:2003-06-12;152

FAO, (2017), Water for Sustainable Food and Agriculture, A report produced for the G20 Presidency of Germany, On line at: https://www.fao.org/3/i7959e/i7959e.pdf.

Fiorentino C., Mancini M., (2020), SFS-h Phytotreatment oxi-nitro rate tested in steady-state on Engineering-UNIBO pilot plant, *Environmental Engineering and Management Journal*, **19**, 1765-1771.

García J., Mujeriego R., Obis J.M., Bou J., (2001), Wastewater treatment for small communities in Catalonia (Mediterranean region), *Water Policy*, **3**, 341-350.

Garfí M., Flores L., Ferrer I., (2017), Life Cycle Assessment of wastewater treatment systems for small communities: Activated sludge, constructed wetlands and high rate algal ponds, *Journal of Cleaner Production*, **161**, 211-219.

Ghosh D., Gopal B., (2010), Effect of hydraulic retention time on the treatment of secondary effluent in a subsurface flow constructed wetland, *Ecological Engineering*, **36**, 1044-1051.

Jiang L., May Chui T.F., (2022), A review of the application of constructed wetlands (CWs) and their hydraulic, water quality and biological responses to changing hydrological conditions, *Ecological Engineering*, **174**, 106459, https://doi.org/10.1016/j.ecoleng.2021.106459.

Kadlec R.H., Wallace S.D., (2009), *Treatment Wetlands*, 2nd Edition, CRC Press, Taylor and Francis Group, Boca Raton, USA.

Kadlec R.H., Knight R.L., Vymazal J., Brix H., Cooper P., Haberl R., (2000), *Constructed Wetlands for Pollution Control: Processes, Performance, Design and Operation*, IWA Publishing, UK.

Mancini M.L., (2004), *Discharge in Coastal Seawater of Treated Wastewater from Riccione WWTP by Estuarine Transition Flow*, International Symposium on Sanitary and Environmental Engineering – SIDISA, 23-26 June, Catania, Italy.

Merino-Solís M.L., Villegas E., De Anda J., López-López A., (2015), The effect of the hydraulic retention time on the performance of an ecological wastewater treatment system: An anaerobic filter with a constructed wetland, *Water*, **7**, 1149-1163.

Smart M.M., Reid F.A., Jones J.R., (1981), A comparison of a persulfate digestion and the Kjeldahl procedure for determination of total nitrogen in freshwater samples, *Water Research*, **15**, 919-921.

UNDRR, (2021), GAR Special Report on Drought 2021, United Nations Office for Disaster Risk Reduction, Geneva, On line at: https://www.undrr.org/publication/gar-special-report-drought-2021

Vymazal J., (2014), Constructed wetlands for treatment of industrial wastewaters: a review, *Ecological Engineering*, **73**, 724-751.

Wang Q., Cao Z., Hu Y., Kong Q., Xu F., Du Y., Zhao C., (2019), Season effects on subsurface constructed wetlands performance: role of radial oxygen loss of *Phragmites australis*, *Clean - Soil, Air, Water*, **47**, 1800428, https://doi.org/10.1002/clen.201800428.

Environmental Engineering and Management Journal
October 2023, Vol. 22, No. 10, 1735-1744
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2023.148

"Gheorghe Asachi" Technical University of Iasi, Romania

REMEDIATION OF DIOXIN-CONTAMINATED SOILS THROUGH THERMAL DESORPTION AND VAPOR MANAGEMENT VIA THERMAL OXIDIZER AT BIÊN HÒA AIRBASE, VIETNAM

Aline Jordens*, **Maël Makoudi, Hatem Saadaoui, Jan Haemers**

Haemers Technologies SA, Chaussée de Vilvorde 104, 1120 Brussels, Belgium

Abstract

During the US-Vietnam War, millions of liters of harmful herbicides, including Agent Orange, were dumped in Vietnam, resulting in severe health issues caused by polychlorinated dibenzo-p-dioxins and dibenzofurans ("dioxins"). Even decades later, dioxin contamination continues to affect the local population. In response to this problem, the Center for Technology Environmental Treatment/Chemical Force (CTET/CF), the GAET Corporation (Vietnam), and HAEMERS Technologies SA (Belgium) have collaborated to establish a joint operation. Their aim is to assess the effectiveness of thermal desorption treatment on dioxin-contaminated soil at Biên Hòa Airbase.

The primary objective of this trial treatment is to demonstrate the capabilities of thermal treatment technology and design in meeting specific targets for dioxins at the site. The goal is to reduce the contamination level from over 17.000 ppt Toxic Equivalents (TEQ) to below 300 ppt TEQ. To achieve this, Haemers Technologies has developed a thermal treatment pilot plant comprising two main units: (i) The thermal pile of 237m³ composed of three types of materials: 187m³ of contaminated soils, 25m³ of contaminated sludges and 25m³ of soil washing cake; (ii) The vapor treatment unit composed of a thermal oxidizer where dioxins are destroyed and a quench tower that rapidly cools the vapor, preventing dioxin reformation. This unit generates no liquid or solid waste. The pilot project has successfully demonstrated that soil can be remediated by heating it to 335°C, with a pollutant removal rate of 99 wt.%. Additionally, dioxins can be destroyed at 1.100°C, achieving a destruction rate of 99.9999 wt.% in the thermal oxidizer. This zero-waste solution offers an improved method for remediating dioxin-contaminated soils, with air emission results meeting the standards set by Vietnam, the European Union (EU), and the United States (US).

Overall, this project showcases an efficient thermal treatment technology for remediating dioxin-contaminated soils. It ensures the complete destruction of all toxic components while enabling soil recycling.

Key words: agent orange, dioxins remediation, thermal conductive heating, thermal oxidizer, zero-waste

Received: May, 2023; Revised final: July, 2023; Accepted: September, 2023; Published in final edited form: October, 2023

1. Introduction

1.1. Site history and project timeline

During the US-Vietnam War, large quantities of herbicides known as the Rainbow agents were sprayed over Vietnam. Biên Hòa Airbase, which served as a joint operating base for the South Vietnam Air Force and the United States Air Force, stored thousands of barrels of Agent Orange, one of the most toxic herbicides used (USAID, 2016). It has been scientifically proven that Agent Orange causes severe health issues, including birth defects, neurological problems, and various types of cancer (Schecter et al., 2009; Young and Cecil, 2011). The composition of Agent Orange consists of 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid, with trace amounts of polychlorinated dibenzo-p-dioxins and dibenzofurans ("dioxins") present as impurities resulting from the production of 2,4,5-

---

[*] Author to whom all correspondence should be addressed: e-mail: aline.jordens@haemers-tech.com; Phone: +32 2 219 13 42

trichlorophenoxyacetic acid. Dioxins are highly insoluble in water, lipophilic, and extremely persistent in the environment (Kulkarni et al., 2008; Mudhoo et al., 2013).

Decades after the Vietnam War came to an end in 1975, the persistence and accumulation of dioxins continue to have adverse effects on the local population (Schecter et al., 2003; Tuyet-Hanh et al., 2015). To improve the living conditions for the residents, it became necessary to take measures to remediate the soil contaminated with dioxins.

The Center for Technology Environmental Treatment/Chemical Force (CTET/CF), the GAET Corporation, and HAEMERS Technologies SA have joined forces to establish a collaborative effort. Their primary objective is to conduct testing and evaluation activities to demonstrate the efficacy of thermal desorption treatment on dioxin-contaminated soils at Biên Hòa Airbase.

A thermal desorption treatment project for dioxin-contaminated soils has already been conducted in Đà Nẵng, Vietnam (USAID, 2010, 2015) and demonstrated the effectiveness of thermal treatment in achieving target levels of dioxins in soil. The main objective of this new operation at Biên Hòa airbase is to demonstrate the effectiveness of the Smart Burners^{TM} technology but, more importantly, to propose an improved solution compared to what has been done in the past, particularly in terms of contaminated vapor management.

Therefore, Haemers Technologies has designed a thermal treatment pilot plant composed of two main units:

- The soil pile, comprising various types of materials, is subjected to thermal treatment.
- The Vapor Treatment Unit (VTU): This unit is responsible for the destruction of dioxins. It comprises a thermal oxidizer, which ensures the complete destruction of dioxins, and prevents the formation of any liquid or solid waste during the process.

Haemers Technologies has undertaken this pilot-demonstration initiative at the Biên Hòa Airforce Base, aiming to implement its specialized technologies for the treatment of soil contaminated with Agent Orange. Although the project started in early 2020, it faced an interruption due to the COVID pandemic. Haemers Technologies returned to the site in late December 2021, resuming its activities and upholding its commitment to the demonstration project. The remediation process was restarted on February 2, 2022, and after a treatment duration of 40 days, the heating phase was concluded on March 14, 2022. The thermal pile successfully attained and sustained the target temperature of 335°C for a minimum of five days.

1.2. Technology outline

In the Haemers Technologies' process (Haemers, 2016) polluted soil is heated by conduction under the action of Smart Burners™ developed by Haemers Technologies. More precisely, steel tubes are inserted into the soil to be remediated. Hot gases, generated by Smart Burners™, circulate in the tubes in order to transfer heat to the soil. This results in the vaporization of the pollutants in the soil when their boiling temperature is reached.

The emitted vapors are extracted through perforated steel tubes, called vapor tubes, and are then either directed to a vapor treatment unit for further treatment or reintroduced into the flame generated by the Smart Burners^{TM} in the case of hydrocarbons pollution.

In *Ex situ* Thermal Desorption (ESTD) mode, heating tubes are inserted horizontally in pre-excavated soils (Fig. 1). ESTD is an on-site or near-site treatment that avoids truck traffic on public roads.

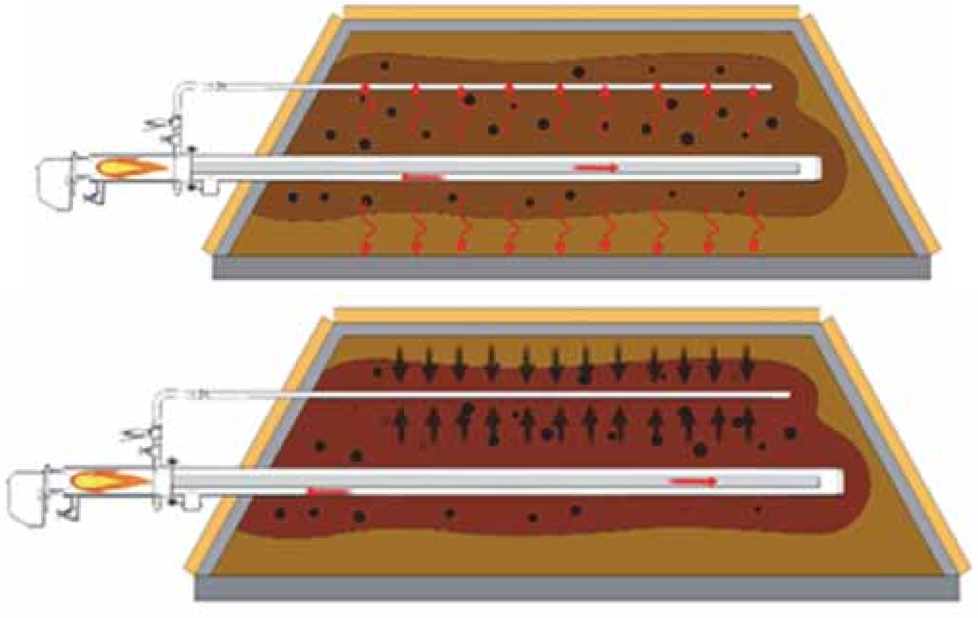


Fig. 1. *Ex situ* Thermal Desorption (ESTD) principle

2. Project design

2.1. Thermal pile design

The *Ex situ* Thermal Desorption (ESTD) takes place in a designated landfill area within Biên Hòa Airbase, where contaminated soils have been stored and restrained over the years. The ESTD is composed of 15 horizontal heating tubes and 13 exchanger tubes (Fig. 2), heating the soil by conduction. The exchanger tubes recover the combustion gases after their passage through the heating tubes, allowing a second passage through the pile and energy optimization. The fan, located at the back of the pile, drives the combustion gases from the burners through the tube network to the chimney. The combustion gases never encounter the contaminated soil and circulate through the tube network until they are released into the atmosphere. Conversely, the polluted vapors generated by the temperature rise in the pile are collected by the vapor tubes placed inside the pile and connected to a collector, placed in front of the pile, leading the polluted vapors to the vapor treatment unit.

The main goal of treatment is to lower the TCDD-TEQ concentration in contaminated soils to target objectives (Table 1), by heating the soil to the target temperature of 335°C. The top of the pile is covered with a layer of gravel, in which more vapor tubes, called secondary vapor tubes, are placed. These secondary vapor tubes are an additional security to avoid any fugitive emission or contamination of the concrete.

The whole pile is then covered with concrete and thermal insulation. The 237 cubic meters pile is made of materials from three origins: 187m^3 are contaminated soils directly extracted from the polluted area, 25m^3 are contaminated sludge and another 25m^3 are washing cake. Soil washing is a remediation technique using physical separation technique to remove contaminants from soils. Particles are separated by size. As a matter, most contaminants tend to be sorbed to clay and silt.

Washing separates those small particles from larger ones (sand and gravel) by breaking adhesive bonds and by mean of filtration. The smaller particles are then filtered and generate a highly contaminated filter-cake (Tran et al., 2022). To avoid the landfill disposal of this residue, the cake is treated in the ESTD pile. In this pilot project the washing cake comes from the Shimizu soil washing installation and was produced in 2019-2020 at Biên Hòa Airbase.

The sludges and washing cakes are arranged in "basins" in the pile of contaminated soil as presented in Fig. 3. The level of contamination of the different materials and their respective treatment objective are listed in Table 1. For soil and sludge materials, initial concentrations are sourced USAID environmental assessment at Biên Hòa Airbase (USAID, 2016). For washing cakes, analyses were performed by an accredited European laboratory on samples before treatment (Eigen method NEN-EN-1948).

2.2. Vapor Treatment Unit

The Vapor Treatment Unit (VTU) is specifically designed to manage the contaminated vapors generated during the soil treatment process and ensure their concentrations are reduced to comply with legal emission standards. There are two primary options available for the treatment of these vapors: condensation and adsorption on activated carbon or thermal oxidation. The first option, condensation and adsorption on activated carbon offers the advantage of low energy consumption. However, it does come with the drawback of producing liquid and solid waste.

The liquid obtained after condensation requires additional treatment, and the activated carbon used in the absorption process becomes a solid hazardous waste that needs proper disposal. In contrast, the second option, Thermal Oxidation, eliminates the need for additional treatment of liquid waste or the disposal of solid waste.

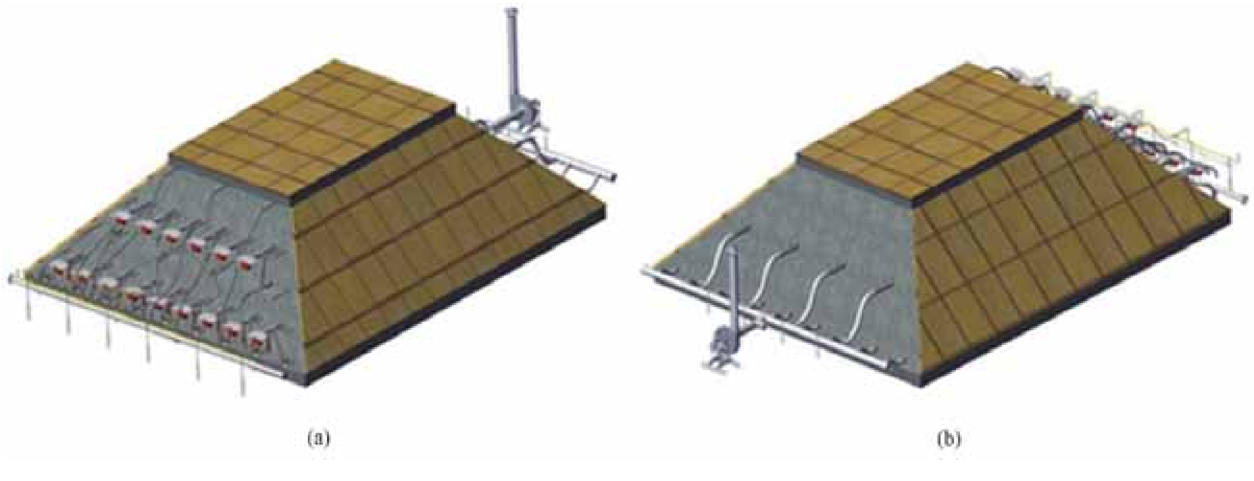


Fig. 2. ESTD design front (a), back (b)

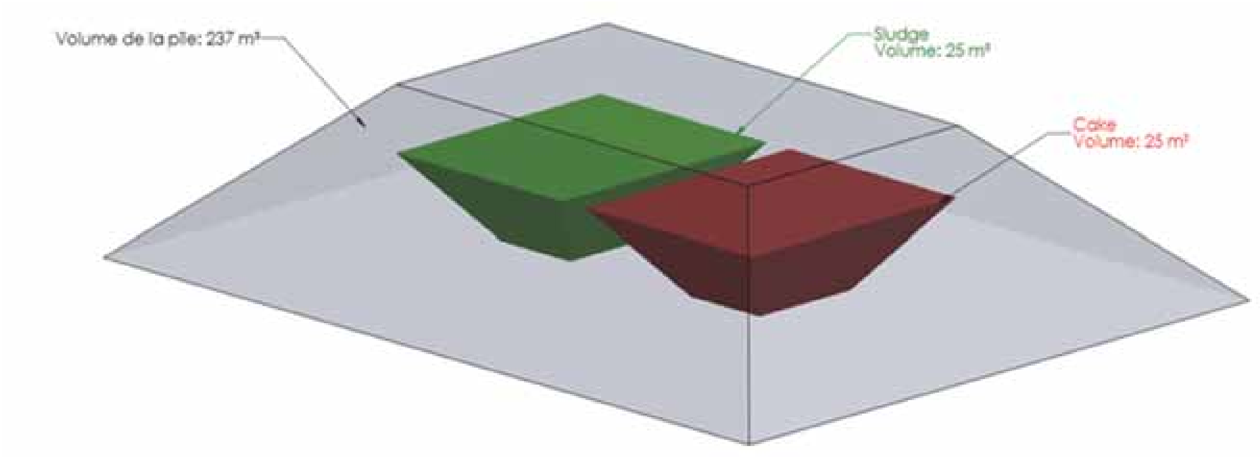


Fig. 3. ESTD composition: 187m³ of contaminated soils (in grey), 25m³ of sludges and 25m³ of washing cake

Table 1. Contaminated materials concentrations

Material	*Unit*	*Initial concentration*	*Treatment goal*	*Target DRE* (%)*
Soil	ppt TEQ	> 11,400	300 (Urban residential) 1200 (Industrial)	97.3 89.5
Sludges	ppt TEQ	> 5,410	150	97.2
Washing cake	ppt TEQ	> 17,200	300	98.2

** Destruction Rate Efficiency*

It achieves the destruction of contaminants through high-temperature combustion. While thermal oxidation may require more energy, it eliminates the complications associated with liquid and solid waste management. An insulated piping network collects the vapours and routes them to the VTU; some condensation occurs, and the condensates are recovered and treated in the thermal oxidizer as well, leaving no contaminated waste (zero waste technology). Energy efficiency for thermal oxidation can be improved by installing a recuperative heat exchanger. The option was judged not suitable for a pilot stage. The chosen design for vapor treatment consists of a Direct Fired Thermal Oxidizer. A direct fired Thermal Oxidizer (also known as a direct-fired oxidizer or afterburner) is an air pollution control technology that is used to treat exhaust gases containing volatile organic compounds (VOCs). The process involves heating the exhaust gas stream to a high temperature in a combustion chamber with a burner and maintaining it at that temperature for a residence time sufficient to allow the oxidation of the VOCs .

In order to achieve a destruction rate efficiency over 99.99%, the following criteria must be met within the oxidation chamber (Gao et al., 2015; Temme et al., 2015):

- temperature of minimum 1.100°C (preferably 1.200°C)
- oxygen content of minimum 6% (preferably 10%)
- residence time of minimum 1 second (preferably 2 seconds)
- good mixing conditions - High Turbulence (Re>>4,000).

Dioxin compounds reformation can happen in the cooling phase, within a temperature range of 200°C to 500°C, with the highest formation occurring at 350°C. The presence of oxygen, chlorine (Cl_2), and hydrocarbons can facilitate the reformation of dioxins. Additionally, factors such as the presence of dust and/or metals can contribute to the formation of dioxins (Buekens et al., 2001; Mukherjee et al., 2016). To avoid the reformation process, the hot gases pass through a quench tower to be cooled quickly enough below 200°C before being released into the atmosphere. To comply with Vietnamese regulations, a maximum temperature of 180°C at the stack has been set. The Vapor Treatment Unit configuration is presented in Fig. 4.

3. Treatment monitoring

The performance of the thermal treatment is evaluated by various parameters: temperature profile in the thermal pile over time, pressure into the soil, emissions at the venting and soil sampling.

3.1. Soil temperature monitoring

The increase in soil temperature is the principal indicator of the progress of decontamination. It is measured at the ‘cold points’ in the soil. A cold point is at the center of the triangle formed by every three tubes and is therefore the furthest point from the heat source (Fig. 5).

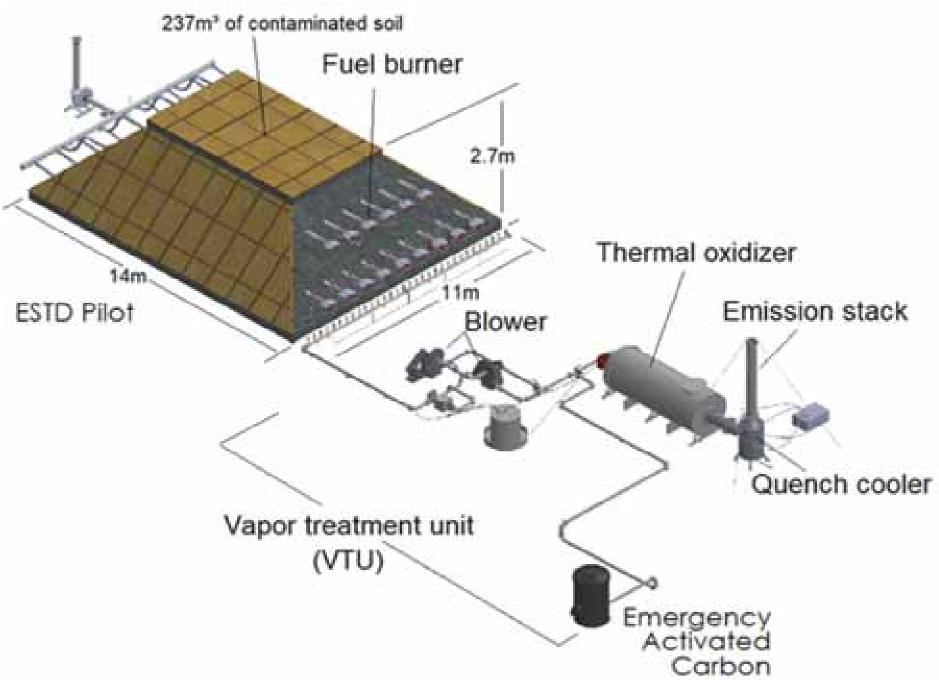


Fig. 4. Vapor Treatment Unit configuration

Temperature measurement is done through thermocouples. Thermocouples are devices consisting of two conductors that produce a temperature-dependent voltage to monitor large temperature ranges. Type-K thermocouples are used, allowing for measurements up to 800°C.

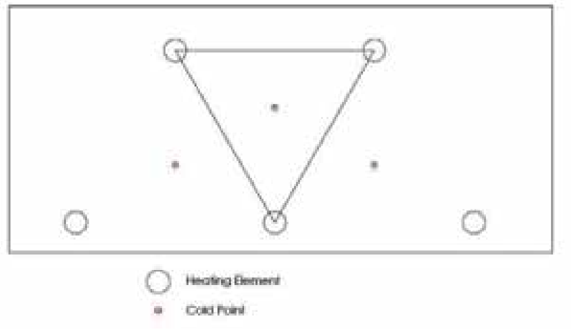


Fig. 5. Cold points

Soil temperature is measured at nine different locations, as described in Fig. 6 - T1 to T9 - and at four different depths within the thermal pile. A total of 36 temperature sensors are placed in the thermal pile.

3.2. Soil pressure monitoring

It is fundamental to control and keep track of the soil pressure during treatment. The aim of this monitoring is to ensure that a negative relative pressure in the soil ($P<P_{atm}$) is maintained, which will consequently prevent fugitive emissions during the treatment. For this project, two pressure wells (P1-P2) were installed and measurements were performed manually every day.

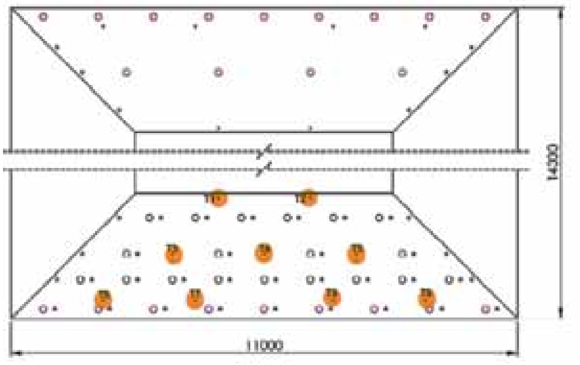


Fig. 6. Temperature monitoring locations

3.3. Emission control

The Vietnam-Russia Tropical Center (VRTC), an accredited Vietnamese laboratory, performed sampling at the outlet of the chimney during the treatment process. Six gas samples were collected between February 8 and 25, 2022, using the United States Environmental Protection Agency (USEPA) method 23 for analysis of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. The sampling equipment consisted of a glass fiber filter, a condenser, a trap, and four impingers with different contents (EPA, 2022).

Sample extraction and analysis followed the EPA method 23 procedures, using Gas Chromatography coupled with High-Resolution Mass Spectrometry. Toxicity Equivalence Factors (TEF) were used to correlate the toxicity of various dioxin and furan compounds, with the most toxic compound, 2,3,7,8-TCDD, having a TEF of 1. Each compound's concentration was multiplied by its respective equivalence factor, and the sum of these values constituted the total toxicity relative to 2,3,7,8-TCDD (Eq. 1) (EPA, 2022).

$$Total\ Equivalent\ Toxicity\ (TEQ) = \sum_{i=1}^{n} Ci \times TEF_i \qquad (1)$$

Toxicity Equivalence Factors (TEF) is established by WHO 2005 TEF (Table 2).

3.4. Soil sampling

Soil samples after treatment were collected in the cooled thermal pile and analysis by an accredited laboratory: Eurofins, Vietnam.

4. Treatment results and discussions

4.1. Soil temperature

4.1.1. Thermographies

Thermographies are heat maps representing the temperature distribution inside the thermal pile. This section presents the thermographies generated at different stages of heat treatment (10, 22, 30 and 40 days of treatment) (Fig. 7). Each thermography illustrates a vertical slice of the thermal pile: the front, the middle and the back of the pile. The evolution of the thermographies enables to visualize the evolution of the heat front in the pile.

The thermographies show that the whole mass of the thermal pile has heated up to the target temperature. After 10 and 22 days, the hot spots are localized next to the heating elements. As the treatment progresses, when 30 and 40 days of treatment are reached, the heat front gradually moves away from the heating tubes towards the so-called cold points (the most distant points from the heating elements).

4.1.2. Average temperature

As the data from thermocouples does not fully represent the global temperature evolution of the soil mass (measurement of coldest points of the thermal pile), Haemers Technologies employs the ANSYS Fluent simulation program to better determine the average temperature of the pile. Haemers Technologies has developed its own algorithm to control their sites and estimate optimal treatment stop. By comparing simulation data with previous sites, a more accurate representation of temperature evolution is achieved (Depasse et al., 2021).

The evolution of the average soil temperature is represented in the green line below. The red line represents the target temperature (335°C) (Fig. 8). The average temperature in the thermal pile has reached the target temperature of 335°C after 35 days of treatment. The target temperature was maintained for five days before stopping thermal treatment.

4.2. Pressure monitoring

Figure 9 shows the evolution of the vacuum in the pile, monitored at both wells (P1 and P2), during treatment. The vertical axis shows the pressure measured (in mbar), the horizontal axis the treatment time. Throughout the treatment process, a vacuum was maintained in the thermal pile, ensuring that the pressure remained below 0 mbar. These results provide evidence that no fugitive emissions occurred during the remediation process. The findings were further supported by ambient air monitoring conducted by the CTET: the ambient air quality remained in conformity throughout the pilot project, for all parameters monitored (dust and noise, volatile organic compounds (VOCs), chlorophenols and dioxins).

4.3. Emissions control results

The results of stack sampling analysis carried out between 08/02/2022 and 25/02/2022 are presented in Table 3 and Fig. 10. The emission standard, represented with the blue line, is 0.1 ng TEQ/Nm³ (or 100 pg TEQ/Nm³). As presented above, the norm is respected, and all emissions are compliant. These results confirm the efficiency of the thermal oxidizer and the proper oxidation of the dioxins inside.

4.4. Soil sampling results

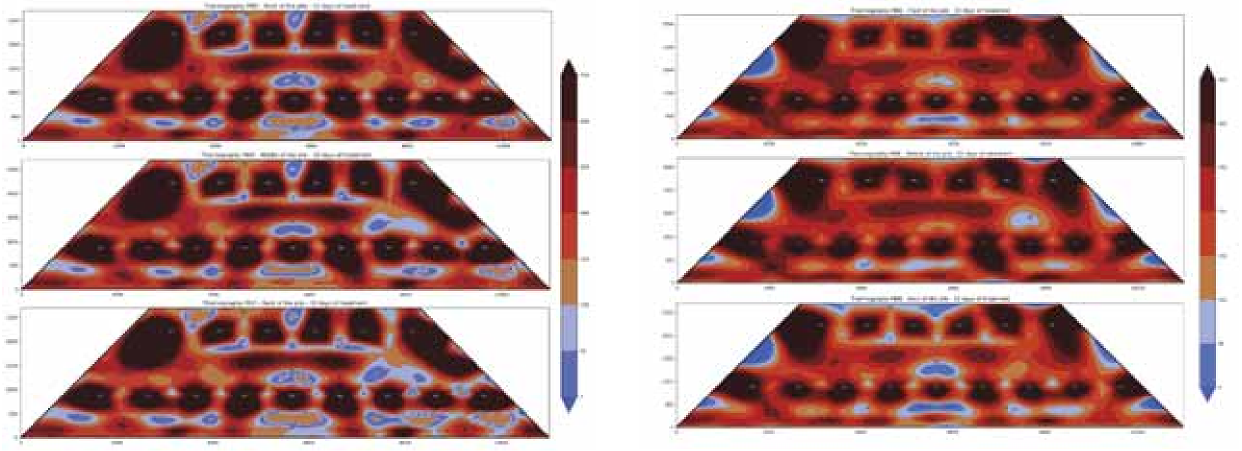
The results of the final sampling are available in Table 4. The two treated soil analysis were respectively performed by two laboratories: Agrolab (Accredited European laboratory) and Eurofins. Treated sludges and washing cake were analysed by Eurofins. As presented in Table 4, the treatment objective of each material (soil, sludges and washing cake) were met. The Destruction Rate Efficiency is over 99% for all samples.

4. Conclusions

In conclusion, the joint operation between CTET/CF, the GAET Corporation, and HAEMERS Technologies SA has successfully demonstrated the effectiveness of thermal desorption treatment on dioxin-contaminated soil at Biên Hòa Airbase. The pilot project has shown that dioxin-contaminated soil can be remediated after being heated to 335°C, and vaporized dioxins can be destroyed at 1,100°C. The thermal treatment technology and design have met the site-specific dioxins target levels, reducing contamination levels to less than 150 ppt TEQ. Soil sampling results confirmed that the treatment objectives were met, with a destruction rate efficiency of over 99% for all samples. The chosen design for vapor treatment consists of a direct-fired thermal oxidizer, which avoids any liquid/solid waste, and ensures that emissions meet Vietnamese, European, and US standards.

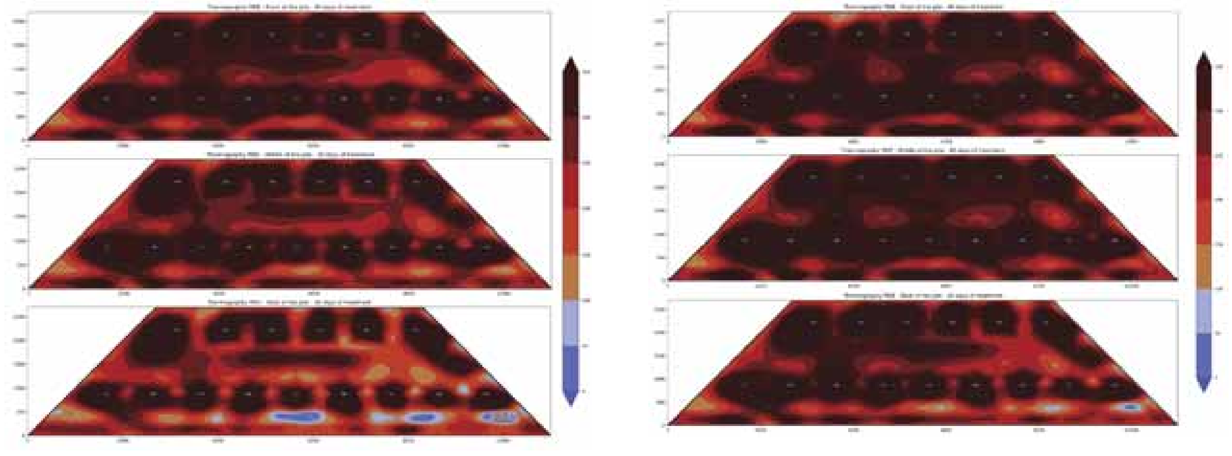
Table 2. *Toxicity Equivalence Factors (TEF)* of the most toxic dioxins and furans components

List number	*Most toxic dioxins and furans components*	*WHO-TEF*
1	**2,3,7,8-TCDD**	**1**
2	1,2,3,7,8-PeCDD	1
3	1,2,3,4,7,8-HxCDD	0.1
4	1,2,3,6,7,8-HxCDD	0.1
5	1,2,3,7,8,9-HxCDD	0.1
6	1,2,3,4,6,7,8-HpCDD	0.01
7	OCDD	0.0003
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PeCDF	0.03
10	2,3,4,7,8-PeCDF	0.3
11	1,2,3,4,7,8-HxCDF	0.1
12	1,2,3,6,7,8-HxCDF	0.1
13	2,3,4,6,7,8-HxCDF	0.1
14	1,2,3,7,8,9-HxCDF	0.1
15	1,2,3,4,6,7,8-HpCDF	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01
17	OCDF	0.0003



10 heating days

22 heating days



30 heating days

40 heating days

Fig. 7. Thermographies after 10, 22, 30 and 40 days of heating
(front, middle and back of the pile)

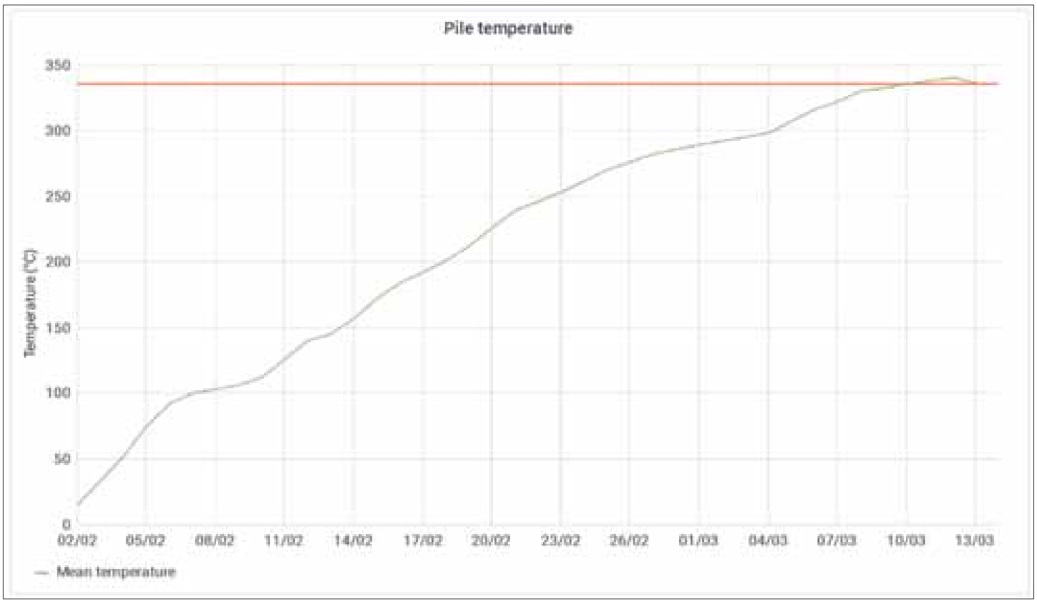


Fig. 8. Average temperature evolution in the thermal pile

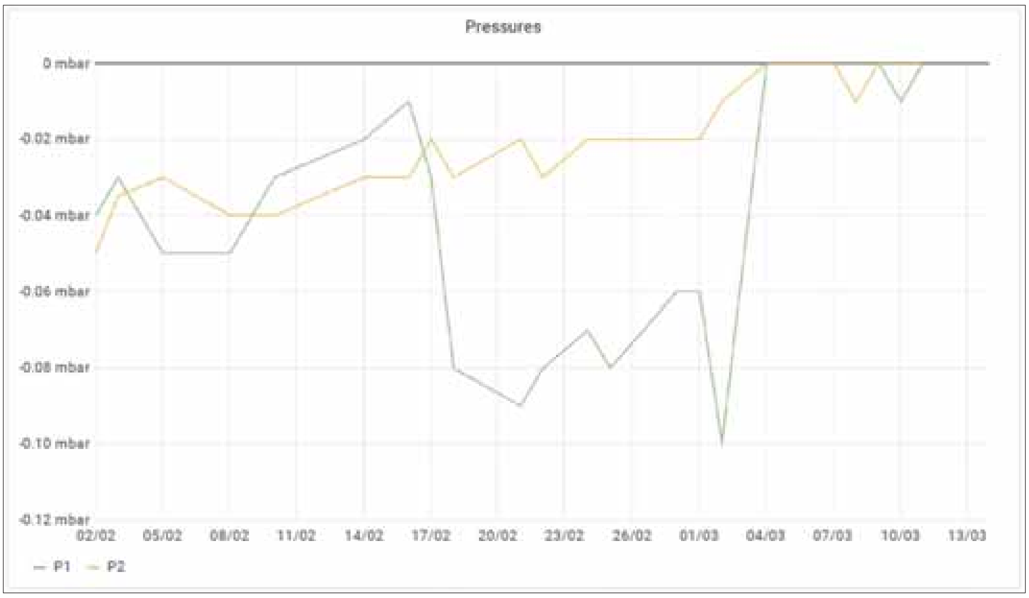


Fig. 9. Soil pressure monitoring during treatment

Table 3. Emission sampling results

Sample	*Unit*	*Concentration*	*Emission standard*	*Sampling date*
1	pg WHO-TEQ$_{2005}$/Nm^3	40.07	100	08/02/2022
2	pg WHO-TEQ$_{2005}$/Nm^3	73.52	100	11/02/2022
3	pg WHO-TEQ$_{2005}$/Nm^3	76.14	100	15/02/2022
4	pg WHO-TEQ$_{2005}$/Nm^3	1.38	100	18/02/2022
5	pg WHO-TEQ$_{2005}$/Nm^3	0.821	100	22/02/2022
6	pg WHO-TEQ$_{2005}$/Nm^3	51.38	100	25/02/2022

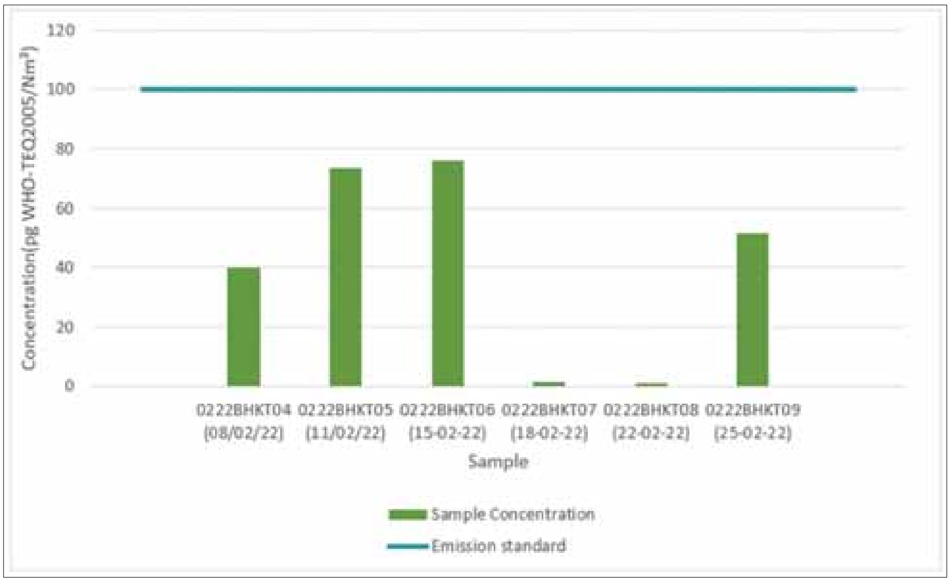


Fig. 10. Emission sampling results

Table 4. Treated soil analysis results

Material	*Unit*	*Initial concentration*	*Treatment goal*	*Treated soil results*	*DRE* (%)*
Soil	ppt WHO-TEQ$_{2005}$	11,400	300 (Urban residential) 1,200 (Industrial)	4.84 96.29	99.96 99.16
Sludges	ppt WHO-TEQ$_{2005}$	5,410	150	ND**	> 99.99
Washing cake	ppt WHO-TEQ$_{2005}$	17,200	300	6.7	99.96

**Destruction Rate Efficiency; **Non-Detected*

Soil temperature, pressure, and emissions control were monitored throughout the treatment, and the results demonstrated the efficiency and success of the thermal treatment.

This zero-waste solution demonstrates an improved and efficient method for remediating dioxin-contaminated soils. Future design improvements could be made, such as adding a heat exchanger to the thermal oxidizer, in order to reduce the energy consumption of such a project.

Overall, the study provides a promising solution for the remediation of dioxin-contaminated soils, with the potential for broader applications in the future.

References

Buekens A., Stieglitz L., Hell K., Huanf H., Segers P., (2001), Dioxins from thermal and metallurgical processes: recent studies for the iron and steel industry, *Chemosphere*, **42**, 729-735.

Depasse Y., Jordens A., Pacella K., Saadaoui H., Haemers J., (2021), *Modelling the Thermal Desorption Soil Treatment*, In: *Book of Abstracts and Proceedings*, AquaConSoil, On line at: https://aquaconsoil.com/assets/Scientific-Programme/ACS2021_BookofAbstracts_incl-proceedings.pdf

EPA, (2022), Air Emission Measurement Center, Method 23 – Dioxins and Furans, United States Environmental Protection Agency, On line at: https://www.epa.gov/emc/method-23-dioxins-and-furans

Gao Y., Chakraborty N., Dunstan T.D., Swaminathan N., (2015), Assessment of Reynolds averaged Navier–Stokes Modeling of scalar dissipation rate transport in turbulent oblique premixed flames, *Combustion Science and Technology*, **187**, 1584-1609.

Haemers J., (2016), System and Method for Treating Porous Materials. s.l. Patent No. WO2016/062757A1.

Kulkarni P.S., Crespo J.G., Afonso C.A.M., (2008), Dioxins sources and current remediation technologies - A review, *Environnement International*, **34**, 139-153.

Mudhoo A., Thayalan G., Muthoora N.J., Muthoora M.N., Oozeer B.Z., Rago Y.P., Ramphul M.P., Valaydon A.K., Kumar S., (2013), *Dioxins and Furans: Sources, Impacts and Remediation*, In: *Pollutant Diseases, Remediation and Recycling*, Lichtfouse E., Schwarzbauer J., Robert D. (Eds.), *Environmental Chemistry for a Sustainable World*, Springer International Publishing, Cham, 479-541.

Mukherjee A., Debnath B., Ghosh S.K., (2016), A Review on Technologies of Removal of Dioxins and Furans from Incinerator Flue Gas, *Procedia Environnemental Sciences*, **35**, 528-540.

Schecter A., Needham L., Pavuk M., Michalek J., Colacino J., Ryan J., Päpke O., Birnbaum L., (2009), Agent Orange exposure, Vietnam War veterans, and the risk of prostate cancer, *Cancer*, **115**, 3369-3371.

Schecter A., Quynh H.T., Pavuk M., Päpke O., Malisch, R., Constable J.D., (2003), Food as a source of dioxin exposure in the residents of Bien Hoa City, Vietnam, *Journal of Occupational and Environmental Medicine*, **45**, 781-788.

Temme J., Wabel T.M., Skiba A.W., Driscoll J.F., (2015), *Measurements of Premixed Turbulent Combustion Regimes of High Reynolds Number Flames*, In: *53rd AIAA Aerospace Sciences Meeting*, American Institute of Aeronautics and Astronautics, Kissimmee, Florida.

Tran H.T., Lin C., Hoang H.G., Bui X.T., Le V.G., Vu C.T., (2022), Soil washing for the remediation of dioxin-contaminated soil: A review, *Journal of Hazardous Materials*, **421**, 126767, https://doi.org/10.1016/j.jhazmat.2021.126767.

Tuyet-Hanh T.T., Minh N.H., Vu-Anh L., Dunne M., Toms L.M., Tenkate T., Thi M.H.N., Harden F., (2015), Environmental health risk assessment of dioxin in foods at the two most severe dioxin hot spots in Vietnam, *International Journal of Hygiene and Environmental Health*, **218**, 471-478.

USAID, (2010), Environmental Remediation at Danag Airport, United States Agency for International Development, On line at: https://pdf.usaid.gov/pdf_docs/PA00KZSS.pdf

USAID, (2015), IPTD® Final Report – Phase I. In Pile Thermal Desorption® (IPTD®) Services, Danang Airport, Vietnam Contract No. Aid-486-C-13-00001, United States Agency for International Development.

USAID, (2016), Environmental Assessment of Dioxin Contamination at Biên Hòa Airbase, United States Agency for International Development, On line at: https://www.usaid.gov/sites/default/files/BH-Final-EA-2016-05-03_EN-reduced.pdf

Young A.L., Cecil P.F., (2011), Agent Orange exposure and attributed health effects in Vietnam veterans, *Military Medicine*, **176**, 29-34.

Environmental Engineering and Management Journal

October 2023, Vol. 22, No. 10, 1745-1751
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2023.149

"Gheorghe Asachi" Technical University of Iasi, Romania

ELECTROCHEMICAL RECYCLING OF RED GYPSUM WASTE: THE ELEDGE PROCESS

Francesco Negri[1,2], Francesco Gallo[1], Flavio Manenti[2*]

[1]Itelyum Regeneration SpA, Via Tavernelle 19, Pieve Fissiraga 26854, Lodi, Italy
[2]Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Milan 20133, Italy

Abstract

Red gypsum is an industrial waste generated by the titanium dioxide industry. Currently, it is mainly used for environmental restoration, but this is not ideal due to problems of geographical availability of suitable sites and environmental issues. Different valorization routes have been proposed, including the utilization of red gypsum in the cement industry or its chemical recycling through thermal processes. These routes either lack the production capacity for an efficient disposal of red gypsum, or propose processes that need severe operating conditions and that generate a significant amount of CO_2 emissions. This paper proposes a novel process for electrochemical recycling of red gypsum based on four fundamental steps: metathesis, electrodialysis, electrolysis, and carbonatation. Preliminary estimates on a process design basis are obtained and analyzed from a phenomenological point of view, leading to the development of mass and energy balances for the process. The advantage of such system is that an industrial plant capable of treating 80000 t/y of $CaSO_4$ on an anhydrous basis leads to the production of 55234 t/y of concentrated H_2SO_4 and 52571 t/y of synthetic $CaCO_3$, coupled with the mineralization of 23131 t/y of CO_2. The process is completely electrified and has a power consumption of 8.5 MW that can be provided entirely from renewables-based power plants, leading to net-negative CO_2 emissions. Tuscany region in Italy is taken as a practical example, where the TiO_2 production industry could benefit from the ELEDGE (ELEttroDialisi di GEssi) process and couple it with a geothermal-based power plant.

Key words: electrochemistry, electrodialysis, recycle, red gypsum, Tuscany

Received: May, 2023; Revised final: June, 2023; Accepted: September, 2023; Published in final edited form: October, 2023

1. Introduction

Worldwide production of titanium minerals in 2022 was estimated at more than 9.5 Mt of equivalent titanium dioxide (TiO_2) content, with China covering more than one third of the mining operations (Statista, 2023). Titanium-containing minerals are included in the so-called "mineral sands" and include ilmenite and rutile, that make up the main feedstock for the industrial production of TiO_2, along with titanium slug. More than 95% of the world's titanium ores are used in TiO_2 production, which is a key compound in the pigment industry. TiO_2 white pigments are mainly used in the paint, plastics, and paper industries, and also in wastewater treatment (Enesca et al., 2009; Gázquez et al., 2014; Porter, 2014; Woodruff et al., 2017; Zarogiannis et al., 2017).

Nowadays, two large-scale industrial processes are available for the synthesis of TiO_2, those being the sulfate process and the chloride process. The increasing popularity of the chloride process is due to its higher performances regarding waste disposal, energy, and quality (Braun et al., 1992). However, the sulfate process is still dominant in China and it is also used for a significant fraction of the European TiO_2 supply chain, with 55% of the total still based on this technology in 2017 (Zarogiannis et al., 2017). The sulfate process includes a filtering and washing step that generates a weak acid effluent that is neutralized by using calcium hydroxide, leading to the production

---

[*] Author to whom all correspondence should be addressed: e-mail: flavio.manenti@polimi.it

of a byproduct named “red gypsum” (Gázquez et al., 2021).

Red gypsum is mainly composed of gypsum dihydrate ($CaSO_4 \cdot 2H_2O$) and other impurities, among which Fe-bearing phases cause the typical red color. The management of this waste is a significant issue for the TiO_2 industry, since it is produced in large amount and has typically no practical use: 7-8 tons of red gypsum are generated for every ton of TiO_2 produced, and the most widespread use for this waste is the environmental restoration of abandoned quarries, mines, and landfills since it is considered an inert and safe material for such purpose (Auer et al., 2017; Protano et al., 2020; Rosli et al., 2020, 2021).

The utilization of red gypsum for environmental restoration may lead to the accumulation of species such as Fe, Ca, Al, Mg, Mn, S in the soil together with an increase of the pH of the area, leading to a slow and complicated revegetation process (Zapata-Carbonell et al., 2019).

Studies have shown that it is possible to use red gypsum to create a waste-based binder to be used in deep in-situ soil stabilization instead of cement, or it can be used directly as a raw material for cement production (Gazquez et al., 2013; Hughes et al., 2011). It has been also proposed to use this waste as a calcium-rich feedstock to be used for the mineralization of CO_2, leading to the possible long-term sequestration of CO_2-rich effluents derived from industrial processes with the formation of $CaCO_3$ (Azdarpour et al., 2014, 2015; Rahmani et al., 2014).

Finally, some solutions that may be classified as chemical recycling have been proposed, one example being the utilization of red gypsum as the pivot of a metal self-enrichment process leading to the co-production of ammonium sulfate and raw materials for the sintering industry (Wu et al., 2019) and another example being a thermal process for the conversion of red gypsum to elemental sulfur and calcium carbonate (De Beer et al., 2014).

The use of red gypsum in the cement and construction industry has a limited scope since the rate of utilization for this waste is subordinated to the production volume of said industry. Moreover, the amount to be used in this area is not arbitrarily large, due to constraints regarding the mechanical and chemical properties of the cement and ligands that are obtained from the gypsum. The chemical recycling route is a far more promising one, since it is disconnected from other industrial sectors and allows to selectively tackle the issue of red gypsum by converting it into useful chemicals. However, the solutions proposed in the literature are few and show some issues, such as the presence of severely endothermic steps such as calcination and thermal reduction that require temperatures above 1000°C, leading to the generation of large amount of CO_2 emissions from fossil fuels combustion.

This paper proposes a novel approach to this problem based on a completely electrified scheme for the electrochemical recycling of red gypsum. This innovative process solution is named ELEDGE (ELEttroDialisi di GEssi, which means Gypsum Electrodialysis in Italian) and it is based on four fundamental steps: metathesis, electrodialysis, electrolysis, and carbonatation, which lead to the complete conversion of red gypsum to diluted sulfuric acid and calcium carbonate. The electrification of the process allows to couple it to a suitable renewables-based power production plant, leading to a net-negative process for what concerns carbon emissions due to the mineralization of a CO_2 stream.

2. Materials and methods

A simplified Block Flow Diagram for the ELEDGE process is shown in Fig. 1, with electrified units highlighted by a lightning symbol. The conversion pathway for red gypsum is here shown only for the main component in its dehydrated form for simplicity ($CaSO_4$). The process is based on four tailored key steps aimed at converting the waste to useful products. First, red gypsum is co-fed with an excess of a concentrated hydrochloric acid solution (HCl) in a dedicated metathesis reactor, leading to the conversion of gypsum to sulfuric acid (H_2SO_4) and calcium chloride ($CaCl_2$). Then, the acidic mixture is treated in an electrodialyzer, a unit in which an electric field is applied to separate ions in solution by also exploiting suitable ion-selective semi-permeable membranes, producing a stream of diluted sulfuric acid and some brine rich in HCl and $CaCl_2$. The excess HCl used for the metathesis step is easily separated and recirculated to the beginning of the process, while the $CaCl_2$ solution enters a dedicated electrolytic cell. The electrolysis of the $CaCl_2$ aqueous solution generates a calcium hydroxide ($Ca(OH)_2$) concentrated stream and gaseous hydrogen (H_2) and chlorine (Cl_2). H_2 and Cl_2 react in a dedicated unit (HCl burner) where HCl is generated and recirculated back to the beginning of the process, thus closing the HCl loop and ensuring that no net consumption of this reactant is necessary to run the process. Finally, the $Ca(OH)_2$ solution is used in a carbonatation reactor to mineralize a CO_2 stream (possibly obtained from a suitable stream of industrial flue gases), converting it into $CaCO_3$. While introducing a new, innovative, and general approach for the chemical recycling of red gypsum that can be applied to any TiO_2 production facility, the technology is especially useful for the TiO_2 plant located in Scarlino, Tuscany, Italy. In fact, the production plant is close to a facility that produces sulfuric acid to be used in the sulfate process. Thus, it is possible to imagine an industrial symbiosis scheme in which red gypsum is treated with the ELEDGE process to produce diluted H_2SO_4 which can then be easily concentrated with the equipment available at the nearby sulfuric acid production plant, maximizing the efficiency of the chemical recycling operation and minimizing the costs and the energy requirements. In addition, the carbonatation reaction allows to mineralize CO_2 emissions that can be obtained from industrial off-gases, leading to the reduction of GHG emissions of the site. Moreover, the production of synthetic $CaCO_3$ can partially substitute the intensive marble quarrying activity for the extraction of natural $CaCO_3$ that is currently conducted in the nearby Massa-Carrara area in Tuscany, Italy. This allows to mitigate the problem of marble powder generated by such activities, which turns into marble sludge in case of rainfall (the so-called "marmettola"), and may lead to environmental issues such as flooding and groundwater pollution (Piccini et al., 2019). Finally, it is also reasonable to imagine a possible coupling of the electrified ELEDGE process with a geothermal-based renewable energy power plant since this type of technology is well-established and popular in many areas of Tuscany region (Reinsch et al., 2017).

More detailed information on the process are shown in the Process Flow Diagram (PFD) in Fig. 2. It is possible to see that the system is a combination of the key operations described previously (metathesis, electrodialysis, electrolysis, carbonatation) and a series of conventional steps, such as filtration, absorption, distillation, evaporation, purging. The process design solution proposed in this paper will proceed with the description of the key steps, without entering the detail of more conventional operations since they are well-known and a detailed evaluation of their performance is outside the scope of this work.

The metathesis step can be carried out in a stirred tank reactor in which red gypsum (rich in $CaSO_4$) and a concentrated solution of hydrochloric acid react according to the reaction shown in (Eq. 1):

$$CaSO_4 + 2HCl \leftrightarrow H_2SO_4 + CaCl_2 \tag{1}$$

The insoluble residue remaining from the metathesis step is filtered out of the system, then the sludge is washed with distilled water to recover water-soluble components, and the resulting solution is recirculated to the process vessel. It is possible to evaluate the performance of this reactive step through a thermodynamic evaluation by using Gibbs free energy and formation enthalpy of the involved chemical species, to be considered as dissolved in aqueous solution (Lange, 1999). The computation of reaction enthalpy and reaction Gibbs free energy at standard conditions highlights two values that are close to zero (ΔH^0_R = -1 kJ/mol and ΔG^0_R = -0.08 kJ/mol). This means that in this reaction, neither the reactants nor the products are favored, and that variations in the operating temperature will have little to no effect on the thermodynamic yield. In order to push the reaction towards the products and ensure high conversion of the gypsum, it is necessary to operate on other parameters, for example by working in large excess of hydrochloric acid. Equilibrium can be studied for this system by solving the system of equations in (Eq. 2), respectively showing the equilibrium condition and the Van't Hoff equation. Since the reaction enthalpy at standard conditions shows a rather small value, the computation of the Van't Hoff equation is performed by considering a constant value for ΔH^0_R, leading to the expression shown in (Eq. 2).

$$\begin{cases} K_{eq}(T) = \prod_{i=1}^{N} a_i^{v_i} \\ Keq(T) = Keq(T_{REF}) \cdot EXP\left[\frac{\Delta H_R^0}{R} \cdot \left(\frac{1}{T_{REF}} - \frac{1}{T}\right)\right] \end{cases} \tag{2}$$

where Keq, T, N, a_i, v_i, T_{REF}, ΔH^0_R, R, are respectively the equilibrium constant, the system temperature, the number of components, the activity for the *i-th* component, the stoichiometric coefficient for the *i-th* component, the reference temperature (298 K), the reaction enthalpy, and the universal gas constant.

The $CaCl_2$-rich brine containing two strong acids (H_2SO_4 and HCl) is then sent to an electrodialyzer. Electrodialysis is a process which is typically used to perform water desalination and salt pre-concentration. It works by applying an electric field to an ionic solution contained inside of a space delimited by anion- and cation- exchange membranes. The electric field combined with the selectivity of the membranes allows to separate the dissolved ions (Strathmann, 2010; Xu and Huang, 2008). There are also innovative approaches based on electrodialysis such as bipolar membrane electrodialysis for the production of acid and bases from corresponding salts, showing that this technology can potentially be applied to a large number of cases in addition to that of water desalting (Huang et al., 2007).

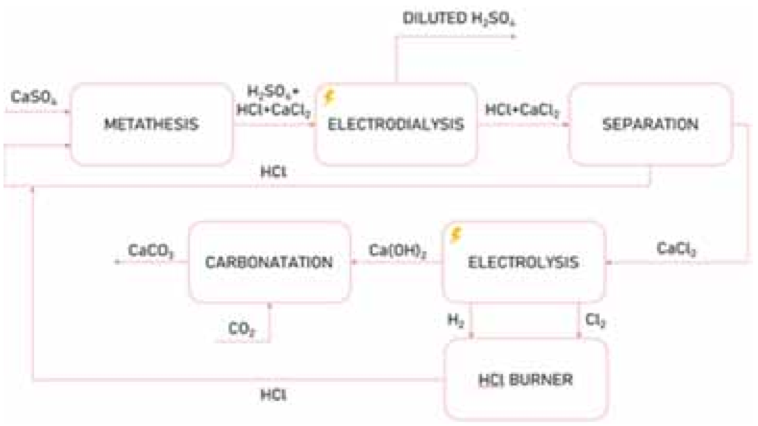


Fig. 1. Block flow diagram for the ELEDGE process

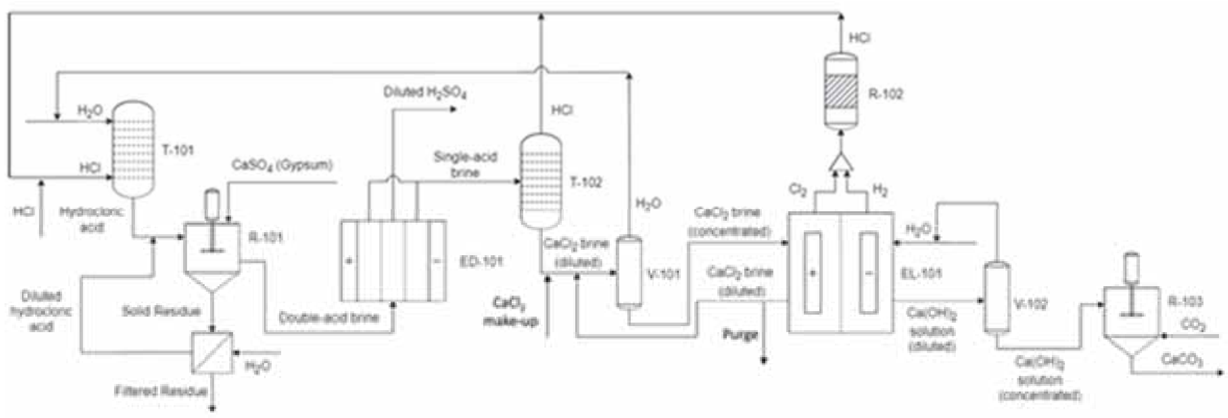


Fig. 2. Process flow diagram for the ELEDGE process

It is interesting to notice that it is possible to use an ion-selective anion-exchange membrane so that a separation between different anions in solution can be achieved on top of the more conventional cation/anion separation. Specifically, it has been shown that it is possible to use semi-permeable membrane for the selective separation of Cl^- and SO_4^{2-} anions (Li et al., 2022). A simplified scheme of an electrodialyzer using this type of anion-selective membrane for the treatment of the $CaCl_2$-rich double-acid brine is shown in Fig. 3. The double-acid brine containing $CaCl_2$, HCl, and H_2SO_4 is fed to the unit and the cations start to migrate towards the cathode by passing through a cationic membrane, while the anions tend to migrate towards the anode by passing through an anionic membrane. However, the use of a Cl^-/SO_4^{2-} anion-selective membrane makes it much more difficult for the larger sulfate ions to pass through the membrane, allowing almost only the Cl^- ion to pass. This leads to the production of diluted sulfuric acid from the central channel, and a single-acid brine containing HCl and $CaCl_2$ from the sides. While the cation/anion separation can be considered as practically complete, the separation efficiency for the anion-selective membrane is not perfect (Li et al., 2022). This is not a problem for the diluted sulfuric acid stream, since it will contain a small amount of HCl easily separable by distillation, due to the very different boiling points of these substances between themselves and water. However, this may generate a problem for the single-acid brine since the leaching of sulfate ions will regenerate $CaSO_4$ that cannot be re-converted to $CaCl_2$ in the following process steps. To avoid its accumulation, it is either necessary to purge it outside of the system and compensate the loss of material with a fresh $CaCl_2$ make-up, or split the effluent from the electrodialyzer and recirculate it to the metathesis section, where $CaSO_4$ will be converted to $CaCl_2$. In this work showing the conceptual design procedure for the process, it has been decided to proceed with the first choice for the sake of simplicity, even if it is less optimal.

The single-acid brine containing HCl and $CaCl_2$ then undergoes a simple distillation to recover pure gaseous HCl from the top, to be recirculated to a water absorption column for the synthesis of the hydrochloric acid solution that is used in the metathesis reactor. The brine, now only containing calcium chloride, is then concentrated and added with a $CaCl_2$ make-up before entering an electrolytic cell for the electrochemical decomposition of the salt. Inspired by the chloralkali process for the industrial production of chlorine and sodium hydroxide, the electrolysis step in the ELEDGE process includes the half-reactions reported in (Eq. 3). They are the same half-reactions that take place in the chloralkali process, those being the oxidation of chloride anions to chlorine at the anode, and the reduction of water to hydrogen and hydroxide anion at the cathode (Schmittinger et al., 2011). The only difference with the chloralkali process is that the cations in this system are Ca^{2+} ions, leading to the production of $Ca(OH)_2$.

$$\begin{cases} 2Cl^- \rightarrow Cl_2 + 2e^- \\ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \end{cases} \tag{3}$$

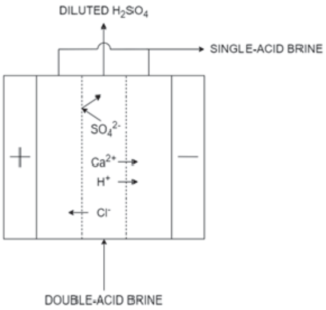


Fig. 3. Electrodialysis step in the ELEDGE process

It is possible to evaluate the performance of this electrochemical cell through a thermodynamic evaluation by starting from standard reduction potentials of the chemical species involved in each half-reaction and shifting them to the real operating conditions by using the Nernst equation, as reported in (Eq. 4).

$$E_{RED} = E^0_{RED} - \frac{RT}{zF} \ln\left(\frac{a_{RED}}{a_{OX}}\right) \tag{4}$$

where: E_{RED} is the half-cell actual reduction potential, the E^0_{RED} is the standard half-cell reduction potential, T is the system temperature, R is the universal gas constant, z is the number of electrons transferred in the half-reaction, F is the Faraday constant, a_{RED} is the activity of the reduced form, a_{OX} is the activity of the oxidized form. A rigorous methodology should include suitable expressions for the activity coefficients of the species involved in the reactions (Thummar et al., 2022). However, it is possible to have a preliminary estimation of the reduction potential by considering the activity of a dissolved species as the concentration, and the activity of a gaseous product as its partial pressure. This is coherent with the preliminary level of the conceptual design procedure introduced in this work.

Chlorine and hydrogen gas produced from the atmospheric electrolytic cell must be compressed and fed to an HCl burner, where gaseous hydrogen chloride is produced through an extremely exothermic reaction, leading to the production of a substantial amount of steam to be used in the plant (Austin and Glowacki, 2000). HCl is then recirculated to the water absorption column to regenerate the 5 M hydrochloric acid solution, thus closing the HCl loop and ensuring that no net consumption of this reactant is needed to run the process.

Finally, the $Ca(OH)_2$ solution produced at the cathode of the electrolytic cell is processed in a carbonatation reactor, where CO_2 bubbled from the bottom is mineralized upon contact with the caustic solution, leading to the production of synthetic $CaCO_3$ (Boynton, 1980; Oates, 2008).

3. Results and discussion

The process design procedure described in this paper allows to choose the optimal operating conditions for the non-conventional unit operations included in the system, followed by a high-level mass balance for a plant based on the ELEDGE process. The thermodynamic study performed in the metathesis step shows that the use of a 5 M hydrochloric acid solution at 80°C corresponds to a $CaSO_4$ conversion higher than 99%. The system temperature has a negligible effect on the thermodynamic yield, but the combination of HCl presence and the choice of operating temperature allows to maximize $CaSO_4$ solubility in the aqueous solution, leading to a great increment in the productivity of the unit. It must be noted that the co-presence of $CaSO_4$ and $CaCl_2$ generated from the metathesis decreases gypsum solubility. However, the choice of operating conditions results in a net increase in $CaSO_4$ solubility, passing approximately from 2 g/L to 20 g/L when referring to its anhydrous form (Li and Demopoulos, 2005). The effluent from the reactor to be purified in the electrodialysis unit is separated in a diluted sulfuric acid stream and a brine containing mainly HCl and $CaCl_2$, with a separation efficiency that can be quantified as follows: 91.71% of the Cl^- ions and 5.44% of the SO_4^{2-} ions pass through the anionic membrane on average (Li et al., 2022). Finally, the brine concentration in $CaCl_2$ and the operating temperature chosen for the electrolytic cell are such that there is a deviation from the standard thermodynamic potential, and the resulting half-cell reduction potentials at the chosen operating conditions lead to an overall thermodynamic electrochemical potential of 1.94 V, which is 12% less than the standard overall thermodynamic potential (2.19 V). With these data, it is possible to perform a high-level mass balance for the system based on the ELEDGE process.

The size of the plant considered for the mass balance refers to an industrial complex capable of treating 80000 t/y of $CaSO_4$ on an anhydrous basis and that has a stream factor of 8000 h/y. The mass balance of the proposed layout, along with the main operating temperatures is reported in Table 1, where the stream names refer to the PFD shown in Fig. 2.

Table 1. Mass balance and operating conditions for the main streams of the ELEDGE process

Stream Name	***$CaSO_4$***	***Hydrocloric acid***	***Double-acid brine***	***Diluted H_2SO_4***	***Single-acid brine***	***$CaCl_2$ brine conc.***	***$Ca(OH)_2$ solution conc.***	***CO_2***	***$CaCO_3$***
Phase	*S*	*L*	*L*	*L*	*L*	*L*	*L*	*G*	*S*
Composition [mol%]									
H_2O	89.4%	82.6%	85.9%	94.5%	78.7%	94.5%	99.976%	0%	89.3%
$CaSO_4$	7.89%	0%	0%	0%	0%	0%	0%	0%	0%
HCl	0%	17.4%	10.8%	1.96%	18.1%	0%	0%	0%	0%
$CaCl_2$	0%	0%	1.67%	0%	3.07%	5.38%	0%	0%	0%
H_2SO_4	0%	0%	1.67%	3.49%	0.17%	0.14%	0%	0%	0%
$Ca(OH)_2$	0%	0%	0%	0%	0%	0%	0%	0%	0%
CO_2	0%	0%	0%	0%	0%	0%	0%	0%	0%
$CaCO_3$	0%	0%	0%	0%	0%	0%	0.024%	0%	0%
Inerts	0%	0%	0%	0%	0%	0%	0%	100%	0%
Flowrate [kmol/h]	932	3528	4361	1981	2381	4233	270221	66	613
MW [kg/kmol]	30	21	23	21	24	23	18	44	27
Mass Flowrate [kg/h]	27500	74884	99884	41896	57988	97945	4867655	2891	16428
Tempe-rature [°C]	25	80	80	25	25	80	80	80	80

The electric energy requirement for the process can be estimated by considering that the steam production from the HCl burner is sufficient to cover all the requirements from the other process units such as the metathesis reactor, the distillation column, and the evaporators. This means that the only electric power required to run the process refers to the electrodialysis and electrolysis steps. For the electrodialysis, a preliminary energy consumption for the system described previously can be obtained from the literature, corresponding to an average value of 0.20 kWh/kg$CaCl_2$ (Li et al., 2022). For the electrolytic cell, it is possible to consider the typical average values for current density and effective electrode area for a standard chloralkali cell, and refer them to the influent calculated for the industrial case, while considering the overall thermodynamic potential calculated as shown in (Eq. 4). The electrolytic cell resulting from the analysis has a specific power consumption of 0.27 kWh/kg$CaCl_2$ (Thummar et al., 2022).

Considering the industrial-scale plant operating with a capacity of 80000 t/y of $CaSO_4$ on an anhydrous basis, this corresponds to a power consumption of 1.6 MW for the electrodialysis, and 6.9 MW for the electrolytic cell, for a total of 8.5 MW. Thus, it is reasonable to imagine the erection of such an electrochemical recycling plant in the Tuscany region and power it completely through renewable geothermal energy since the total installed capacity for this type of renewables system in the region in 2023 is 915 MW provided by 33 power plants, with 20 MW to be installed in the following years (Regione Toscana, 2023). The resulting electrochemical recycling plant is effectively a net-negative carbon emissions process, with the utilization of 0.29 kgCO_2/kg$CaSO_4$ through mineralization.

4. Conclusions

The design of an electrochemical recycling process for red gypsum waste was described in its most important parts: metathesis, electrodialysis, electrolysis, and carbonatation.

A thermodynamic analysis was performed for the metathesis step in order to find the optimal operating conditions. An electrodialysis unit based on the use of a Cl^-/SO_4^{2-} anion-selective membrane was illustrated in terms of separation efficiency and general performance, followed by the evaluation of the real overall thermodynamic potential of an electrolytic cell. The carbonatation section was introduced and described in detail.

The ELEDGE process can be used in an industrial plant capable of treating 80000 t/y of $CaSO_4$ on an anhydrous basis, obtaining, after suitable purification steps aimed at removing excess water and other contaminants, 55234 t/y of concentrated H_2SO_4 and 52571 t/y of synthetic $CaCO_3$, while also mineralizing 23131 t/y of CO_2, with an electric consumption of 8.5 MW that can be entirely provided by renewables such as geothermal energy for the case of titanium dioxide industry in Tuscany region, Italy. The renewables-based electrochemical recycling process is a net-negative CO_2 emissions process, due to the mineralization of a CO_2-rich stream.

References

Auer G., Woditsch P., Westerhaus A., Kischkewitz J., Griebler W., Rohe M., Liedekerke M., (2017), *Pigments, Inorganic, 2. White Pigments*, In: *Ullmann's Encyclopedia of Industrial Chemistry*, John Wiley & Sons, 1-36.

Austin S., Glowacki A., (2000), *Hydrochloric Acid, in: Ullmann's Encyclopedia of Industrial Chemistry*, John Wiley & Sons.

Azdarpour A., Asadullah M., Junin R., Manan M., Hamidi H., Mohammadian E., (2014), Direct carbonation of red gypsum to produce solid carbonates, *Fuel Processing Technology*, **126**, 429-434.

Azdarpour A., Asadullah M., Junin R., Mohammadian E., Hamidi H., Daud A.R.M., Manan M., (2015), Extraction of calcium from red gypsum for calcium carbonate production, *Fuel Processing Technology*, **130**, 12-19.

Boynton R.S., (1980), *Chemistry and Technology of Lime and Limestone*, 2nd Edition, Wiley & Sons, New York.

Braun J.H., Baidins A., Marganski R.E., (1992) TiO_2 pigment technology: a review, *Progress in Organic Coatings*, **20**, 105-138.

De Beer M., Maree J.P., Liebenberg L., Doucet F.J., (2014), Conversion of calcium sulphide to calcium carbonate during the process of recovery of elemental sulphur from gypsum waste, *Waste Management*, **34**, 2373-2381.

Enesca A., Andronic L., Duta A., (2009), Wastewater treatment using optimized TiO2 photocatalytic properties, *Environmental Engineering and Management Journal*, **8**, 753-758.

Gázquez M.J., Bolívar J.P., Garcia-Tenorio R., Vaca F., (2014), A Review of the production cycle of titanium dioxide pigment, *Materials Sciences and Applications*, **5**, 441-458.

Gazquez M.J., Bolivar J.P., Vaca F., García-Tenorio R., Caparros A., (2013), Evaluation of the use of TiO_2 industry red gypsum waste in cement production, *Cement and Concrete Composites*, **37**, 76-81.

Gázquez M.J., Contreras M., Pérez-Moreno S.M., Guerrero J.L., Casas-Ruiz M., Bolívar J.P., (2021), A Review of the commercial uses of sulphate minerals from the titanium dioxide pigment industry: The case of Huelva (Spain), *Minerals*, **11**, 575, https://doi.org/10.3390/min11060575.

Huang C., Xu T., Zhang Y., Xue Y., Chen G., (2007), Application of electrodialysis to the production of organic acids: State-of-the-art and recent developments, *Journal of Membrane Science*, **288**, 1-12.

Hughes P.N., Glendinning S., Manning D.A.C., White M.L., (2011), Use of red gypsum in soil mixing engineering applications, *Proceedings of the Institution of Civil Engineers - Geotechnical Engineering*, **164**, 223-234.

Lange N.A., (1999), *Lange's Handbook of Chemistry*, 15 Edition, McGraw-Hill, New York, USA.

Li F., Guo Y., Wang S., (2022), Pilot-Scale Selective Electrodialysis for the Separation of Chloride and Sulphate from High-Salinity Wastewater, *Membranes*,

12, 610, https://doi.org/10.3390/membranes12060610.

Li Z., Demopoulos G.P., (2005), Solubility of CaSO4 Phases in Aqueous HCl + $CaCl_2$ Solutions from 283 K to 353 K, *Journal of Chemical & Engineering Data*, **50**, 1971-1982.

Oates J.A.H., (2008), *Lime and Limestone: Chemistry and Technology, Production and Uses*, Wiley & Sons, New York.

Piccini L., Di Lorenzo T., Costagliola P., Galassi D.M.P., (2019), Marble slurry's impact on groundwater: The case study of the Apuan Alps karst aquifers, *Water*, **11**, 2462, https://doi.org/10.3390/w11122462.

Porter R., (2014), *Mineral Sands Industry (Fact Book)*, ILUKA, Perth, Australia.

Protano G., Baroni D., Bianchi S., Russo C., Salleolini M., (2020), Assessing the impact on groundwater chemistry of an environmental restoration performed using industrial solid waste from TiO_2 production, *Applied Geochemistry*, **120**, 104666, https://doi.org/10.1016/j.apgeochem.2020.104666.

Rahmani O., Junin R., Tyrer M., Mohsin R., (2014), Mineral carbonation of red gypsum for CO_2 sequestration, *Energy Fuels*, **28**, 5953-5958.

Regione Toscana, (2023), Geothermal Energy - Tuscany Region, (in Italian), On line at: www.regione.toscana.it/-/geotermia

Reinsch T., Dobson P., Asanuma H., Huenges E., Poletto F., Sanjuan B., (2017), Utilizing supercritical geothermal systems: a review of past ventures and ongoing research activities, *Geothermal Energy*, **5**, 16, https://doi.org/10.1186/s40517-017-0075-y

Rosli N.A., Aziz H.A., Selamat M.R., Lim L.L.P., (2020), A mixture of sewage sludge and red gypsum as an alternative material for temporary landfill cover, *Journal of Environmental Management*, **263**, 110420, https://doi.org/10.1016/j.jenvman.2020.110420.

Rosli N.A., Aziz H.A., Selamat M.R., Lim L.L.P., Zawawi M.H., (2021), Effect of compaction on physical properties of a sewage sludge and red gypsum mixture as intermediate landfill cover, *Construction and Building Materials*, **289**, 123153, https://doi.org/10.1016/j.conbuildmat.2021.123153.

Schmittinger P., Florkiewicz T., Curlin L.C., Lüke B., Scannell R., Navin T., Zelfel E., Bartsch R., (2011), *Chlorine*, In: *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH.

Statista, (2023), Titanium production worldwide by country 2022, On line at: www.statista.com/statistics/759972/mine-production-titanium-minerals-worldwide-by-country/

Strathmann H., (2010), Electrodialysis, a mature technology with a multitude of new applications, *Desalination*, **264**, 268-288.

Thummar K., Abang R., Menzel K., De Groot M.T., (2022), Coupling a chlor-alkali membrane electrolyzer cell to a wind energy source: dynamic modeling and simulations, *Energies*, **15**, 606, https://doi.org/10.3390/en15020606.

Woodruff L.G., Bedinger G.M., Piatak N.M., (2017), *Titanium* (USGS Numbered Series No. 1802- T), U.S. Geological Survey, *Reston*, https://doi.org/10.3133/pp1802T.

Wu H., Feng Y., Li H., He S., Bian Z., (2019), Red gypsum utilization and acidic wastewater treatment based on metal self-enrichment process, *Science of The Total Environment*, **691**, 9-15.

Xu T., Huang C., (2008), Electrodialysis-based separation technologies: A critical review, *AIChE Journal*, **54**, 3147-3159.

Zapata-Carbonell J., Bégeot C., Carry N., Choulet F., Delhautal P., Gillet F., Girardclos O., Mouly A., Chalot M., (2019), Spontaneous ecological recovery of vegetation in a red gypsum landfill: Betula pendula dominates after 10 years of inactivity, *Ecological Engineering*, **132**, 31-40.

Zarogiannis P., Cockcroft L.J., Halliday R., (2017), Analysis of the socio-economic impacts of a harmonized classification of carcinogen category 2 for titanium dioxide (TiO2), RPA Risk & Policy Analysts, On line at: https://rpaltd.co.uk/uploads/report_files/titanium-dioxide-918.pdf

Environmental Engineering and Management Journal

October 2023, Vol. 22, No. 10, 1753-1758
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2023.150

"Gheorghe Asachi" Technical University of Iasi, Romania

SYNTHESIS OF BIO-BASED WOOD ADHESIVE

Salise Oktay[1,3]*, Nilgün Kızılcan[2], Başak Bengü[3]

[1]*Istanbul Technical University, Graduate School of Science Engineering and Technology Department of Polymer Science and Technology*
[2]*Istanbul Technical University, Faculty of Science and Letter, Department of Chemistry*
[3]*Kastamonu Entegre Ağaç San. Tic. A.Ş.*

Abstract

The wood-based panel industry plays a crucial role in facilitating the industrial production of everyday products like particleboard and fiberboard, which are commonly used in flooring, furniture, and more. Key inputs for board production include thermoset resins, which act as binders. Traditionally, resins based on urea-formaldehyde, melamine-formaldehyde, and melamine-urea-formaldehyde are widely used due to their reactivity and cost-effectiveness. However, the sustainability of these resins is a growing concern, and stricter regulations regarding formaldehyde emissions are impacting the industry.

In response to this challenge, this study introduces a bio-based resin formulation, utilizing corn starch and Mimosa tannin as alternatives to formaldehyde-based resins. The choice of corn starch and Mimosa tannin as raw materials is motivated by their chemical compatibility and ready availability. The study involved the determination of the solids and gel times of the synthesized resins. Additionally, laboratory-scale board production was undertaken to assess the performance of the newly developed resin formulations. The mechanical and physical properties of the resulting boards, along with formaldehyde content, were measured. Mechanical test results were evaluated in accordance with the EN 312 standard.

The findings suggest that the developed resin formulations show promise for particleboard production suitable for interior applications, as they generally meet the standard requirements for mechanical properties.

Key words: corn starch, furanic derivatives, Mimosa tannin, wood adhesive

Received: May, 2023; Revised final: October, 2023; Accepted: October, 2023; Published in final edited form: October, 2023

1. Introduction

Formaldehyde-based thermoset resins, including urea-formaldehyde, melamine-formaldehyde, and melamine-urea-formaldehyde, have found extensive utility in the wood-based panel industry due to their cost-effectiveness and high reactivity, as corroborated by numerous studies (Ji et al., 2017; Kim, 2009; Liu et al., 2018; Nuryawan et al., 2017; Perminova et al., 2019; Philbrook et al., 2005). These resins have been instrumental in manufacturing various products integral to our daily lives, such as particleboard and fiberboard, which serve as fundamental components in flooring, furniture, and more.

However, despite their practical advantages, formaldehyde-based resins present substantial drawbacks, particularly in terms of sustainability and their contribution to formaldehyde emissions. These concerns have curtailed their widespread adoption.

Formaldehyde-based resins, being derived from non-renewable sources, are entwined with the issue of formaldehyde emissions, a prominent environmental pollutant with adverse implications for human health and ecological well-being. As a result, there has been a growing emphasis on research and development aimed at formulating wood adhesives that are both sustainable and devoid of formaldehyde, echoing the industry's shift towards greener and more responsible practices (El Mansouri et al., 2007; Liu et

---

* Author to whom all correspondence should be addressed: e-mail: salise.oktay@keas.com.tr; Phone: +902165543587

al., 2018; Moubarik et al., 2010, 2013; Yang et al., 2013; Zhao et al., 2016).

Within the academic domain, attention has increasingly gravitated towards starch and tannin-based wood adhesive formulations as promising avenues to produce natural, formaldehyde-free wood adhesives. These materials have been favored for their compatible chemical composition and eco-friendly attributes. However, it is recognized that bio-based resins, despite their sustainable advantages, tend to exhibit comparatively lower reactivity when juxtaposed with traditional formaldehyde-based adhesives. Consequently, this study embarks on the task of synthesizing a starch-tannin-based resin endowed with heightened reactivity, thus striving to bridge this performance gap (Ahmad et al., 2020; Gu et al., 2019; Kuakpetoon and Wang, 2008; Pizzi, 1979; Sumathirathne and Karunanayake, 2017; Tondi, 2017).

The paramount objective of this research revolves around the creation of a renewable, eco-conscious resin formulation that stands as a compelling alternative to formaldehyde-based counterparts. In this context, starch and tannin were judiciously chosen as raw materials owing to their harmonious chemical makeup and environmentally sustainable attributes. The outcome of this effort revealed a resin formulation that not only exhibited excellent mechanical properties but also, importantly, showcased minimal formaldehyde emissions when utilized in the production of particleboards. As a collective testimony to these findings, it becomes evident that the newly developed starch and tannin-based wood adhesive formulations have the potential to be effectively harnessed within the wood-based panel industry as efficient binders. In doing so, they aptly address and mitigate the critical concerns associated with conventional formaldehyde-based adhesives, thereby propelling the industry towards a more sustainable and eco-friendly trajectory.

2. Experimental

2.1. Chemicals and reagents

Corn starch (CS) was obtained by Sunar Mısır (Adana, Turkey). Amylose and moisture content of the CS were 25.3% and 11.9% by weight on a dry basis, respectively. Wattle bark (Mimosa) tannin (MT) was purchased from Bondtite Pty. Ltd (Dorpspruit, South Africa). The moisture content of the MT was 7% by weight on a dry basis. Laboratory-scale particleboards were manufactured in Kastamonu Entegre Ağaç San. Tic. A.Ş. Besides, mechanical, physical, and formaldehyde content tests of the produced boards were also carried out in Kastamonu Entegre.

2.2. Synthesis of tannin-based wood adhesive

Primarily for resin synthesis with 46% solid content by weight, 1110 g of tannin was mixed into 1110 g of distilled water and dispersed at room temperature using a mechanical stirrer. Finally, hexamine (HMTA) was added to the resin system as a hardener. The hardener content used was 10% by weight of the resin solid content. Finally, the pH value of the resin was adjusted to the range 8-9 with a 40 wt.% NaOH aqueous solution.

2.3. Synthesis of starch-based wood adhesive

A quantity of 350 g of corn starch was added to 1000 g of distilled water and mixed at room temperature using a mechanical stirrer. Then, 75 g of sugar and 70 g of urea were added. Finally, 70 g of furfural was added to the system and the pH value of the resin was adjusted to the range of 8-9 with 40% NaOH.

2.4. Physical properties: Solid content and viscosity determination

Firstly, about 1.5 g of synthesized wood adhesives were poured into a piece of aluminum foil and then dried at 120°C in an oven for 2 hours. After drying, the dried sample was taken out of the oven. Following that, the dried sample was reweighed. The solid content by percentage (S) of the tannin-based adhesive was determined according to Eq. (1).

$$S = \frac{M_2 - M_0}{M_1 - M_0} x\ 100\% \qquad (1)$$

where: S was solid content, M_0 was the mass of aluminum foil, M_1 was the mass of aluminum foil and adhesive sample and M_2 was the mass of aluminum foil and dry adhesive sample+.

The calculated solid content value was an average of three replicates (Zhao et al., 2018a). The viscosity of the prepared adhesives at 20°C was measured using Brookfield CAP 2000+ instrument at 200 rpm. An average of three test results was presented.

2.5. Fourier transform infrared (FT-IR) spectroscopy

The chemical structure of the cured tannin-based wood adhesive sample was characterized by Fourier transform infrared spectroscopy (FT-IR). FT-IR analyses were carried out by using Bruker Tensor 37 spectrophotometer and the samples were scanned between 400 and 4000 cm^{-1}. To obtain a cured tannin adhesive sample, the synthesized tannin-based wood adhesive of 55 g and an HMTA of 2.5 g were added sequentially to a beaker, and the HMTA was dissolved completely in the resin. The pH value of the resin was adjusted to the range 8-9 with a 40 wt.% NaOH aqueous solution. 2 g of the prepared resin sample and stir bar was placed in the test tube. Then, as soon as the test tube was immersed in boiling water, the chronometer was started and the resin was mixed with the rod.

The chronometer was stopped when the resin took solid form. The recorded time was determined as the curing time. After the cured resin samples were completely dried, FT-IR analyses of the samples were carried out.

2.6. Particleboard preparation and testing

Particleboards are mainly composed of three layers which are 2 surface layers (SL) and 1 core layer (CL). Laboratory scale particleboards of dimensions 500 mm x 500 mm x 12 mm were prepared. The total resin solid by weight was 12% for the surface layers and 7% for the core layer. Particleboard samples bonded with the developed bio-based resin formulations were assembled and hot-pressed at 200°C, for 4 minutes press time. In general, it is known that the core layer of the particleboard determines the mechanical properties, and the formaldehyde content is determined by the surface layer.

Therefore, in the study, tannin-based resin with higher mechanical strength was used in the core layer, and corn starch-based resin was used in the surface layer. Particles were dried to approximately 4% moisture content before the application of resin. The aimed board density was 700 kg/m^3. All tests were conducted by appropriate European Standards. Internal bond (IB), bending strength (BS), modulus of elasticity (MOE), and surface soundness of the produced particleboards were performed according to EN 319, EN 310, and EN 311 test standards, respectively (Wager and Kleinert, 2011).

2.7. Formaldehyde content by perforator method

The formaldehyde content of the manufactured particleboards was measured according to the European Norm (EN 12460-5), also called the perforator method. It is used to determine the formaldehyde content of the uncoated and non-laminated wood-based board. In this method, the amount of formaldehyde (mg) within the 100 g sample was measured.

Firstly, formaldehyde was extracted from the test samples by boiling toluene and transferred into de-mineralized water. After that, the formaldehyde content of this aqueous solution was determined photometrically (Oktay et al., 2021).

3. Results and discussion

3.1. Physical properties: Solid content and viscosity determination

Resin solid content and viscosity significantly affect the processability of adhesives in a board production line. The solid content of the tannin and starch-based resin was 46%. The viscosity values for tannin and starch-based wood adhesives were 350 and 30 mPa-s, respectively. The resin solid content was at a level that prevented excessive moisture during board pressing, and the resin viscosity was such that it could spread evenly on the chips. Additionally, it was observed that the resin solid content and viscosity obtained were similar to those of commercial formaldehyde-based wood adhesives (Zhao et al., 2018a).

3.2. Fourier transform infrared (FT-IR) spectroscopy

The chemical structure of the cured tannin-based adhesive sample was illuminated with FT-IR and their spectra are shown in Fig. 1. As could be seen from Fig. 1, the detected bands at 1587 and 1458 cm^{-1} in the Mimosa tannin spectrum which were attributed to the aromatic -C=C- stretching, disappeared in the cured resin spectrum possibly due to the increment of the aromatic ring substitution of tannin. Likewise, compared with the Mimosa tannin spectrum, the band at 1148 cm $^{-1}$ related to the C–O and O–H groups of resorcinol molecule of mimosa tannin, disappear after the reaction. Besides, three new peaks at around 1010 cm^{-1}, 1230 cm$^{-1,}$ and 1605 cm^{-1} which were respectively ascribed to the antisymmetric deformation of -C–O–C- in ether groups, presence of –C-N- groups, and formation of the azomethine groups (–CH=N-) were detected in the FT-IR spectrum of the cured tannin-based resin (Peña et al., 2009).

Moreover, to elucidate the chemical structures of the cured corn starch-NaOH and corn starch-NaOH-sugar mixtures, FT-IR analyses were performed. Their spectra are shown in Fig. 2. As could be seen from Fig. 2, compared with the corn starch spectrum, the broadband at around 3300 cm^{-1} related to the hydroxyl groups of the starch gradually weakened in the cured corn starch-NaOH and corn starch-NaOH-sugar mixtures. This could be attributed to the reducing –OH content after oxidization. Likewise, the band at 1147 $^{-1}$ cm disappeared. Besides, two new peaks were detected in the FT-IR spectrum of the cured corn starch-NaOH and cornstarch-NaOH-sugar at around 1560 cm$^{−1}$ and 1410 cm^{-1}. These peaks were ascribed to the –COO$^-$Na$^+$ group on the starch molecule chains (Yaacob et al., 2011). On the other hand, compared to the corn starch and cured corn starch-NaOH spectra, a new peak at 778 cm$^{−1}$ was detected according to the FT-IR spectrum of the cured corn starch-NaOH-sugar mixture, which was related to the unsubstituted CH=CH group of 5-hydroxymethyl-2-furfural (5-HMF) ring (Zhao et al., 2018a).

It was known that sugar decomposes at high temperatures and produces furanic derivatives such as 5-HMF (Fig. 3) (Tondi et al., 2012; Zhao et al., 2016; Zhao et al., 2018b). It was known that the chemical interaction between corn starch and 5-HMF with dimethylene ether bridges was possible. These observations revealed that chemical interactions between corn starch and NaOH occurred in the cured corn starch-NaOH mixture. In the cured corn starch-NaOH-sugar mixture, in addition to the interaction of corn starch and NaOH, a possible interaction between corn starch and 5-HMF could be formed.

3.3. Particleboard preparation and testing

To examine the performance of the developed resin formulation, at least 3 laboratory-scale particleboards were produced. The physical (thickness and density) and the mechanical test results (internal bond, surface soundness, bending strength, and modulus of elasticity) of the particleboards were illustrated and compared with similar studies in the literature in Table 1.

Since the boards were intended to be used in a dry environment, water uptake and thickness swelling tests were not performed.

All of the obtained results showed that the produced board by using a developed bio-based resin formulation met the standard values and was comparable with similar studies' results. In addition, the formaldehyde content of the produced boards is significantly lower and originates from the wood itself (Oktay et al., 2022).

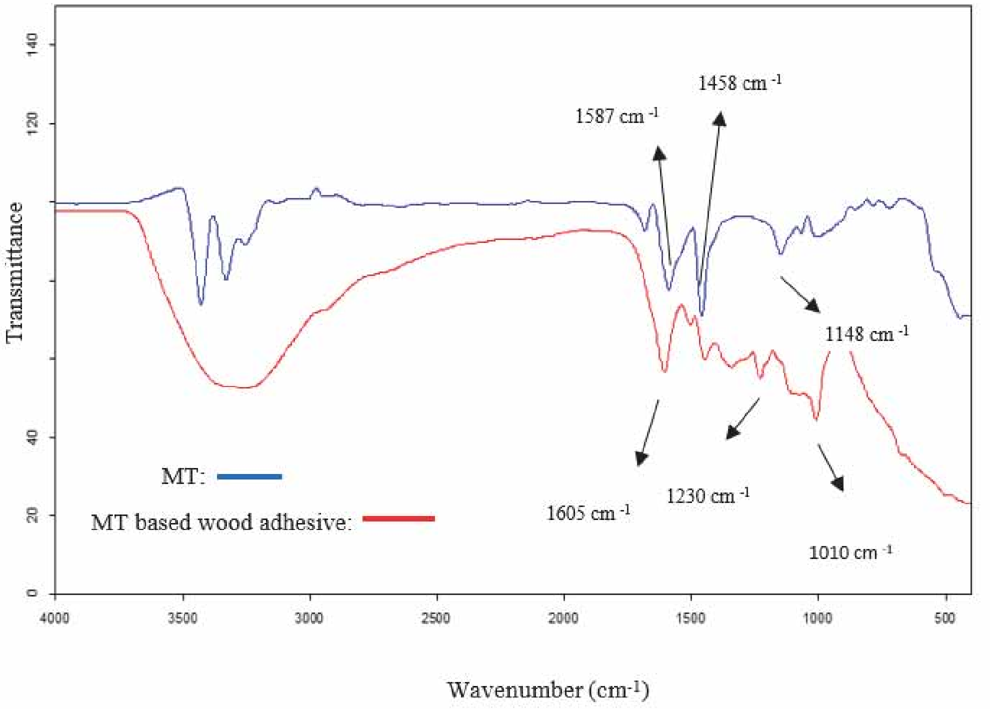


Fig. 1. FT-IR spectra of the Mimosa tannin and cured tannin-based resin

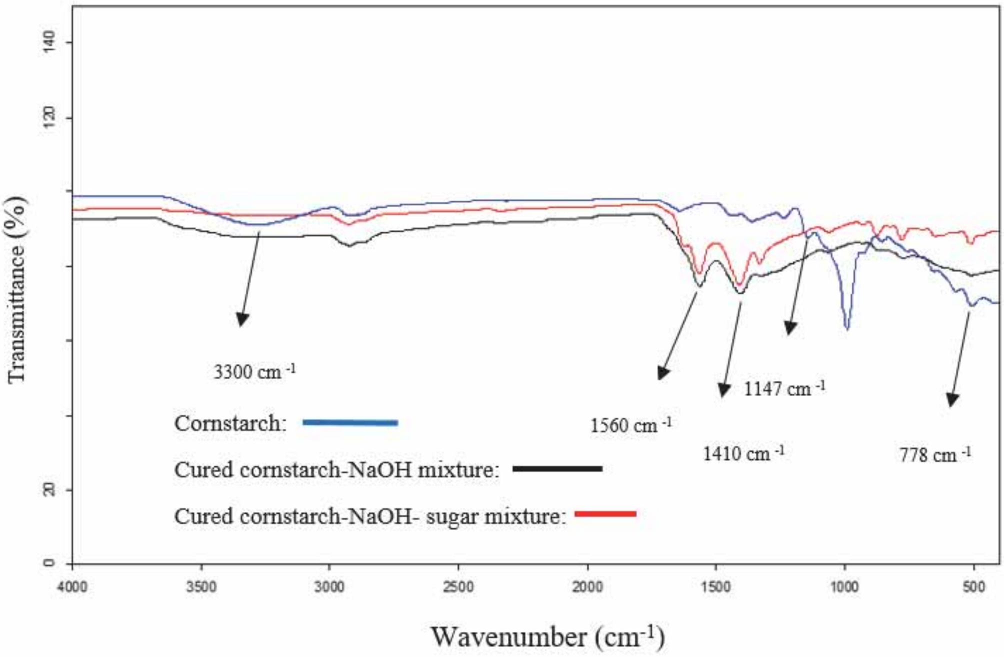


Fig. 2. FT-IR spectra of the corn starch, cured corn starch-NaOH mixture, and cured corn starch-NaOH- sugar mixture

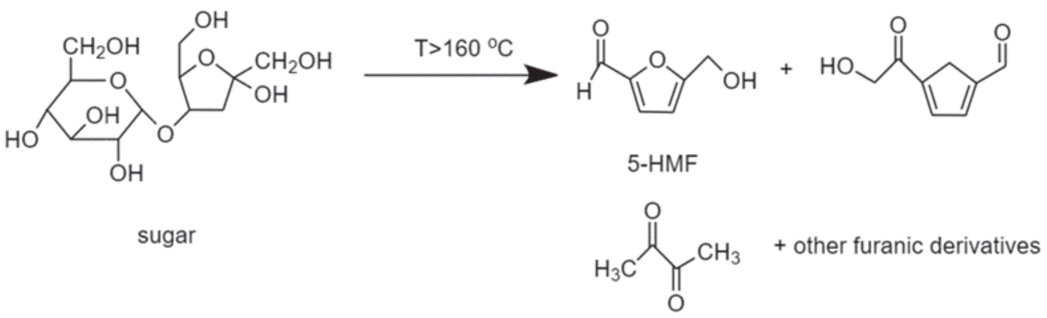


Fig. 3. Thermal decomposition of sugar at high temperatures

Table 1. Particleboards test results

Hybrid resin formulation (by weight%)		***Thickness mm Density kg/m^3***	***IB N/mm^2***	***MOE N/mm^2***	***MOR N/mm^2***	***Surface soundness N/mm^2***	***FA content (mg/100g)***
Resin 1 35% CS 7% furfural 7.5% sucrose 7% urea	**Resin 2** 50% MT 10% HMTA	11.08 739	0.60	2843	15.07	1.14	1.36
Oktay et al., 2021		10.47 761	0.97	2220	10.36	1.34	0.94
Oktay et al., 2022		11.45 695	0.43	2472	11.14	0.72	0.92
P2 class std.		6<x≤13	> 0.40	> 1800	> 11	> 0.80	-

4. Conclusions

We have proposed sustainable, environmentally friendly, cost-effective, and formaldehyde-free corn starch and tannin-based wood adhesive formulations. The chemical structure of the cured adhesive samples confirmed that the desired crosslinked network was successfully achieved. Additionally, to determine the performance of the prepared resin formulations, we produced laboratory-scale particleboards. Their physical and mechanical properties were determined, and their formaldehyde content values were measured.

All of the obtained test results demonstrated that the boards made with the developed bio-based resin formulations generally satisfied the exigencies of panels for interior fittings used in dry medium (P2) according to European norms EN 312 (2010). Besides, good mechanical properties, the panels produced with the prepared formaldehyde-free resin formulations had significantly lower formaldehyde content. The low formaldehyde content of the boards produced with the prepared resins was not due to the resin but from the natural structure of the wood raw material.

All of the obtained results showed that the developed bio-based resin formulations have a high potential to be used for producing interior-grade particleboard.

Acknowledgements

The authors would like to thank the Scientific and Technical Research Council of Turkey (TUBITAK) - 2244 - Istanbul Technical University-Kastamonu Entegre Ağaç Sanayi - Project No: 118C107. The authors acknowledge funding from the Research Fund of the Istanbul Technical University, Turkey (ITU BAP; Project No.: TDK-2021-43282 and THD-2022-44082).

References

Ahmad A.N., Lim S.A., Navaranjan N., Hsu Y.I., Uyama H., (2020), Green sago starch nanoparticles as reinforcing material for green composites, *Polymer*, **202,** 122646, https://doi.org/10.1016/j.polymer.2020.122646.

El Mansouri N.E., Pizzi A., Salvadó J., (2007), Lignin-based wood panel adhesives without formaldehyde, *Holz als Roh - und Werkstoff*, **65**, 65-70.

Gu Y., Cheng L., Gu Z., Hong Y., Li Z., Li C., (2019), Preparation, characterization and properties of starch-based adhesive for wood-based panels, *International Journal of Biological Macromolecules*, **134,** 247-254.

Ji X., Li B., Yuan B., Guo M., (2017), Preparation and characterizations of a chitosan-based medium-density fiberboard adhesive with high bonding strength and water resistance, *Carbohydrate Polymers*, **176,** 273-280.

Kim S., (2009), Environment-friendly adhesives for surface bonding of wood-based flooring using natural tannin to reduce formaldehyde and TVOC emission, *Bioresource*

Technology, **100**, 744-748.

Kuakpetoon D., Wang Y.J., (2008), Locations of hypochlorite oxidation in corn starches varying in amylose content, *Carbohydrate Research*, **343**, 90-100.

Liu M., Wang Y., Wu Y., He Z., Wan H., (2018), “Greener” adhesives composed of urea-formaldehyde resin and cottonseed meal for wood-based composites, *Journal of Cleaner Production*, **187**, 361e371, https://doi.org/10.1016/j.jclepro.2018.03.239

Moubarik A., Allal A., Pizzi A., Charrier F., Charrier B., (2010), Preparation and mechanical characterization of particleboard made from maritime pine and glued with bio-adhesives based on corn starch and tannins, *Maderas: Ciencia y Tecnologia*, **12**, 189-197.

Moubarik A., Mansouri H.R., Pizzi A., Charrier F., Allal A., Charrier B., (2013), Corn flour-mimosa tannin-based adhesives without formaldehyde for interior particleboard production, *Wood Science and Technology*, **47**, 675-683.

Nuryawan A., Risnasari I., Sucipto T., Heri Iswanto A., Rosmala Dewi R., (2017), Urea-formaldehyde resins: Production, application, and testing, *IOP Conference Series: Materials Science and Engineering*, **223**, 012053, http://doi.org/10.1088/1757-899X/223/1/012053.

Oktay S., Kızılcan N., Bengü B., (2021), Development of bio-based corn starch - Mimosa tannin - sugar adhesive for interior particleboard production, *Industrial Crops and Products*, **170**, 113689, https://doi.org/10.1016/j.indcrop.2021.113689.

Oktay S., Kızılcan N., Bengü B., (2022), Environment-friendly corn starch and tannin-based wood adhesives for interior particleboard production as an alternative to formaldehyde-based wood adhesives, *Pigment and Resin Technology*, https://doi.org/10.1108/PRT-06-2022-0075.

Peña C., De La Caba K., Retegi A., Ocando C., Labidi J., Echeverria J.M., Mondragon I., (2009), Mimosa and chestnut tannin extracts reacted with hexamine in solution, *Journal of Thermal Analysis and Calorimetry*, **96**, 515-521.

Perminova D.A., Malkov V.S., Guschin V., Eisenreich N., (2019), Influence of glyoxal on curing of urea-formaldehyde resins, *International Journal of Adhesion and Adhesives*, **92**, 1-6.

Philbrook A., Blake C.J., Dunlop N., Easton C.J., Keniry M.A., Simpson J.S., (2005), Demonstration of co-polymerization in melamine-urea-formaldehyde reactions using 15N NMR correlation spectroscopy, *Polymer*, **46**, 2153-2156.

Pizzi A., (1979), The chemistry and development of tannin/urea–formaldehyde condensates for exterior wood adhesives, *Journal of Applied Polymer Science*, **23**, 2777-2792.

Sumathirathne L.D., Karunanayake L., (2017), Synthesis of novel porous tannin-phenol-formaldehyde cation exchange resin from Terminalia arjuna (Kumbuk), *Journal of the National Science Foundation of Sri Lanka*, **45**, 219-227.

Tondi G., (2017), Tannin-Based copolymer resins: Synthesis and characterization by solid state 13C NMR and FT-IR spectroscopy, *Polymers*, **9**, 223, http://doi.org/10.3390/polym9060223.

Tondi G., Wieland S., Wimmer T., Schnabel T., Petutschnigg A., (2012), Starch-sugar synergy in wood adhesion science: Basic studies and particleboard production, *European Journal of Wood and Wood Products*, **70**, 271-278.

Wager E., Kleinert S., (2011), Responsible research publication: international standards for authors, *Macedonian Journal of Chemistry and Chemical Engineering*, **35**, 29-33.

Yaacob B., Amin M.C.I.M., Hashim K., Bakar B.A., (2011), Optimization of reaction conditions for carboxymethylated sago starch, *Iranian Polymer Journal (English Edition)*, **20**, 195-204.

Yang L., Liu J., Du C., Qiang Y., (2013), Preparation and properties of cornstarch adhesives, *Advance Journal of Food Science and Technology*, **5**, 1068-1072.

Zhao X.F., Peng L.Q., Wang H.L., Wang Y.B., Zhang H., (2018a), Environment-friendly urea-oxidized starch adhesive with zero formaldehyde-emission, *Carbohydrate Polymers*, **181**, 1112-1118.

Zhao Z., Miao Y., Yang Z., Wang H., Sang R., Fu Y., Huang C., Wu Z., Zhang M., Sun S., Umemura K., Yong Q., (2018b), Effects of sulfuric acid on the curing behavior and bonding performance of tannin-sucrose adhesive, *Polymers*, **10**, 651, https://doi.org/10.3390/polym10060651.

Zhao Z., Umemura K., Kanayama K., (2016), Effects of the addition of citric acid on tannin-sucrose adhesive and physical properties of the particleboard, *BioResources*, **11**, 1319-1333.

Environmental Engineering and Management Journal

October 2023, Vol. 22, No. 10, 1759-1766
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2023.151

"Gheorghe Asachi" Technical University of Iasi, Romania

MANAGEMENT AND POSSIBLE VALORIZATION OF BIOPLASTICS SEPARATED FROM ORGANIC FRACTION OF MUNICIPAL SOLID WASTE

Giorgia Pellegrino[1,2]*, Paola Zitella[1], Alexia Boulanger[1], Barbara La Licata[1], Debora Fino[2]

[1]*Environment Park S.p.a, Via Livorno 60, 10144, Torino, Italy*
[2]*Department of Applied Science and Technology, PolitecnicoDi Torino, Corso Duca Degli Abruzzi 24, 10129 Torino, Italy*

Abstract

Italian law requires bioplastics to meet precise degradability criteria under aerobic conditions to be treated with Organic Fraction Municipal Solid Waste (OFMSW) but does not provide specific controls on anaerobic degradation capacity. The result is longer composting times for bioplastics than OFMSW. The marketing and use of biodegradable single-use products, such as shopper bags, sidesteps the problem of using common plastics without completely solving it. Therefore, there is a need to identify technological solutions that allow for the complete degradation of biodegradable plastics without the need to modify the process in place in organic waste treatment plants. For this purpose, on biodegradable plastics composed mainly of starch and PBAT, anaerobic digestion tests were carried out to assess whether the degradation kinetics are consistent with the digestion hydraulic retention time of the organic fraction. Alongside this process, pre-treatment tests involving chemical hydrolysis and commercial enzymes were conducted. The tests were performed on laboratory and pilot scales, using organic matter and culture medium for methanogenic bacteria growing also in comparison with Clostridia consortia and both in mesophilic and thermophilic conditions. During the tests, samples were collected after 30 and 55 days of reaction. Microplastic content was analysed in terms of weight loss and presence of PBAT building blocks: adipic acid, terephthalic acid, and 1,4-butanediol. The results showed that both types of pre-treatments increase the degradation yield of bioplastics at different processing times. These results lead the way for the prospect that pre-treated biodegradable plastics can be delivered along with organic waste to existing anaerobic digestion and could increase the quantities normally handled in the aerobic composting plants.

Key words: anaerobic digestion, bioplastic, chemical pre-treatment, enzyme, PBAT

Received: May, 2023; Revised final: October, 2023; Accepted: October, 2023; Published in final edited form: October, 2023

1. Introduction

According to European Bioplastics, an association representing the interests of the bioplastics industry in Europe, a plastic material is defined as bioplastic if it is "biobased, biodegradable, or has both properties" (https://www.european-bioplastics.org/bioplastics/). For a bioplastic to be "biobased," it must come, even partially, from renewable sources, while for it to be biodegradable, it is sufficient for the polymer to be digestible into simpler monomers by microorganisms in the environment (Comanita et al., 2015; Venturelli et al., 2021). The two properties are not directly related: some polymers are 100% biobased but not biodegradable, and some are 100% obtained from fossil sources but are biodegradable. Indeed, biodegradability has little to do with the polymer source but more to do with the chemical bonds in the polymer structure.

When the biodegradation of the polymer occurs in a manner and time frame compatible with those of industrial or household degradation of organic waste, the bioplastic is also called "compostable". The

---

* Author to whom all correspondence should be addressed: e-mail: giorgia.pellegrino@envipark.com; Phone: 0112257232

spread of biodegradable and compostable plastics has gained momentum in some Countries after European Directive 2019/904 banned single-use plastic products. Bioplastic (BP) can be disposed of and processed with organic waste, but only if it meets the compostability criteria of EN 13432. The problem arises because the standard refers to the mode and time of aerobic digestion, which is much longer than that required by a standard municipal solid waste anaerobic digester (Kosheleva et al., 2023). Different pre-treatments can be applied to promote bioplastic degradation and their digestion by the microorganisms (Mohee et al., 2008). Calabro et al. (2020) conducted an experiment using Mater-Bi, previously treated by different pre-treatment methods: mechanical shredding, chemical pre-treatment with NaOH for 24 hours and aerobic digestion using an aerobic inoculum from a sludge plant activated. Mechanical trituration has no significant effect, while chemical pre-treatment with NaOH was the most effective because it makes the polymer more accessible to enzymes, increasing both methane yields and sample mass loss. In contrast, aerobic digestion slowed the growth of the aerobic consortium, inhibiting biogas production.

In the literature are mentioned several enzymes of the hydrolase class, synthesized by bacteria, adhere to the surface of the substrate and degrade it (Muroi et al., 2017; Suzuki et al., 2014; Zumstein et al., 2017). Among the enzymes readily available on the market are RoL lipase extracted from *Rhizopus oryzae* (SIGMA Catalog No. 80612) and an FsC-like cutinase isolated from *Fusarium solani* (NOVOZYM 51032) (Urbanek et al., 2020). These two enzymes completely degrade very thick films of Mater-Bi within 20 hours at a pH of 6 at a temperature of 20°C.

This paper studied the action of enzymatic and chemical pre-treatment on BP bags subjected to anaerobic digestion afterward.

2. Materials and methods

The chemical and enzymatic pre-treatment effects were studied on BP bags composed of 70 percent polybutylene adipate co-terephthalate (PBAT), 20 percent starch, and 10 percent additives (Venturelli et al. 2021). The weight decrease of plastics over time is the critical parameter studied to evaluate the effectiveness of pre-treatment.

2.1. Laboratory-scale chemical pre-treatment and anaerobic digestion

For this activity, were used HCl and NaOH supplied by Sigma Aldrich. The tests were conducted in 500-mL Duran bottles.

Carried out: nine tests with NaOH under different concentrations and process conditions; two pre-treatments with hydrochloric acid and one alkaline pre-treatment followed by anaerobic digestion. The Table 1 shows the operating conditions of the several tests performed. Having selected, thanks to the observation of weight decrease of the polymer, the best pre-treatment conditions among those tested, the experimentation continued with the replication of the test followed by anaerobic digestion. Was performed the pre-treatment test followed by anaerobic digestion by mixing 10 mL of 25% NaOH and 7g of BP in 320 mL of water, with a pH of 12.2 and a process temperature of 50°C. The test lasted for 96 hours. Then 10% v/v digestate was added and started the anaerobic digestion process. The anaerobic digestion lasted 16 days.

2.2. Laboratory-scale enzymatic pre-treatment

The enzymes used were amylase from *Bacillus licheniformis*, amylase from *Bacillus amyloliquefaciens*, and esterase from *Bacillus subtilis*. The enzymes were all supplied by Sigma Aldrich. The tests were conducted in 500-mL Duran bottles.

For the enzyme pre-treatment, were set up three bottles for each amylases enzymes (two for the test at different enzyme concentrations and one for the blank for each enzyme), two bottles for the esterase at varying BP content, and two bottles containing amylase from *Bacillus amyloliquefaciens* and esterase, added at two different times, to evaluate the synergy of the two enzymes in the pre-treatment process. Process parameters such as pH, temperature, buffer, and reaction times utilized are given in Table 2, while Table 3 shows a review of the test setup.

Each plastic bag was divided into equal parts weighed. The pieces were placed in the oven at 55 °C for 30 minutes; then, they were dried in the desiccator for 30 minutes and weighed again. In each bottle was placed a certain amount of bioplastic (Table 3). The bottles were placed in the shaken bath at 55 °C. After 24 hours, was sampled one piece of bioplastic from the test bottles and one from the blank bottle. The plastic pieces were rinsed in distilled water and placed in the oven at 55°C overnight; afterward, they dried again in the desiccator for 30 minutes. The sampling procedure was carried out every 24 hours and at the end of the tests. In each bioplastics sampling, 8 mL of liquid was taken from both the test bottle and the blank bottle to later test for the presence of sugars (Megazyme's K-MASUG kit) and stored in the freezer.

In tests conducted with both enzymes, 2.5 mg esterase (Test 3) and 20 µL amylase (Test 4), the bottles were placed in a shaker at 55 °C for an additional 48 hours, with sampling every 24 hours. After drying, the samples were weighed, and the weight loss was estimated. The bioplastic pieces were stored in a dry place.

2.3. Laboratory-scale anaerobic digestion tests

Following the initial screening on the effectiveness of enzymatic pre-treatments on the degradation of plastics, several anaerobic digestion tests were conducted to evaluate the effect of the pre-treatments performed on the degradation kinetics of bioplastics. These tests were carried out at 50 °C with consortia of methanigenic bacteria and at 37 °C with consortia of Clostridia-type bacteria in the presence or absence of Organic Fraction Municipal Solid Wastes (OFMSW) and a specific medium (Perz et al., 2016; Yagi et al., 2014). Non-pre-treated BPs were used as a comparison. Again, as with the pre-treatments, degradation efficiency was studied by analyzing weight decreases as principal parameter. Table 4 shows the summary of the tests performed. The unpretreated bioplastic pieces were placed in the oven at 55°C for 30 minutes and then in the desiccator for 30 minutes.

After drying, the bioplastics were weighed. In the bottle test without pre-treatment, was added 0.6 g of bioplastic per bottle. In the test with pre-treatment, was added the amount of bioplastic remaining after enzymatic action. Fresh OFMSW consisting exclusively of fruit and vegetable waste was shredded. Medium for Clostridia and methanigenic bacteria were prepared, with the composition shown in the Table 5. Anaerobic digestion tests were carried out in 500 mL Duran bottles with a total filling volume of 375 mL.

Table 1. Operating conditions of chemical pre-treatments

Test (%)	*Base or Acid quantity (mL)*	*Bioplastic quantity (g)*	*Water (mL)*	*pH*	*Temperature (°C)*	*HRT (h)*
NaOH, 25	10	7	330	12.3	50	96
NaOH, 25	0.5	7	330	10	50	168
NaOH, 25	0.75	7	330	12	50	192
NaOH, 25	0.25	8.5	330	11	50	144
NaOH, 25	0.094	8.5	330	11.5	50	144
NaOH, 25	0.25	8.5	330	12	50	144
NaOH, 25	6	7	330	13.5	50	384
NaOH, 25	8	7	330	13.5	50	384
NaOH, 25	10	7	330	13.6	50	384
HCl, 37	0.028	8.5	330	3	25	144
HCl, 37	0.001	8.5	330	5	25	144

Table 2. Summary of the process parameters of the enzymatic tests performed

Enzyme	*Buffer*	*pH*	*Temperature (°C)*
Bacillus licheniformis	citrate	5	50
Bacillus amyloliquefaciens	phosphate	7	50
Bacillus subtilis	phosphate	7.5	30

Table 3. Tests carried out with the different enzymes studied

Test	*Type of enzyme*	*Enzyme quantity*	*Biopolymer quantity (g)*	*HRT (h)*
L1	Amilase (*B. licheniformis*)	2 mg	7	48
L2		4 mg	7	48
A1	Amilase (*B. amyloliquefaciens)*	20 µL	7	48
A2		40 µL	7	48
Test 1	Esterase (*B. subtilis*)	2.5 mg	3.5	65
Test 2		2.5 mg	1.7	65
Test 3	Amilase + Esterase	20 µL + 2.5 mg	3.5	48 + 48
Test 4	Esterase + Amilase	2.5 mg + 20 µL	3.5	48 + 48

Table 4. Summary of anaerobic digestion conditions tested

Test	*Colture*	*pH*	*T (°C)*	*Medium (mL)*	*OFMSW (mL)*	*Water (mL)*	*Digestate (mL)*	*Total volume (mL)*	*Pretreat-ment*	*HRT (d)*
D1	Clostridia	5	37	337.5	-		37.5	375	-	111
D2	Clostridia	5	37	-	-	337.5	37.5	375	-	111
D3	Methanigenic	7	50	337.5	-		37.5	375	-	76
D4	Methanigenic	7	50	-	-	337.5	37.5	375	-	76
FD1	Clostridia	5	37	37.5	300	-	37.5	375	-	111
FD1*	Clostridia	5	37	37.5	300	-	37.5	375	A1 o L1	111
FD2*	Methanigenic	7	50	37.5	300	-	37.5	375	A1 o L1	56
FD4*	Methanigenic	7	50	37.5	250	-	87.5	375	A2 o L2	86
FD5*	Clostridia	5	37	37.5	250	-	87.5	375	A2 o L2	86
FD6*	Clostridia	5	37	37.5	300	-	37.5	375	Prova 1	49
FD7*	Clostridia	5	37	37.5	300	-	37.5	375	Prova 3	49
FD8*	Methanigenic	7	50	37.5	300	-	37.5	375	Prova 2	49
FD9*	Methanigenic	7	50	37.5	300	-	37.5	375	Prova 4	49

Table 5. Medium for Clostridia and methanogenic bacteria

Reagent	*Medium Clostridia (g)*	*Medium methanigenic (g)*
Distillate water	675	675
$NaHCO_3$	0.324	3.375
NH_4Cl	0.206	0.675
KH_2PO_4	0.102	0.202
$FeCl_3$ $6H_2O$	0.007	-
Yeast extract	0.021	-
NaCl	-	0.405
Glucose	-	13.5

All bottles were placed in anaerobiosis (nitrogen flow for 15 min under a chemical fume hood). At the end of this step, the 0.5 L bottles were sealed with a cap. Was attached an anaerobiosis indicator, appropriately activated with distilled water. A one liter or 3 L Tedlar bag was attached to each bottle's cap to collect the gases produced during the fermentation process. The bottles were placed in the shaking bath at 37 °C or in the 50°C orbital shaker. Each time a bottle was opened for sampling, the pH was measured to monitor its trend and put back into anaerobiosis as described above. The bioplastic samples were rinsed and then placed in an oven at 55°C for 2-3 hours or overnight (in the case of enzymatically pre-treated bioplastics) so that they dry well; then, they are placed in a desiccator for 30 minutes. After drying, the samples are weighed, and the loss incurred over time is estimated.

2.4. Pilot-scale enzymatic pre-treatment and anaerobic digestion tests

Enzymatic pre-treatment testing of pilot-scale bioplastics took place in the pilot plant consisting of a 7l reactor (LAMBDA Minifor Fermenter). The reactor is placed on a housing equipped with a coil for temperature control and connected to two peristaltic pumps that control its pH by withdrawing controlled amounts of H_2SO_4 or NaOH from two bottles placed on the base of the reactor support. Temperature and pH are measured with the probe. After filling the reactor, temperature, pH, and stirring values are set via the control panel integrated into the reactor housing.

BP bags were cut into squares of about 10x10 cm, weighed (initial weight of 0.21 g each), and subjected to enzymatic pre-treatment to promote their degradation during anaerobic digestion tests by methanigenic bacteria. In the 7 L reactor, 35 g of so-cut bags (i.e., about 166 squares), 3.30 L of phosphate buffer (100 mM, pH 7), 200 µl of α-amylase from *Bacillus amyloliquefaciens* and 25 mg of an esterase from *Bacillus subtilis* were placed, according to the protocol developed after laboratory-scale enzymatic pre-treatment trials. The reactor was kept stirring at a constant temperature of 55°C for 48 hours. Samples of bioplastics were taken from the reactor after 18, 24, 36, and 48 hours to monitor their weight change.

After 48 hours of enzymatic pre-treatment, the reactor was emptied. The bioplastics were put back into the reactor while the buffer was discarded. The OFSMW, consisting mainly of fruit and vegetable waste, was shredded and slightly diluted with water. To the 5 L reactor, already containing the pre-treated bioplastics, 3 L of OFMSW, 375 mL of digestate containing the methanogenic bacteria, and 375 mL of the medium, whose recipe is given in Table 5, were added, with a final volume of about 4 L. Finally, was set a temperature of 50°C and constant stirring. To achieve anaerobiosis and to promote the initial stirring of the mixture, nitrogen was insufflate from the bottom of the reactor for about one hour. On samples was performed a FOS/TAC assay by titration with 0.1 N sulfuric acid to monitor and maintain this parameter in line with optimal values for anaerobic digestion.

After 30 and 55 days from the start of the test, digestate samples were taken and sent to a certified laboratory to quantify the weight change and to evaluate the degradation of PBAT into its three monomers: adipic acid, terephthalic acid, and 1,4-butanediol.

2.5. Quantification of weight loss and the presence of terephthalic acid, adipic acid and 1,4-butanediol

For weight loss quantification, samples were diluted with water and allowed to be decanted overnight. After filtering out the supernatant, the solid was rinsed several times with water and filtered; all the solid was then dried in an oven at 80°C and weighed.

For terephthalic acid quantification, the water in each sample was directly analysed through an HPLC-UV, employing a Phenomenex Sinergi Hydro 250 x 4.6 mm, 4µm column and eluting with a water +0.1% phosphoric acid/acetonitrile mixture. The wavelength of detection was 254 nm.

For adipic acid quantification, it was derivatised in acidic methanol and then determined in GC-MS, with a VF-17ms column.

For 1,4-butanediol, methanol was directly injected into a GC-MS system, equipped with a VF-17ms column, for sample dilution.

3. Results and discussion

3.1. Laboratory-scale chemical pre-treatment and anaerobic digestion

Due to the dissolution of the samples, it wasn't possible to proceed with evaluations of the effectiveness of the treatment in terms of weight decrease. Therefore, analytical evaluations were made to assess whether some fundamental components of the polymer were separated as bond degradation results. Thus, 1,4 butanediol, adipic acid, and terephthalic acid were searched in the hydrolysate. The only quantifiable compound in the pre-treated hydrolysates was 1,4 butanediol. The percentage by weight of the compound found in the hydrolysate varied from a minimum of 0.265% to a maximum of 0.626%, depending on the pre-treatment performed. The maximum found corresponds to a conversion of about 30% w/w of the converted BP to 1,4 butanediol.

The NaOH addition in the bioreactor prevents acidification of the medium, prolongs the acidogenic for at least two weeks, and promotes hydrolysis of the bioplastic (Garcia-Aguirre et al., 2019). Comparable results were also achieved by Hobbs et al. (2019), using a PLA-based starting BP. In the study, alkali pretreatment at 21°C was critical to allow near-complete solubilization of the polymer (about 97%) after 15 days. In the present work, performing tests at a temperature of 50°C probably allowed the treatment time to be cut down, speeding up the breakdown of the polymer's internal bonds and resulting in BPs that were no longer visually detectable as early as 4 days. Treatments with hydrochloric acid proved to be less effective than those with caustic soda. The anaerobic digestion test proved effective in that, although already reduced to a powdery state in solution after chemical pre-treatment, the plastics were no longer visually detectable after anaerobic digestion.

3.2. Laboratory-scale enzymatic pre-treatment

Below are the trends of plastic weight decrease detected during the tests conducted; the blank tests were performed with the same reaction parameters but without the enzyme.

About the experiments involving *Bacillus licheniformis* (L1 and L2), it can be seen that the increase of the enzyme in solution does not result in a corresponding increase in the decrease in the weight of the bioplastics; moreover, there is not much difference between the decrease in the blank tests and those with the enzyme. Tests A1 and A2 (*Bacillus amyloliquefaciens*) show a decrease in weight that increases proportionately with the doubling of the enzyme concentration. In 48 h, 16% of the total bioplastic can be hydrolyzed. Tests with *Bacillus subtilis* esterase for cleavage of ester bonds (Test 1 and Test 2) do not denote direct efficacy in hydrolysing plastics. The trend outlined follows that of the blank tests. Tests 3 and 4 were carried out to assess whether esterases have an ester bond-breaking effect for improving the efficacy of amylases used in combination; the enzyme used was *B. amyloliquefaciens* since it was proved more efficient than *B. licheniformis*.

The tests showed that switching enzymes does not result in a different decrease in weight. The two effects add up to achieve a weight decrease of slightly less than 20%. The generated maltose concentration was evaluated for the pre-treatment tests. The analysis of maltose concentrations in the hydrolysates is consistent with the findings for weight decreases.

3.3. Laboratory-scale anaerobic digestion tests

It can be shown that enzymatic pre-treatment promotes higher degradation of bioplastic samples during anaerobic digestion trials by methanogenic bacteria: microbial enzymes, depolymerases or esterase, break down polymers into fragments easily assimilated for the microbial consortium in the digestate (Abraham et al., 2021).

Plastics that were pre-treated and processed in digestion with methanigens were all found to be unsampled after fermentation, in contrast to plastics that were not subjected to enzymatic pre-treatment, which achieved a maximum percentage reduction in weight of plastic samples of about 70%. However, this value represents an excellent result when compared with other data in the literature (Abraham et al., 2021). The degradation trend could be influenced by several factors attributable to different anaerobic digestion plants, for example, specific microbial consortium or the chemical characteristics of the digestate. In the future, it is relevant to study the influence of these factors to make it easier to reproduce the implemented method on an industrial scale.

In addition, trials in which pre-treatment had been done with esterases (in which the immediate result of pre-treatment did not seem significant) led in subsequent tests with methanogenic bacteria to a stepwise effect on kinetics. After 49 days, timing not too dissimilar to some industrial digestion processes (Ruggero et al., 2020), the plastics were no longer sampleable, an effect achieved with the other enzymatic pre-treatments after 56 and 86 days.

3.4. Pilot-scale enzymatic pre-treatments and anaerobic digestion tests

From the data shown in Table 6, it can be established that enzymatic pre-treatments caused a 27% reduction in the weight of bioplastics, a result in line with what was obtained during laboratory-scale tests. Furthermore, from these results, it could be assumed that an enzymatic pre-treatment equal to that carried out would present its process optimization after 24h. After ten days of the test, the digestate had a much more liquid consistency, while the bioplastics had a flakes appearance, evidence that the hydrolysis phase had been triggered. Another study achieved similar results after 30 days of anaerobic batch digestion (Kosheleva et al., 2023).

Infrared spectrometry analysis showed that the microparticles present were all PBAT microplastics. The results of the tests are shown in Table 7. As can be seen after 30 days, the concentration of PBAT was reduced by 70%, from 7000 mg/L to 2106 mg/L, degrading into its three monomers, mainly into adipic acid.

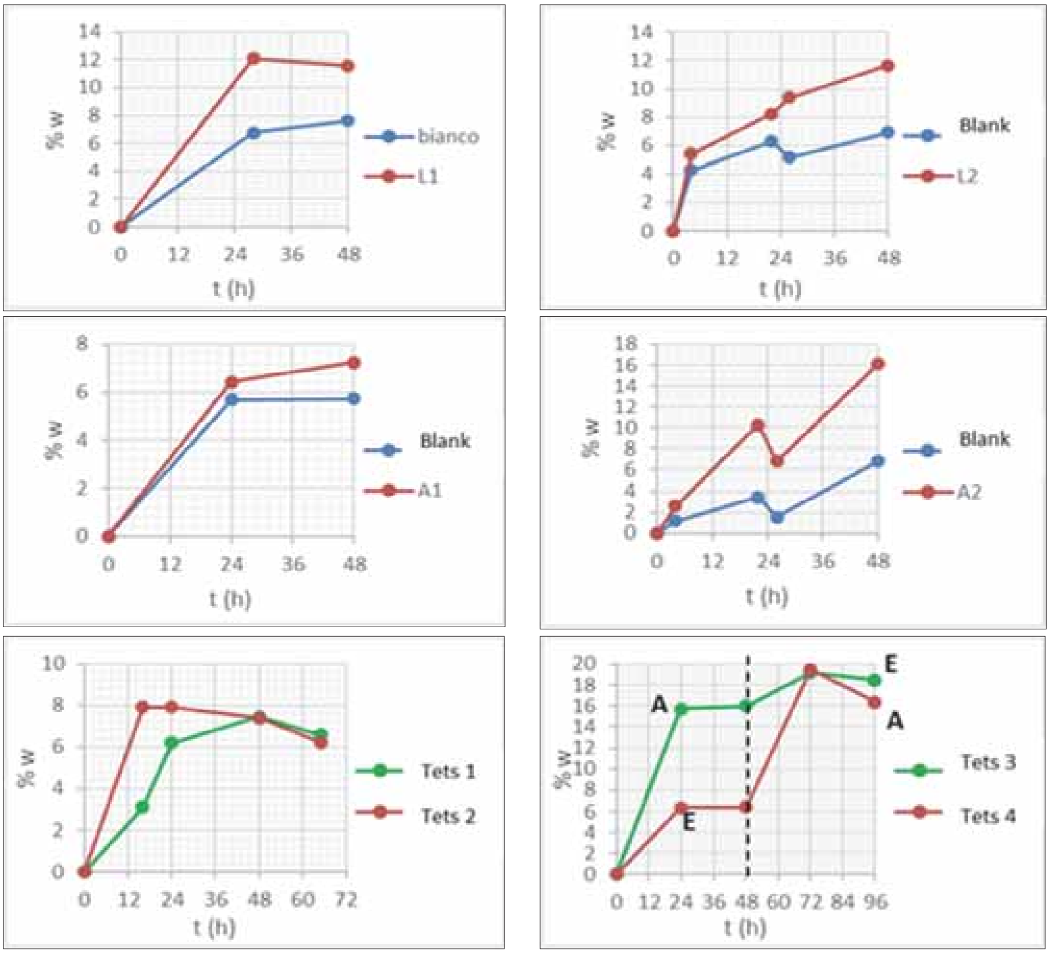


Fig. 1. Weight decreases over time

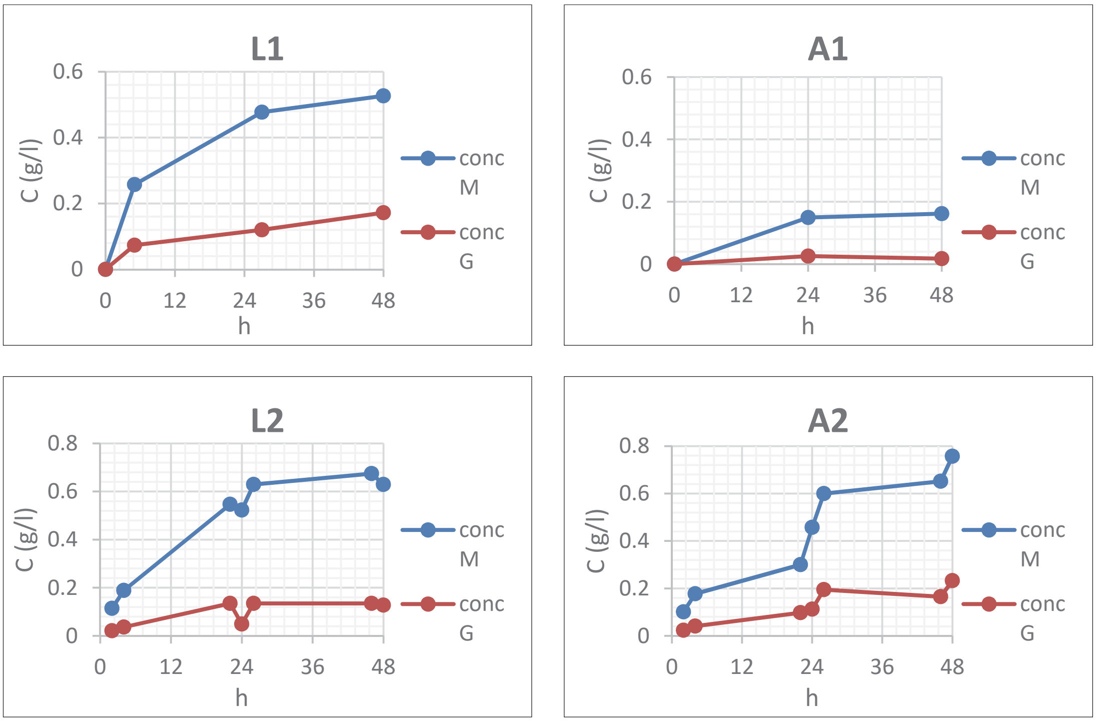


Fig. 2. Trend of maltose and glucose concentration in the hydrolyzate

Table 6. Weight variation during bioplastic enzymatic treatments

	Dry weight (g)	*Weight loss (%)*
18 h	0.2049	2.4
24 h	0.1595	24.0
36 h	0.1553	26.0
48 h	0.1530	27.1

Table 7. Bioplastics degradation rate and concentration of adipic acid, terephthalic acid, and 1,4-butanediol

	After 30 days	*After 55 days*
Degradation (%)	70	97
Adipic acid (mg/L)	130	167
Terephthalic acid (mg/L)	13.6	21.3
1,4-butanediol (mg/L)	33.8	76.6

In light of the results achieved and comparing the chemical and enzymatic pretreatment results, it is found that enzymes are more effective in breaking the polymer's internal bonds, allowing all three building blocks to be released, albeit in different ways, thus promoting the digestion of PBAT by methanigenic bacteria.

4. **Conclusion**

Anaerobic digestion seems to be a great way to dispose of BP-based waste. In addition, the efficiency of the process increases when chemical or enzymatic pretreatment is used. Both technologies have limitations, so the choice falls to the most efficient method. For the results achieved, it seems to be the enzymatic one.

The results show degradation efficiencies of up to 30 % with 96 hours of alkaline treatment and about 20 % with 72 hours of biological treatment. The results of the pilot tests confirmed the degrading ability of the enzymes and supported the hypothesis of possible industrial use: the effects can already be seen after only 24 hours of treatment by adding the enzymes all at once. Afterward, an anaerobic digestion test was performed with a degradation efficiency of 70 % after 30 days of digestion. Studies on the same polymer have obtained fewer exciting results, with degradations of up to 15% after 55 days at 50°C. These results are very positive and suggest that the retention time of industrial anaerobic digestion plants could be compatible with a high degradation rate of bio-plastics digested together with the OFMSW, provided that enzymatic pre-treatment is carried out beforehand.

Complete degradation of bioplastics should be allowed by enzymatic pre-treatment at the head of an anaerobic digestion process followed by aerobic digestion. They lead the way for further tests to confirm and refine the conclusions obtained and described in this paper and to develop complete and efficient industrial supply chains dedicated to the valorization of bio-plastics.

Acknowledgements

The tests described in this paper were conducted within the "Saturno" project (https://saturnobioeconomia.it/) funded by FinPiemonte. We are grateful to all project partners for their cooperation and contribution to the results obtained.

References

Abraham A., Park H., Choi O., Sang B., (2021), Anaerobic co-digestion of bioplastics as a sustainable mode of waste management with improved energy production – A review, *Bioresource Technology*, **322**, 124537, https://doi.org/10.1016/j.biortech.2020.124537.

Calabro P.S., Folino A., Fazzino F., Komilis D., (2020), Preliminary evaluation of the anaerobic biodegradability of three biobased materials used for the production of disposable plastics, *Journal of Hazardous Materials*, **390**, 121-653.

Comanita E.-D., Ghinea C., Hlihor R.-M, Simion I.-M., Smaranda C., Favier L., Rosca M., Gostin I., Gavrilescu M., (2015), Challenges and oportunities in green plastics: an assessment using the ELECTRE decision-aid method, *Environmental Engineering and Management Journal*, **14**, 689-702.

Garcia-Aguirre J., Esteban-Gutiérrez M., Irizar I., González-Mtnez de Goni J., Aymerich E., (2019), Continuous acidogenic fermentation: Narrowing the gap between laboratory testing and industrial application, *Bioresource Technology*, **282**, 407-416.

Hobbs S.R., Parameswaran P., Astmann B., Devkota J.P., Landis A.E., (2019), Anaerobic codigestion of food waste and polylactic acid: effect of pretreatment on methane yield and solid reduction, *Advances in Materials Science and Engineering*, **2019**, 1-6.

Kosheleva A., Gadaleta G., De Gisi S., Heerenklage J., Picuno C., Notarnicola M., Kuchta K., Sorrentino A, (2023), Co-digestion of food waste and cellulose-based bioplastic: From batch to semi-continuous scale investigation, *Waste Management*, **156**, 272-281.

Mohee R., Unmar G.D., Mudhoo A., Khadoo P., (2008), Biodegradability of biodegradable/degradable plastic materials under aerobic and anaerobic conditions, *Waste Management*, **28,** 1624-1629.

Muroi F., Tachibana Y., Soulenthone P., Yamamoto K., Mizuno T., Sakurai T., Kobayashi Y., Kasuya K., (2017), Characterization of a poly(butylene adipate-co-terephthalate) hydrolase from the aerobic mesophilic bacterium Bacillus pumilus, *Polymer Degradation and Stability*, **137**, 11-22.

Perz V., Hromic A., Baumschlager A., Steinkellner G., Pavkov-Keller T., Gruber K., Bleymaier K., Zitzenbacher S., Zankel A., Mayrhofer C., Sinkel C., Kueper U., Schlegel K., Ribitsch D., Guebitz G.M., (2016), An esterase from anaerobic clostridium hathewayi can hydrolyze aliphatic-aromatic polyesters, *Environmental Science and Technology*, **50,** 2899-2907.

Ruggero F., Carretti E., Gori R., Lotti T., Lubello C., (2020), Monitoring of degradation of starch-based biopolymer film under different composting conditions, using TGA, FTIR and SEM analysis, *Chemosphere*, **246**, 125770, https://doi.org/10.1016/j.chemosphere.2019.125770.

Suzuki K., Noguchi M.T., Shinozaki Y., Koitabashi M., Sameshima-Yamashita Y., Yoshida S., Fujii T., Kitamoto H.K., (2014), Purification, characterization, and cloning of the gene for a biodegradable plastic-degrading enzyme from Paraphoma-related fungal strain B47-9, *Applied Microbiology and Biotechnology*, **98,** 4457-4465.

Urbanek A.K., Mirończuk A.M., García-Martín A., Saborido A., De la Mata I., Arroyo M., (2020), Biochemical properties and biotechnological applications of microbial enzymes involved in the degradation of polyester-type plastics, *Biochimica et Biophysica Acta - Proteins and Proteomics*, **1868**, 140315, https://doi.org/10.1016/j.bbapap.2019.140315.

Venturelli V., Dolci G., Catenacci A., Malpei F., Grosso M., (2021), Evaluation of the anaerobic degradation of food waste collection bags made of paper or bioplastic (in Italian), *Ingegneria dell'Ambiente*, **8**, 221-234.

Yagi H., Ninomiya F., Funabashi M., Kunioka M., (2014), Mesophilic anaerobic biodegradation test and analysis of eubacteria and archaea involved in anaerobic biodegradation of four specified biodegradable polyesters, *Polymer Degradation and Stability*, **110**, 278-283.

Zumstein M.T., Rechsteiner D., Roduner N., Perz V., Ribitsch D., Guebitz G.M., Kohler H. P.E., McNeill K., Sander M., (2017), Enzymatic hydrolysis of polyester thin films at the nanoscale: Effects of polyester structure and enzyme active-site accessibility, *Environmental Science and Technology*, **51**, 7476-7485.

Environmental Engineering and Management Journal

October 2023, Vol. 22, No. 10, 1767-1774
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2023.152

"Gheorghe Asachi" Technical University of Iasi, Romania

LIFE CYCLE ASSESSMENT OF THE PRODUCTION OF NATURAL AND RECYCLED AGGREGATES FOR CONCRETE: A CASE STUDY IN THE PROVINCE OF BRESCIA

Andrea Piccinali[1]*, Irma Cavallotti[2], Giovanni Plizzari[1], Sabrina Sorlini[1]

[1]Department of Civil, Environmental, Architectural Engineering and Mathematics, University of Brescia, 25123 Brescia, Italy
[2]ICA – Società di Ingegneria Chimica per l'Ambiente, Kilometro Rosso, 24126, Bergamo Italy

Abstract

The construction sector in Europe consumes about 50% of the total available raw materials, using enormous quantities of natural resources and soil from which these raw materials are extracted. At the same time, construction and demolition waste (CDW) accounts for about 35% of all waste produced both at the European and national levels, with approximately 60 million tonnes produced annually in Italy alone. The aim of this study, using the Life Cycle Assessment (LCA) methodology, was to analyse the environmental performance of the production process of recycled aggregates (RA) from CDW compared to natural aggregates (NA) for concrete production. In terms of overall environmental impact, the LCA highlighted that the production of recycled aggregates from construction and demolition waste has a significantly lower impact compared to the extraction of natural aggregates from quarries. The results of the LCA confirmed the importance and environmental advantages of using recycled aggregates in the construction sector, as they contribute to reducing the extraction of natural resources and the overall environmental impact of the production process. However, it is important to note that the actual assessment of environmental impact also depends on various specific factors of the case study, such as the technologies employed, transportation distances, and the management of CDW.

Key words: construction and demolition waste, life cycle assessment, natural aggregates, recycled aggregates

Received: May, 2023; Revised final: July, 2023; Accepted: September, 2023; Published in final edited form: October, 2023

1. Introduction

As is now well known, one of the global themes of the new millennium is undoubtedly the fight against climate change. In this sense, Europe has been implementing sustainable policies for some time now aimed at safeguarding our planet, which is rapidly heading towards irreversible climate change. These policies, in addition to being aimed at all production sectors, also aim to raise awareness among the population about a more conscious use of resources. The adoption of a circular economy plays a key role in this challenge, as it counters the linear model of production and consumption by aiming to maximize the reuse, recycling and restoration of existing resources. Through the circular economy, resource use can be optimized, reducing pressure on natural sources and helping to ensure access to valuable mineral resources for future generations (Agrawal, 2023).

According to Eurostat studies, in 2020, the total amount of waste produced in the 27 member states of the European Union from all economic activities amounted to 2.151 million tonnes, and in particular, the amount of waste produced by construction and demolition activities is the highest and represents about 37% of all waste produced (including municipal solid waste) (Eurostat, 2022). Italy, with a production of about 66 million tonnes of CDW, is the fourth European country in terms of construction and demolition waste production, after France, Germany, and the Netherlands. Regarding the recovery of these wastes, depending on the individual country, recovery

---

[*] Author to whom all correspondence should be addressed: e-mail: a.piccinali@unibs.it

rates range from 70 to 95%, according to Eurostat (Eurostat, 2022).

According to official data from ISPRA, Italy fully reflects the European situation; in fact, the recovery rate of CDW (excluding excavated soil and rocks) is over 78%, which is above the 70% target set by Directive 2008/98/EC for 2020 (ISPRA, 2022). At the same time, the construction industry, in addition to being the largest producer of waste contributes significantly to the environmental crisis as it is one of the sectors most responsible for land use, energy and resource consumption, with an incidence of around 30% on total energy consumption and 40% on material consumption (IEA, 2022).

To identify and measure the energy and materials utilized throughout the entire life cycle of a product, including the emissions that are released into the environment such as greenhouse gases, toxic substances, and waste, Life Cycle Assessment (LCA) methodology is gaining increasing prominence and importance. As seen, the use of recycled aggregates can widely replace natural aggregates, and the goal is to improve their quality to increase their possibilities of use (Piccinali et al., 2022). However, most studies focus on the utilization of RA as a substitute for NA and the impacts associated with their use in concrete production (Hossain et al, 2016; Jian et al., 2021; Turk et al., 2015) or on different methods of C&D waste management, without emphasizing their production process (Kucukvar et al., 2014, Liu et al. 2020).

For this reason, this work aims to analyze the entire life cycle of the production of RA and extraction of NA only, identifying and evaluating opportunities for environmental improvement, in the specific case of a treatment plant located in the province of Brescia. The evaluation also focused on the environmental impacts generated by the transport of C&D waste from the construction site to the plant, which is the most critical factor (Colangelo et al., 2018; Mah et al., 2018; O'Brien et al., 2009).

2. Material and methods

The study was conducted applying the LCA methodology according to the UNI EN ISO 14040:2021 and UNI EN ISO 14044:2021 (Ente italiano di normazione, 2021a, 2021b) standards respectively titled "Environmental management - Life cycle assessment - Principles and framework" and "Environmental management - Life cycle assessment - Requirements and guidelines", and implemented using the PCR (product category rules) in accordance with UNI EN ISO 15804:2021 "Sustainability of construction works - Environmental product declarations - Product category rules for construction products" (Ente italiano di normazione, 2021c).

2.1. LCA methodology

The criterion for evaluating the environmental impact of the production of both types of aggregates is based on the LCA methodology. The two UNI EN ISO standards that regulate the application of LCA provide for four different iterative phases, including 1) Goal and scope definition, 2) life cycle inventory (LCI) analysis, 3) life cycle impact assessment (LCIA) calculation and 4) results interpretation (Fig. 1).

The first phase of LCA study sets the goals and scope, including the functional unit (FU), system boundary, and data requirements for the life cycle inventory (LCI). Selecting these parameters is crucial, as the FU provides a basis for comparing results. The second one, the LCI phase involves collecting necessary data for the elementary flow from processes involved in the product linked to the FU, while the third phase, the LCIA converts this information to environmental impact scores. The LCIA methodology must be determined before LCI data collection, in line with the defined study goal and scope. The final phase is results interpretation, which includes identifying significant issues, evaluating completeness, sensitivity, and consistency, drawing conclusions, stating limitations, and making recommendations. Impact categories refer to the categories expressed by the 15804:2021 methodology.

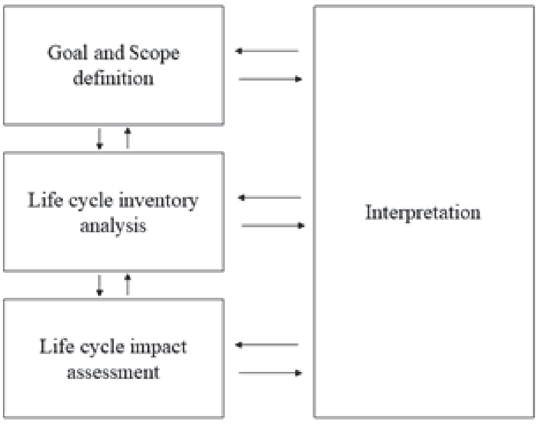


Fig. 1. Phases of an LCA (adapted from UNI EN ISO 14040:2021)

2.1.1. Goal and scope definition and functional unit

This work aims to identify the environmental impacts during the life cycle related to the production of natural aggregate and recycled aggregate from construction and demolition waste for concrete production. Both types of aggregates, recycled and natural, were analyzed so that once produced, they had the same function and were both certified according to the UNI EN 12620:2019 standard "Aggregates for concrete" so that they could be compared with each other.

The functional unit used for the study is 1 ton of aggregate produced and ready to be used in a concrete production plant.

2.1.2. System boundaries and case study

The system boundaries for both analyses conducted are defined as "from cradle to gate", according to what is expressed in UNI EN ISO 15804:2021. These boundaries encompass the A1-A3 product phases, which include the extraction of raw materials (only applicable in the case of natural aggregates), transportation of raw materials, and product manufacturing. While some studies include option A4, which considers the transportation impact of construction products from the manufacturer to the construction site during the construction process stage, it was not taken into account in this study as the focus was solely on A1-A3.

The case study, from which primary data for analysis was collected, is a treatment plant located in the province of Brescia. This site is particularly unique because a quarry for extracting virgin material is also present in the same area.

As regards the RA production, once demolished mainly from small demolitions, the CDW is transported to the plant. Upon arrival at the plant, after verifying the necessary documentation and checking for non-hazardousness, the CDW is unloaded in a designated area and sorted according to its EWC code. Before being crushed, the waste undergoes a preliminary process of removing iron and reducing its volume through the use of a mechanical clamp. Finally, there is a manual removal phase for other materials such as plastics or wood present in the CDW, which are collected separately. In this case, no specific mechanical removal processes such as flotation or air injection are required. However, the quantity of such materials is very low as there is already a preliminary manual removal phase at the construction site. Once the preliminary processes are completed, the material is moved from the deposit area to the crusher's mouth by a wheel loader. The mobile crusher is a machine that allows the granulometric reduction of CDW through a crushing process, while at the same time separating the metallic materials still present within the waste. The crushed CDW, not yet RA, is stored in designated lots awaiting a leaching test to confirm the cessation of its waste qualification.

As regards the NA, the extraction is carried out using a dredger that excavates inside a water basin. This dredger operates on electric current. Once extracted, the natural aggregate is transported via conveyor belts to a sieve that is responsible for separating it into different sizes (gravel and sand of different dimensions). During this process, there is no need to wash the aggregates as they are extracted directly from a water basin. As a result, there are several piles of different sizes at the output of the sieve, which are then moved to storage yards using dumpers. Fig. 2 graphically represents the system boundaries under analysis. Regarding the production of recycled aggregates, the environmental impact analysis process begins immediately after demolition, when construction and demolition waste is transported to the plant.

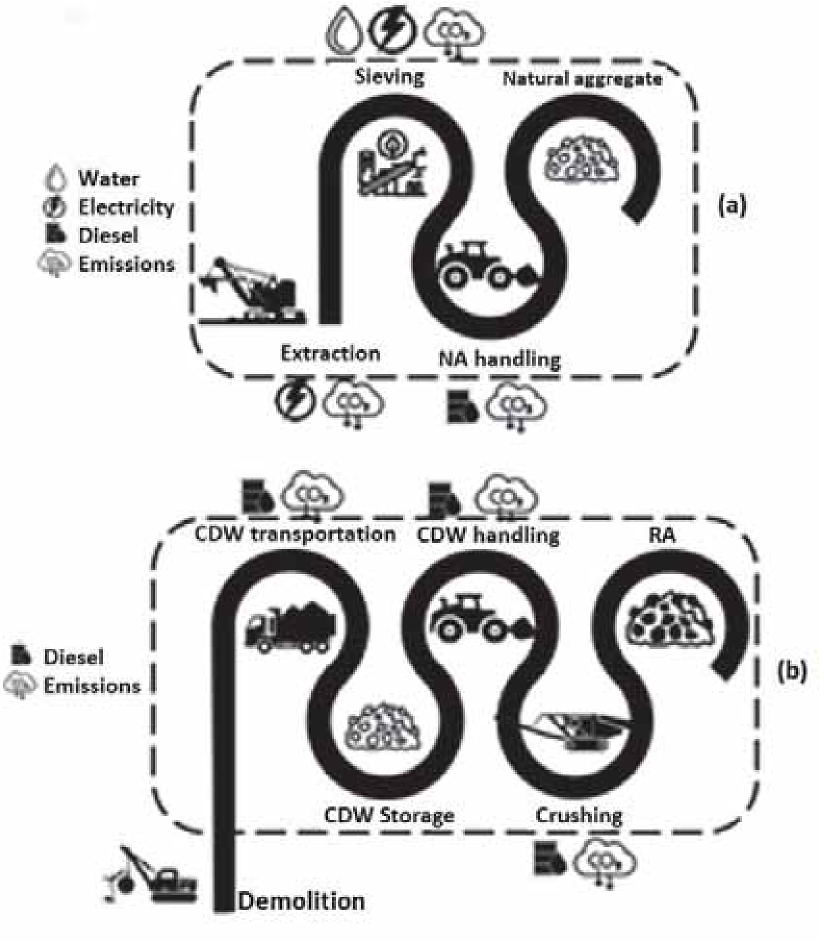


Fig. 2. (a) System boundary of the natural aggregate extraction process (b) System boundary of the recycled aggregate production process

2.2. Data collection and inventory analysis

The inventory of the production phase of both types of aggregate is based on primary data collected directly from the production plant of these two aggregates. When data collection was not possible due to a lack of information, the Ecoinvent v3.6 database (allocation, cut-off by classification) was used.

Technical visits and site inspections were carried out at the plant under analysis to collect the inventory data necessary to quantify the flows of materials, energy, and environmental emissions associated with the production process. Specifically, to better represent the studied reality in this LCA analysis, all processes related to the extraction and processing phases of natural inert materials and the treatment of C&D waste for RA production were adequately reconstructed based on the collected operational data. Regarding the process of extraction and processing of NA, the electrically powered extraction dredge and the fixed processing plant, also powered by electricity, were considered. On the other hand, for the process of C&D waste treatment, the mobile plant (MOBY 1001 jaw crusher) powered by diesel fuel was considered. Quantifications of the total amount of material treated per day are listed in Table 2, to facilitate then the possible reconstruction of environmental impacts obtained in data processing.

After evaluating the daily quantities processed by the treatment plants, information was collected on the energy consumption of the single stages, as well as The consumption of internal transport in the treatment plant. Especially, Information collected was about the consumption of electricity (extraction dredge and fixed plant), diesel fuel (mobile plant and handling equipment), and water (washing natural aggregates and for dust suppression that may arise during the handling and discharge of materials from conveyor belts). Information about the specific consumptions are listed in Table 3. It should be noted that, since the C&D waste treatment process is a dry process, no water consumption is expected during its operation.

Furthermore, after evaluating the consumption and quantities processed, the required processing times have also been taken into consideration. Taken directly at the plant, they refer to the time required to crush one ton of C&D waste, the extraction of one ton of AN, and the time required to transport the processed materials from one point of the plant to another. As for the loader, the times also refer to the time required to load the mobile crushing plant. These are listed in Table 4.

The data for which it was necessary to use the Ecoinvent database mainly refer to energy sources whose origin could not be reconstructed in order to better calculate the environmental impact of the processes in the boundaries of the study.

2.3. Life cycle impact assessment

The impact categories chosen in accordance with the UNI 15804:2021 standard and all the impact categories provided by this standard have been used and analyzed. SimaPro 9.1 was used to build the LCIA model and impact analysis. The following impact categories have been evaluated: *climate change; ozone depletion; ionizing radiation; photochemical ozone formation; particulate matter; human toxicity, non-cancer; human toxicity, cancer; acidification; eutrophication, freshwater; eutrophication, marine; eutrophication, terrestrial; ecotoxicity, freshwater; land use; water use; resource use, fossils; resource use, minerals, and metals.* For all the impact categories, individual emission factors were identified so that the amounts of emissions associated with specific categories per unit of output could be calculated. Then, total emissions were calculated by multiplying the activity data by the relevant emission factors.

After that, to represent and compare the individual impact categories with each other, it was necessary to apply the different normalization factors related to each of them. The characterization factors are listed in Table 5.

Table 2. Quantity of excavated NA and processed CDW daily

Treatment	***NA***	***RA***
	t/day	***t/day***
Natural aggregates extraction dredge	2500	---
Natural aggregates fixed processing plant	2000	---
Mobile plant for CDW treatment	---	155

Table 3. Processes energy and water consumption

Treatment Machinery	***Diesel***	***Electric Energy***	***Water***
	L/t	***(kWh/t)***	***L/t***
Natural aggregates extraction dredge	---	1.6	---
Natural aggregates fixed processing plant	---	1.75	1.25
Mobile plant for CDW treatment	0.14	---	---
Loader	0.07	---	---

Table 4. Processes duration

Treatment machinery	***Time (min)***
Natural aggregates extraction dredge	0.27
Natural aggregates fixed processing plant	0.27
Mobile plant for CDW treatment	0.4
Loader	0.4

Table 5. Normalization factor for each impact category

Impact category	***Normalization factor***
Climate change	0.0001235
Ozone depletion	18.64
Ionizing radiation	0.000237
Photochemical ozone formation	0.02463
Particulate matter	1680
Human toxicity, non-cancer	4354
Human toxicity, cancer	59173
Acidification	0.018
Eutrophication, freshwater	0.6223
Eutrophication, marine	0.05116
Eutrophication, terrestrial	0.005658
Ecotoxicity, freshwater	0.00002343
Land use	0.00000122
Water use	0.00008719
Resource use, fossils	0.00001538
Resource use, minerals and metals.	15.71

2.4. Life cycle interpretation

For both studies conducted (RA, NA), the environmental impacts of each main compartment are assessed in the Climate change category to determine which is the hot spot of the treatment solution, in order to define the best solution to reduce the environmental impact generated by the production of recycled aggregate.

3. Results and discussion

Before assessing the individual impact categories as explicitly required by UNI EN 15804:2021, an assessment of the overall impacts in terms of CO_2eq was carried out. This assessment is very important because it shows the Global Warming Potential (GWP) of individual products to be compared. Subsequent diversification into impact categories is seen as necessary to specify the individual environmental effects of individual production steps. Figure 3 represents the total environmental impacts related to the production of AN and RA. As regards the total environmental impacts, 2.47 kgCO_2eq for AN and 4.7 kgCO_2eq for AR are released into the atmosphere during the production process. In this case, regarding the transport of the recycled aggregate from the production site to the treatment plant alone produces 3.43 kgCO_2eq accounting for about 70% of the total. The outcome demonstrates that RA production has a higher harm compared to NA extraction.

After the first assessment conducted on the total impacts, analyses have been also developed on all other impact categories as depicted in Fig. 4. Regarding the results obtained from this analysis, with the exception of Eutrophication freshwater, Land use and Water use, all other categories have impacts for natural aggregate ranging from 80% to 30% less for natural aggregate in comparison with recycled aggregate.

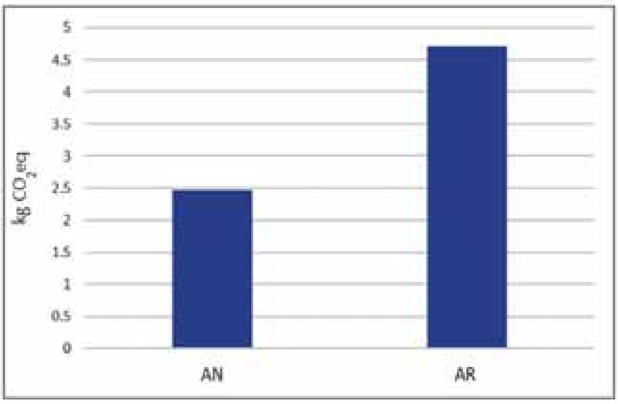


Fig. 3. Global warming potential related to NA and RA

Specifically, the impact categories that obtained a higher difference are *photochemical ozone formation*, *particulate matter*, and *eutrophication marine*, for all three the difference is about 80 percent between the two types of aggregate, directly referring to the use of diesel.

In fact, the combustion of fossil fuels, such as the diesel used by trucks, generates high amounts of NOx, which contributes to the eutrophication and acidification of the environment (Ferronato et al., 2022) and increases air pollution due to the increase in particulate matter (Borghi et al., 2018).

In contrast, for the impact category referring to climate change, expressed in kgCO$_2$ eq, the difference in environmental impact is about 50 percent. On the other hand, the impact categories of eutrophication freshwater, land use, and water use, which have less impact for RA compared to NA, are due to the direct extraction of material from the water and the greater consumption of soil caused by the area affected by the extraction plant (Luo et al., 2022). As for the water use category, the high difference is due to the processing plant of natural aggregates (NA) that uses water for washing the aggregates, unlike the recycled aggregates (RA) that use a dry production system (Renzulli et al., 2016). According to Marinković et al. (2010), the outcome shows that the production of natural aggregates has a lower impact compared to recycled aggregates. However, due to the different operations involved in the production of RA, a hotspot analysis is needed to investigate the main impact contributors.

3.1. Recycled aggregates production hotspot analysis

The impact of RA production on the environment is illustrated in Fig. 5 for all impact categories. In this case, the transportation of C&D waste from the construction site to the treatment plant represents the largest environmental burden in all categories of the RA production process as confirmed by Blengini and Garbarino (2010). In fact, in most non-toxic categories, the transportation of CDW is a major contributor to the overall impact results (Butera et al., 2015).

In this specific case, for average transportation distances of 20 km, the impact due to the transportation of materials varies from 65% to 97% for different impact categories. Despite all processes for the production of recycled aggregates running on diesel, the average transportation distance remains the primary source of environmental impact in all analyzed impact categories.

Specifically, it ranges from a maximum value of 97% for mineral resource utilization and land use, to a minimum value of 65% for the Human toxicity cancer category. As for the other 14 categories, impacts due to transport are about 70-75% of the total. This result has been consistently found in various literature studies focusing on this topic. In fact, the feasibility of a waste scenario is highly dependent on transportation distance and diesel use (Mah et al., 2018; Papadaki et al., 2022).

Therefore, based on the results obtained from natural aggregate extraction, it was decided to develop additional scenarios that would reduce transportation distances. It has been decided, in fact, to reduce the transportation distance of the CDW to 0 km, as it is the same distance traveled by the NA since it is produced and processed in the same facility. As demonstrated in Fig. 6, eliminating transportation distances leads to a significant decrease in environmental impacts.

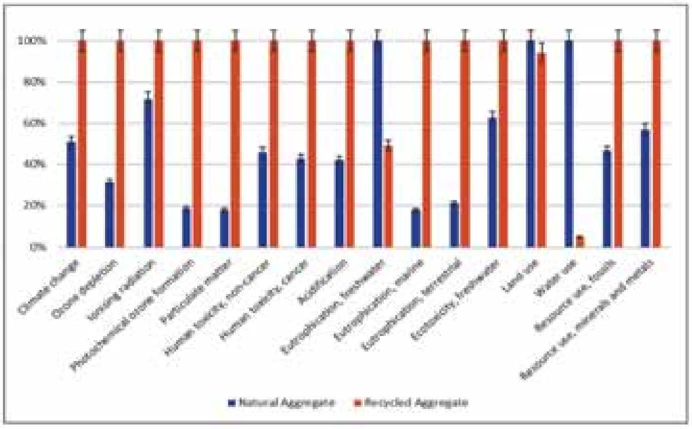


Fig. 4. Environmental impacts for RA and NA for each impact category

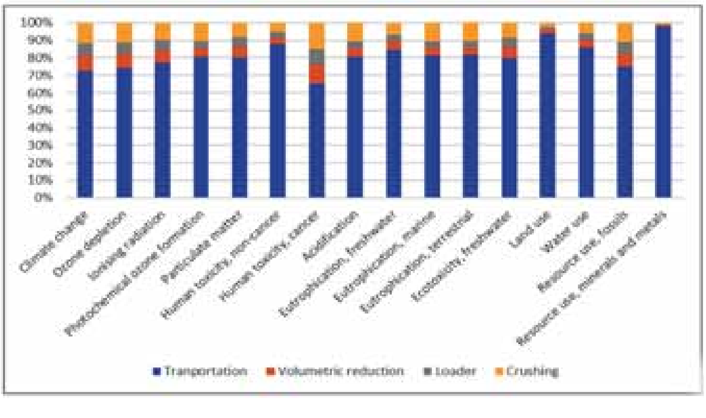


Fig. 5. RA production percentage contribution relative to each impact category

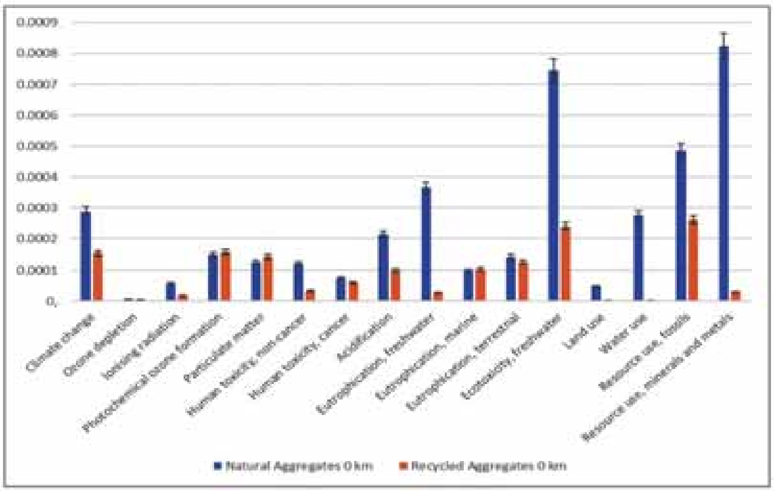


Fig. 6. Normalized impacts calculated for each impact category (No distance considered)

For all impact categories except photochemical ozone formation, particulate matter, and eutrophication in marine environments, the elimination of the transportation distances in the case of the production of recycled aggregates, still have an impact higher than the one for NA extraction, while all other categories show a considerable reduction with decreasing transportation distances (Butera et al., 2015). The result for these impact categories is due not only to the impact of transportation but also to the numerous processing operations carried out on-site, reducing the transportation of CDW alone would not lead to excessive savings (Borghi et al., 2018; Butera et al., 2015).

Specifically, when it comes to the freshwater ecotoxicity category, it shows one of the biggest disparities between the two types of aggregates, second only to the resource use of minerals and metals. This is primarily because of the water usage for washing NA, and, by the modeling of the Italian energy mix production, which, at the Italian level incorporates 14% hydroelectric energy (Borghi et al. 2018). The analysis of the subsystems in the recycling chain has confirmed the essential role of transportation and emphasizes the need for a better understanding and efficient management of the collection and distribution network. If there are excessive distances or the use of inefficient collection systems, it can compromise the overall environmental performance. (Blengini and Garbarino, 2010)

Considering zero transport distances, a reduction of environmental impacts by over 70% is achieved compared to the case study. However, this scenario was proposed to enable a pure comparison between the aggregate production stages. This is useful since our case study represents an exceptional case where CDW is delivered to the plant to produce RA, while AN is extracted directly from the quarry. The comparison between aggregate production processes is extensively studied in the literature.

Numerous studies, including Hossain et al. (2016) and Simion et al. (2013), have confirmed the lower environmental impact of AR production compared to AN without considering transportation distances from the production sites to the treatment plants.

4. Conclusions

In conclusion, this paper conducted a comprehensive Life Cycle Assessment (LCA) analysis to compare the environmental performance of recycled aggregates (RA) derived from construction and demolition waste (CDW) with natural aggregates (NA). Considering the case study, the LCA analysis determined that when accounting for waste transportation to the treatment facility, the production of RA has a significantly higher environmental impact compared to the extraction of NA. This finding highlights the importance of evaluating transportation and the need for careful material delivery planning to reduce environmental impacts.

However, when transportation is not considered and only the production processes is evaluated, a substantial reduction in environmental impacts for the production of RA compared to NA has been demonstrated.

Nevertheless, it is crucial to consider site-specific factors, such as waste management practices, transportation distances, and the energy mix used by the treatment plant when assessing the environmental impact of aggregate production. Local circumstances and infrastructure play a significant role in determining the overall environmental performance of each option.

Further research and case studies are encouraged to investigate specific contexts, advancements in recycling technologies, and waste management practices. This will enable improvements in environmental performance and promote the widespread adoption of recycled aggregates in construction projects.

Acknowledgements

This work is developed within the Ph.D. research project "Study of sustainable solutions for the use of recycled materials in the construction sector", financed by ANCE Brescia. The authors wish to thank ANCE Brescia for the support during the research work development and data collection at the CDW treatment plants.

References

Agrawal R., Bhagia S., Satlewal A., Ragauskas A.J., (2023), Urban mining from biomass, brine, sewage sludge, phosphogypsum and e-waste for reducing the environmental pollution: Current status of availability, potential, and technologies with a focus on LCA and TEA, *Environmental Research*, **224,** 0013-9351.

Blengini G.A., Garbarino E., (2010), Resources and waste management in Turin (Italy): the role of recycled aggregates in the sustainable supply mix, *Journal of Cleaner Production*, **18**, 1021-1030.

Borghi G., Pantini S., Rigamonti L., (2018), Life cycle assessment of non-hazardous Construction and Demolition Waste (CDW) management in Lombardy Region (Italy), *Journal of Cleaner Production*, **184**, 815-825.

Butera S., Christensen T.H., Astrup T.F., (2015), Life cycle assessment of construction and demolition waste management, *Waste Management*, **44**, 196-205.

Colangelo F., Petrillo A., Cioffi R., Borrelli C., Forcina A., (2018), Life cycle assessment of recycled concretes: A case study in southern Italy, *Science of the Total Environment*, **615**, 1506-1517.

Ente italiano di normazione, (2021a), UNI EN ISO 14044:2021 - Environmental management - Life cycle assessment - Requirements and guidelines, (in Italian).

Ente italiano di normazione, (2021b), UNI EN ISO 14040:2021 - Environmental Management - Life cycle assessment - Principles and framework, (in Italian).

Ente italiano di normazione, (2021c), UNI EN 15804:2021 - Sustainability of buildings - Environmental product declarations - Development framework rules by product category, (in Italian).

Eurostat, (2022), Eurostat – Statistics, On line at: https://ec.europa.eu/eurostat/databrowser/view/env_wasgen/default/table?lang=en

Ferronato N., Guisbert Lizarazu G.E., Gorritty Portillo M.A., Moresco L., Conti F., Torretta V., (2022), Environmental assessment of construction and demolition waste recycling in Bolivia: Focus on transportation distances and selective collection rates *Waste Management and Research*, **40**, 793-805.

Hossain M.U., Poon C.S., Lo I.M.C., Cheng J.C.P., (2016), Comparative environmental evaluation of aggregate production from recycled waste materials and virgin sources by LCA, *Resource Conservation and Recycling*, **109**, 67-77.

IEA, (2022), Building Analysis, On line at: https://www.iea.org/reports/buildings

IISP, (2022), Special waste report 2022, (in Italian), On line at: https://www.isprambiente.gov.it/it/pubblicazioni/rapporti/rapporto-rifiuti-speciali-edizione-2022

Jian S.M., Wu B., Hu N., (2021), Environmental impacts of three waste concrete recycling strategies for prefabricated components through comparative life cycle assessment, *Journal of Cleaner Production*, **328**, 129463, https://doi.org/10.1016/j.jclepro.2021.129463.

Kucukvar M, Egilmez G, Tatari O., (2014), Evaluating environmental impacts of alternative construction waste management approaches using supply-chain-linked life-cycle analysis, *Waste Management & Research*, **32**, 500-508.

Liu J, Huang Z, Wang X., (2020), Economic and Environmental Assessment of Carbon Emissions from Demolition Waste Based on LCA and LCC, *Sustainability*, **12**, 6683, https://doi.org/10.3390/su12166683.

Luo W., Liu S., Hu Y., Hu D., Kow K.W., Pang C., Li B., (2022), Sustainable reuse of excavated soil and recycled concrete aggregate in manufacturing concrete blocks, *Construction and Building Materials*, **342**, 127917, https://doi.org/10.1016/j.conbuildmat.2022.127917.

Mah C.M., Fujiwara T., Ho C.S., (2018), Life cycle assessment and life cycle costing toward eco-efficiency concrete waste management in Malaysia, *Journal of Cleaner Production*, **172**, 3415-3427.

Marinković S., Radonjanin V., Malešev M., Ignjatović I., (2010), Comparative environmental assessment of natural and recycled aggregate concrete, *Waste Management*, **30**, 2255-2264.

O'Brien K.R., Ménaché J., O'Moore L.M., (2009), Impact of fly ash content and fly ash transportation distance on embodied greenhouse gas emissions and water consumption in concrete, *International Journal of Life Cycle Assessment*, **14**, 621-629.

Papadaki D., Nikolaou D.A., Assimakopoulos M.N., (2022), Circular environmental impact of recycled building materials and residential renewable energy, *Sustainability*, **14**, 4039, https://doi.org/10.3390/su14074039.

Piccinali A., Diotti A., Plizzari G., Sorlini S., (2022), Impact of recycled aggregate on the mechanical and environmental properties of concrete: A review, *Materials*, **15,** 1818, https://doi.org/10.3390/ma15051818.

Renzulli P.A., Notarnicola B., Tassielli G., Arcese G., Di Capua R., (2016), Life Cycle Assessment of steel produced in an italian integrated steel mill, *Sustainability*, **8**, 719, https://doi.org/10.3390/su8080719.

Simion I.M., Fortuna M.E., Bonoli A., Gavrilescu M., (2013), Comparing environmental impacts of natural inert and recycled construction and demolition waste processing using LCA, *Journal of Environmental Engineering and Landscape Management*, **21**, 273-287.

Turk J., Cotič Z., Mladenovič A., Šajna A., (2015), Environmental evaluation of green concretes versus conventional concrete by means of LCA, *Waste Management*, **45**, 194-205.

Environmental Engineering and Management Journal

“Gheorghe Asachi” Technical University of Iasi, Romania

73 Mangeron Blvd., 700050, Iasi, Romania
Tel./Fax. +40-232-271759, PO 10, BOX 2111,
URL: http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
e-mail: eemjournal@yahoo.com, eemjoffice@yahoo.com

INSTRUCTIONS FOR AUTHORS

1. Introduction

Environmental Engineering and Management Journal (EEMJ) is an international medium for publication of Original Papers, Reviews, Case Studies, Book Reviews on the fundamentals, applications in environmental engineering and technologies, applied environmental sciences, environmental health, management, sustainable development, education for sustainability. Advertising is also accepted with contractual payment forms.

Submission of a manuscript implies that the work described has not been published before (except in the form of an abstract or as part of a published lecture, review, or thesis); that it is not under consideration for publication elsewhere; that its publication has been approved by all coauthors, if any, as well.

Papers, books for review, offers to review, suggestions and commercials (advertising) should be submitted to the Editor-in-Chief. All papers will be published in English. Non-English speaking authors should seek the advice of a professional language expert or an English speaker to help translate the paper.

2. Legal requirements

The author(s) guarantee(s) that the manuscript is/will not be published elsewhere in any language without the consent of the copyright holders, that the rights of third parties will not be violated, and that the publisher will not be held legally responsible should there be any claims for compensation.
Authors wishing to include figures or text passages that have already been published elsewhere are required to obtain permission from the copyright holder(s) and to include evidence that such permission has been granted when submitting their papers. Any material received without such evidence will be assumed to originate from the authors.

The author(s) are encouraged to transfer the copyright of the article to the publisher upon acceptance of an article by the journal, using the Authors' Warranty and Assignment of Copyright agreement. This transfer enables the Editor to protect the copyrighted material for the authors, but does not relinquish the authors' proprietary rights. The publication of an article is conditioned by the signature of the author to whom correspondence should be addressed on this Authors' Warranty and Assignment of Copyright that is provided by the Editor.

Ethics in publishing

For information on ethics in publishing for journal publication please read the **Important notice for authors** on journal website.

Conflict of interest

All authors are requested to disclose any actual or potential conflict of interest such as any financial, personal or other relationships with other people or organizations concerning the submitted work that could inappropriately influence, or be perceived to influence, their work.

3. Editorial procedure

For original papers, 7000 words are accepted (including Abstract, Keywords, References, Figures and Tables), processed with MS editing facilities.

For review papers (critical evaluation of existing data, defined topics or emerging fields of investigation, critical issues of public concern), 15000 words are accepted (including Abstract, Keywords, References, Figures and Tables).

Manuscripts should be written in US English (American or British usage is accepted, but not a mixture of these) and submitted electronically, in .docx format to the Editor-in-Chief, at one **(only one)** of the following e-mail addresses:

eemjournal at yahoo.com, eem_journal at yahoo.com, eemjeditor at yahoo.com, eemj_editor at yahoo.com, eemj.office at yahoo dot com, eemj_office at yahoo dot com

Please be sure to include your full affiliation and e-mail address.

When submitting the manuscript, it is mandatory to include a cover letter to the editor. The cover letter must state:

- that all authors mutually agree that the manuscript can be submitted to EEMJ
- that the manuscript contains the original work of the authors
- the novelty in results/findings, or significance of results
- that the manuscript has not already been published, or is not under consideration for publication elsewhere

Manuscripts are evaluated first in the Editorial Office (as a preliminary condition for acceptance) in terms of meeting the requirements of the journal, including attempts of plagiarism.
The author is responsible for the accuracy of the whole paper and references. Authors will be notified about the registration of their contribution. Only those contributions which conform to the following instructions can be accepted for the peer-review process. Otherwise, the manuscripts are returned to the authors with observations, comments and annotations.
The peer review process is decisive for paper acceptance. It could be done in several stages, depending on the revision quality of the manuscript in accordance with the requirements of paper evaluators. Please do not transmit electronic data or requirements to the publisher until your manuscript has been reviewed and accepted for publication. Please follow the instructions below.

A minimum of four suitable potential reviewers should be provided by the authors. Please provide their name, e-mail address and institutional affiliation. When compiling the list of potential reviewers please consider the following important criteria: they must be knowledgeable about the subject area of the manuscript; they must not be from the authors' own institution or country; they should not have recent (less than five years) joint publications with any of the authors. However, the final choice of reviewers is at the editors' discretion.

4. Manuscript preparation

Authors must follow the instructions for authors strictly, failing which the manuscripts would be rejected without review. Editors reserve the right to adjust the formatting style to conform to the standards of the journal.

Manuscripts should be concise, in 1.5 line spacing, and should have 2 cm all over margins. The font should be Times New Roman of size 12 points. The numbering of chapters should be in decimal form. Ensure that each new paragraph is clearly indicated, using TAB at 1.00 pts.

The text layout should be in single-column format. Keep the layout of the text as simple as possible. Most formatting codes will be removed and replaced on processing the manuscript. However, do use bold face, italics, subscripts, superscripts etc. Ass the line numbering and page numbers. To avoid unnecessary errors it is strongly advised to use the "spell-check" and "grammar-check" functions of your word processor.

Title page will contain

- A concise and informative title (Times New Roman bold, all caps of size 14 points); the maximum length of the title should be maximum 100 letters and spaces;
  The full name(s) of the author(s) (first name, then last name, with Times New Roman bold 12 points) should be written below the title. The affiliation(s) and complete postal address(es) of the author(s) will be provided immediately after the full name of the authors and will be written with Times New Roman 12 points. When the paper has more than one author, their name will be followed by a mark (Arabic numeral) as superscript; for the corresponding author, an asterix will be added using *Word_Insert_Reference_Footnote_Symbol* sequence.
  Also, the full and e-mail addresses, telephone and fax numbers of the corresponding author will be provided in the footer of the first page, as: Author to whom all correspondence should be addressed: email..., Phone..., Fax... .
- **Abstract:** each paper must be preceded by an abstract presenting the most important results and conclusions in no more than 250 words. Do not include citations, Figures, schemes in the Abstract.
- **Keywords:** three to five keywords should be supplied after the Abstract for indexing purposes, **ordered alphabetically**, using American spelling and avoiding general and plural terms and multiple concepts (avoid, for example, "and", "of"). Be sparing with abbreviations: only abbreviations firmly established in the field may be eligible.
- The text of the paper should be divided into **Introduction, Materials and Methods (or Experimental), Results and Discussion,**

Conclusions, References (for papers dealing with environmental management, policy, education etc., the Experimental part can be replaced by a case-studies presentation).

1. Introduction

State the objectives of the work and provide an adequate background, avoiding a detailed literature survey or a summary of the results.

2. Material and methods (or Experimental)

Provide sufficient detail to allow the work to be reproduced. Methods already published should be indicated by a reference: only relevant modifications should be described.

3. Results and Discussion

Results should be clear and concise. Discussion should explore the significance of the results of the work, not repeat them. Avoid extensive citations and discussion of published literature.

4. Conclusions

The main conclusions drawn from results should be presented in a short Conclusions section. Do not include citations in this section.

Formulae, symbols and abbreviations Formulae will be typeset in Italics (preferably with the Equation Editor of Microsoft Office 2003) and should be written or marked as such in the manuscript, unless they require a different styling. The formulae should be numbered on the right side, between brackets:

$$a^3 = 3M / 4N \qquad (1)$$

Always refer in the text to the Equations as (Eq. 1), Eqs. (1-4) etc., not as “the following Equation” or “Equation below”)

The more complex Chemical Formulae should be presented as Figures.

Abbreviations should be defined when first mentioned in the abstract and again in the main body of the text and used consistently thereafter.

SI units must be used throughout.

Footnotes should be avoided.

References The list of References should only include works that are cited in the text and that have already been published. References should be cited in the text in brackets (Harvard style) as in the following examples: for references with a single author: (Chisti, 1989), for references with two authors: (Gavrilescu and Roman, 1996), for references with three or more authors: (Moo-Young et al., 1999).

References should be alphabetically listed at the end of paper, with hanging at 0.6 pts., with complete details, as follows:

Books: Names and initials of the authors, year (between brackets), chapter title, title of the book, editors, edition, volume number, publisher, place, page number:

Mauch K., Vaseghi S., Reuss M., (2000), *Quantitative Analysis of Metabolic and Signaling Pathways in Saccharomyces cerevisiae*, In: *Bioreaction Engineering*, Schugerl K., Bellgardt K.H. (Eds.), Springer, Berlin Heidelberg New York, 435-477.

Faber K., (2000), *Biotransformations in Organic Chemistry - A Textbook*, vol. VIII, 4th Edition, Springer, Berlin-Heidelberg-New York.

Handbook, (1951), *Handbook of Chemical Engineer*, vol. II, (in Romanian), Technical Press, Bucharest, Romania.

Symposia volumes: Names and initials of the authors, year, paper title, symposium name, volume number, place, date, page numbers:

Clark T.A., Steward D., (1991), *Wood and Environment*, Proc. 6th Int. Symp. on Wood and Pulping Chemistry, Melbourne, June, 25-28, vol. 1, 493-498.

Journal papers: Names and initials of authors, year (between brackets), full title of the paper, full name of the journal (italic), volume number (bold), first and last page numbers:

Tanabe S., Iwata H., Tatsukawa R., (1994), Global contamination by persistent organochlorines and their ecotoxicologcial impact on marine mammals, *Science of the Total Environment*, **154**, 163-177.

Danilova I., Sharipova M., (2020), The practical potential o bacilli and their enzymes for industrial production, *Frontiers in Microbiology*, **11**, 1782, https://doi.org/10.3389/fmicb.2020.01782

Patents: Names and initials of authors, year, patent title, country, patent number (italic):

Grant P., (1989), Device for Elementary Analyses. USA Patent, No. *123456*.

Dissertations: Names and initials of authors, year (between brackets), title, specification (PhD Thesis, MSc Thesis), institution, place:

Aelenei N., (1982), *Thermodynamic study of polymer solutions* (in Romanian), PhD Thesis, Institute of Macromolecular Chemistry Petru Poni, Iasi, Romania.

Stanciulescu D., (2004), *Environmental impact assessment generated by C.E.T.1 Company, Iasi* (in Romanian), MSc Thesis, Gheorghe Asachi Technical University of Iasi, Romania.

Star K., (2008), *Environmental risk assessment generated by natural hazards*, MSc Thesis, Institute of Hazard Research, Adelaide, Australia.

Legal regulations and laws, organizations: Abbreviated name, year (between brackets), full name of the referred text, document type, author, URL address:

ESC, (2007), Improving access to modern energy services for all fundamental challenge, Economic and Social Council, ENV/DEV/927, On line at: http://www.un.org/News/Press/docs/2007/envdev927.doc.htm

USEPA, (2007), Biomass Conversion: Emerging Technologies, Feedstocks, and Products, Sustainability Program, Office of Research and Development, EPA/600/R-07/144, U.S. Environmental Protection Agency, Washington, D.C., On line at: http://www.epa.gov/Sustainability/pdfs/Biomass%20Conversion.pdf

EC Directive, (2000), Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000, on the incineration of waste, Annex V, *Official Journal of the European Communities*, **L 332**/91, 28.12.2000, Brussels, Belgium.

GD, (2004), Governmental Decision no. 1076/2004 surnamed SEA Governmental Decision, regarding the procedure for strategic environmental impact assessment for plans or programs, *Romanian Official Monitor*, Part I, no. 707 from 5th of August, 2004, Bucharest, Romania.

Web references: The full URL should be given in text as a citation, if no other data are known. If the authors, year, title of the documents are known and the reference is taken from a website, the URL address has to be mentioned after these data.

Burja C., Burja V., (2008), Adapting the Romanian rural economy to the European agricultural policy from the perspective of sustainable development, MPRA, Munich Personal RePEc Archive, On line at: http://mpra.ub.uni-muenchen.de/7989/1/MPRA_paper_7989.pdf

Web references must not be listed separately, after the reference list.

All references must be provided in English with a specification of original language in round brackets, placed immediately after the title of the work.

Citation in text Please ensure that every reference cited in the text is also present in the reference list (and vice versa).
Do not cite references in the abstract and conclusions.
Unpublished results, personal communications as well as URL addresses are not recommended in the reference list.
Citation of a reference as "in press" implies that the item has been accepted for publication.

Papers which have been accepted for publication should be included in the list of references with the name of the journal and the specification "in press".

Reference style *Text*: All citations in the text may be made directly (or parenthetically) and should refer to:

- *single author*: the author's name (without initials, unless there is ambiguity) and the year of publication: "as previously demonstrated (Smith, 2007)"; "as Smith (2007) demonstrated"
- *two authors*: both authors' names and the year of publication: (Arnold and Sebastian, 2008; Smith and Hansel, 2006; Stern and Lars, 2009)
- *three or more authors*: first author's name followed by "et al." and the year of publication: "As has recently been shown (Werner et al., 2005)...", "Kramer et al. (2000) have recently shown..."

Citations of groups of references should be listed first alphabetically, then chronologically

Examples: "as demonstrated (Aden, 1996a, 1996b, 1999; Allan and Jones, 1995; Allan and Jones, 2000; Alan et al., 1997; Allan et al., 2003)".

Abbreviations

Define all abbreviations at their first mention in the Abstract. Also, define all abbreviations at their first mention in manuscript body. Ensure the consistency of abbreviations throughout the article.

Acknowledgements

Include acknowledgements in a separate section at the end of the article before the references and do not, therefore, include them on the title page, as a footnote to the title or otherwise. List here those individuals who provided help during the research (e.g., providing language help, writing assistance or proof reading the article, data processing, software development, funding supports etc.).

Footnotes

Footnotes must be avoided. Do not include footnotes as citations or in the Reference list.
Table footnotes
Indicate each footnote in a table with a superscript lowercase letter.

Tables

Draw the Tables in grid format using a basic, solid line style without shadows.
Ensure that the data presented in Tables do not duplicate results described in Figures or elsewhere in the paper.

Figures

Number Figures consecutively in accordance with their appearance in the text. All illustrations should be provided in camera-ready form, suitable for reproduction, which may include reduction without retouching.
Photographs, charts and diagrams are all to be referred to as Figure(s) and should be numbered consecutively, in the order to which they are referred.
Figures may be inserted preferably as black line drawings. They should be pasted on, rather than taped, since the latter results in unclear edges upon reproduction.
Ensure that each illustration has a caption, placed below the Figure. A maximum limit of 8 Figures are allowed per manuscript.
A caption should comprise a brief title (not on the Figure itself) and a description of the illustration. Keep text in the illustrations themselves to a minimum but explain all symbols and abbreviations used. Multiple Figures can be expressed as one Figure (for e.g. 1a, 1b, 1c etc...), while retaining the maximum limit of 6.

ALL Figures must be submitted in either .jpg or .tiff format with a very good resolution (but do not submit graphics that are disproportionately large for the content).

Figures and Tables must be embedded in the text.

Refer/cite the Figures and Tables before they are places in the manuscript, using their number (“as shown in Table 1”, “as illustrated in Fig. 3”). Avoid citations as: “in the following Table”, “as presented in Figure below”.

Proofs
Proofs will be sent to the corresponding author (by e-mail) and should be returned within maximum 72 hours of receipt. Corrections should be restricted to typesetting errors; any other changes may be charged to the authors. The authors should work on the final proof sent to the corresponding author, as .docx, by the Editor, so as to keep changes and corrections recommended by the Editor. Authors are asked to submit their finally corrected manuscript as an attachment, in maximum 72 h, to one of the above-mentioned e-mail addresses, as .docx, together with *Author’s warranty and agreement*, signed by the corresponding author or all authors.

Finally, the corresponding authors are asked to check the final proof, as .pdf within maximum 48 h and agree with the final form of the manuscript.

5. Page charge

There is no charge per printed page for regular papers.

6. Reprints

The corresponding author will be provided with a .pdf file containing the paper, via e-mail, free of charge. A hard copy of the issue containing the paper can be provided on request, for a fee. This request will be formulated when the final form of the manuscript (the electronic one) is provided.

7. Additional procedures for the editorial management of *Environmental Engineering and Management Journal*

Printed copies of papers or issues can be delivered on request with payment.

An author cannot appear on more than two papers per regular issue. An author cannot appear on more than three papers in a Guest Editor/Conference issue.

The evaluation/peer-review process of manuscripts submitted for Guest Editor/Conference issues published according to journal editorial procedure and policy will be handled and evaluated as with regular manuscripts, so that only consistent papers will be published. The manuscripts must be sent at least six months before the presumed data of publication. Those manuscripts which do not fulfill the journal requirements will be rejected. This is to discourage superficiality in the development of the manuscript, from formal and scientific points of view.

No more than 190-200 pages and no more than 20 papers are acceptable for regular issues. No more than 220 pages and no more than 25 papers are opportune for special issues. The number of pages is based on the published version of an article, not on the submitted version (for instance, when page breaks are changed and when images are enlarged for easier viewing).

A regular issue can include, as an exception, a number of 25 papers as a maximum. This situation could appear when subscribers to our journal ask for early publication of their already accepted papers, against the position in the list of accepted papers. The annual subscription is **575 Euro**, and the subscribers may ask for early publication of one accepted paper per subscription. If the authors of a newly-registered manuscript ask for a rapid evaluation of their manuscript (in maximum 3 months after its registration), a deposit of **300 Euro** shall be paid in advance. If the manuscript is deemed unsuitable for publication, the authors will not be eligible for a refund, so no amount of money will be refunded following the rejection of manuscripts.

In all cases, the corresponding author will send a signed Requirement letter to the Editor-in-Chief, according to the Editorial Policy and Procedures. All payment will be made in the Journal account and will be confirmed according to the legal procedures, based on delivered invoice and tracking of the fee payment.

The journal could publish maximum six Guest Editor issues, according to the Editorial Policy and Procedures.

Automated software is used for checking against plagiarism. In order to avoid false results, the generated reports are cautiously checked and confirmed by journal staff. We do not send plagiarism reports to authors. Any manuscripts which do not prove to be at least 90% original will be rejected. The rejection for plagiarism may arise at any phase of the editorial / review process, even if the manuscript was accepted for publication. The authors are solely responsible for the originality of their submission.

Therefore, any manuscript should be carefully checked for such inconsistencies before submitting to EEMJ.

The authors are required to follow academic publishing rules, to adhere to the principles of scientific ethics and to sign the Authors' warranty and Copyright transfer.

Detailed information concerning these issues may be found on the EEMJ website, under Editorial Procedure and Policy.

October 2023 vol. 22 No. 10 *ISSN 1582-9596*

Environmental Engineering and Management Journal is edited by the
Publishing House **ECOZONE** of the
Academic Organization for Environmental Engineering and Sustainable Development
(OAIMDD)
71 Mangeron Blvd., 700050-Iasi, Romania

“Gheorghe Asachi” Technical University of Iasi