# 4th International Conference on Sustainable Chemical & Environmental Engineering

SUST
ENG
2025

1 - 4 September 2025

Thessaloniki, Greece

hybrid event

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**organizers**

Design of Environmental Processes Lab

**Technical University of Crete**
School of Chemical and Environmental Engineering

Cyprus University of Technology

Dear friends and colleagues,

I am pleased to invite you to the **4th International Conference on Sustainable Chemical and Environmental Engineering (SUSTENG 2025)**, between **1st to 4th September 2025.**

The conference is organized by the "Design of Environmental Processes Laboratory", of the School of Chemical and Environmental Engineering, Technical University of Crete and the Cyprus University of Technology.

The **SUSTENG 2025** Conference will take place both with physical and virtual presence.

The conference aims to encourage the exchange of knowledge between academicians, scientists and engineers on hot issues and current developments in chemical and environmental engineering through sustainable perspective. The participants will have the opportunity to present their recent research findings on an extended spectrum of conference topics and be informed about new challenges, future trends, and technological innovations on sustainable processes following the principles of circular economy.

After the completion of the conference, all abstracts/full papers will be published in the **SUSTENG 2025** Conference Proceedings with ISBN number, while selected manuscripts will be published to at least one Special Issues at high IF scientific journals.

The conference Chair

**Petros Gikas**

Professor

Head of the "Design of Environmental Processes Lab"

School of Chemical and Environmental Engineering

Technical University of Crete, Greece

# SESSIONS OF SUSTENG 2025

**Session 1: Biochemical engineering and green chemistry**

**Session 2: Valorization of food waste**

**Session 3: Wastewater management**

**Session 4: Solid waste management and greenhouse gas monitoring**

**Session 5: Modeling and optimization in energy and environment**

**Session 6: Circular economy in waste management**

**Session 7: Sustainable agriculture and waste management**

**Session 8: Sustainable water management and reuse**

**Session 9: Biosolids management and valorization**

**Session 10: Life cycle assessment**

## Scientific committee:

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Zouboulis, Anastasios, Aristotle University of Thessaloniki, Greece

# SUSTENG 2025- PROGRAMME AT A GLANCE

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|---|---|
| **DAY 1 – Monday 1 September \| Susteng 2025** | |
| Aristotle University Research Dissemination Center (KEDEA) | |
| **Registration** | **14:00 - 16:00** |
| **Session 1: Biochemical engineering and green chemistry** | **16:00 - 18:00** |
| **Welcome Speeches**<br>**Stavros Kalafatis-Vice Minister of Development**<br>**Konstantinos Gioutikas-Vice Governor of Thessaloniki**<br>**Stelios Angeloudis-Mayor of Thessaloniki**<br>**Dimitris Aslanidis, Mayor of the Municipality of Pavlos Melas**<br>**Kyriakos Anastasiadis-Rector of the Aristotle University of Thessaloniki**<br>**Michael Zervakis-Rector of the Technical University of Crete**<br>**George Savaidis-Dean of the Faculty of Engineering, Aristotle University of Thessaloniki**<br>**Vasileios Zaspalis-School of Chemical Engineering, Aristotle University of Thessaloniki**<br>**Aris Gorogias-President at Hellenic Association of Chemical Engineers**<br>**Michael Geranis-President of the Regional Association of Solid Waste Management Agencies of Central Macedonia**<br>**Yiannis Tsouloftas-President of the Local Government Organization of Limassol District, Cyprus** | **18:00 - 18:30** |
| **PLENARY LECTURE: Professor Petros Gikas** | **18:30 - 19:15** |
| **Welcome reception** | **19:30 - 22:00** |
| **DAY 2 – Tuesday 2 September \| Susteng 2025** | |
| Aristotle University Research Dissemination Center (KEDEA) | |
| **Session 2: Valorization of food waste** | **09:30 - 10:45** |
| ***Coffee break - Posters viewing*** | ***10:45 - 11:00*** |
| **Session 3: Wastewater management** | **11:00 - 12:30** |
| **PLENARY LECTURE: Professor Güçlü Insel** | **12:30 - 13:15** |
| ***Lunch break*** | ***13:15 - 14:45*** |
| **Session 4: Solid waste management and greenhouse gas monitoring** | **14:45 - 16:30** |
| **PLENARY LECTURE: Professor Paraschos Melidis** | **16:30 - 17:15** |
| **Session 5: Modeling and optimization in energy and environment** | **17:15 - 19:00** |

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| **Gala dinner** | **20:30 - 23:00** |
| **DAY 3 – Wednesday 3 September \| Susteng 2025** | |
| Aristotle University Research Dissemination Center (KEDEA) | |
| **Session 6: Circular economy in waste management** | **09:30 - 10:45** |
| ***Coffee break - Posters viewing*** | ***10:45 - 11:00*** |
| **PLENARY LECTURE: Professor Jacek Dach** | **11:00 - 11:45** |
| **Session 7: Sustainable agriculture and waste management** | **11:45 - 13:15** |
| ***Lunch break*** | ***13:15 - 14:45*** |
| **PLENARY LECTURE: Professor Konstantinos Kakosimos** | **14:45 - 15:30** |
| **Session 8: Sustainable water management and reuse** | **15:30 - 16:15** |
| **Session 9: Biosolids management and valorization** | **16:15 - 18:30** |
| **Session 10: Life cycle assessment** | **18:30 - 19:15** |
| **Closing ceremony** | **19:15 - 19:45** |
| **DAY 4 - Thursday 4 September \| Susteng 2025** | |
| **Conference excursion at the capital of ancient Macedonia Aegae, in Vergina, and the grave of Philip II, father of Alexander the Great, and the Byzantine town of Veria** | **09:00 - 17:00** |

SUST ENG 2025

# SUSTENG 2025

# PROGRAMME

| **DAY 1 – Monday 1 September \| Susteng 2025** | |
|---|---|
| Aristotle University Research Dissemination Center (KEDEA) | |
| **Registration** | **14:00 - 16:00** |
| **Session 1: Biochemical engineering and green chemistry**<br>**Chair: Emine Çokgör, Manal Haj Zaroubi** | **16:00 - 18:00** |
| **Anaerobic production of biosurfactants from contaminated soils: a waste valorization approach to soil remediation**<br>M. Puddu, G. Beretta, S. Saponaro and E. Sezenna | 16:00 - 16:15 |
| **Carbon dioxide capture from actual industrial flue gas using microalgae**<br>G. Makaroglou, P. Gikas | 16:15 - 16:30 |
| **From lab to pilot scale Microalgae-based Photobioreactors: statistical optimization of 3rd generation biofuel production**<br>A. Pavlou, G. Penloglou and C. Kiparissides | 16:30 - 16:45 |
| **Willow (salix acmophylla boiss.) Leaf and Branch Extracts Inhibit in *vitro* Sporulation of Coccidia (Eimeria spp.) from Goats**<br>M. Haj-Zaroubi, N. Mattar, S. Awabdeh, R. Sweidan, A. Markovics, J. D. Klein and H. Azaizeh | 16:45 - 17:00 |
| **Optimization of high-added value terpenes recovery from genetically engineered Saccharomyces cerevisiae and Yarrowia lipolytica strains**<br>A. Moschona, C. Gerasi, M. Moumin, F. Tsakiroglou, A. Assimopoulou and S.I. Patsios | 17:00 - 17:15 |
| **Valorization of Invasive Macroalgae (Asparagopsis armata and Sargassum spp.) as Sources of Immune-Enhancing Aquafeed Ingredients: Recovery and In-Vitro Fish Digestibility Assessmen**<br>S. Papadaki, C. Stergiopoulos , N. Tricha and M. Krokida | 17:15 - 17:30 |
| **Life cycle assessment of systems exploiting microalgae for the wastewater treatment**<br>G. Dolci, M.J.F.A. Nichilo, M. Grosso, and L. Rigamonti | 17:30 - 17:45 |

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| **Efficient mechanochemical synthesis of conjugated porous (macro)molecules via multiple Sonogashira couplings and their energy storage application**<br>R. S. Rao, A. Shunnar, B. Pirzada, E. Oueis, A. B. Lowe and J. Shaya | 17:45 - 18:00 |
| **Welcome Speeches**<br>**Stavros Kalafatis-Vice Minister of Development**<br>**Konstantinos Gioutikas-Vice Governor of Thessaloniki**<br>**Stelios Angeloudis-Mayor of Thessaloniki**<br>**Dimitris Aslanidis, Mayor of the Municipality of Pavlos Melas**<br>**Kyriakos Anastasiadis-Rector of the Aristotle University of Thessaloniki**<br>**Michael Zervakis-Rector of the Technical University of Crete**<br>**George Savaidis-Dean of the Faculty of Engineering, Aristotle University of Thessaloniki**<br>**Vasileios Zaspalis-School of Chemical Engineering, Aristotle University of Thessaloniki**<br>**Aris Gorogias-President at Hellenic Association of Chemical Engineers**<br>**Michael Geranis-President of the Regional Association of Solid Waste Management Agencies of Central Macedonia**<br>**Yiannis Tsouloftas-President of the Local Government Organization of Limassol District, Cyprus** | **18:00 - 18:30** |
| **PLENARY LECTURE: Professor Petros Gikas**<br>**Energy Self-Sustainable Wastewater Treatment Plants**<br>**Chair: Güçlü Insel, Jacek Dach** | **18:30 - 19:15** |
| **Welcome reception** Aristotle University Research Dissemination Center (KEDEA) | **19:30 - 22:00** |
| **DAY 2 – Tuesday 2 September \| Susteng 2025** | |
| Aristotle University Research Dissemination Center (KEDEA) | |
| **Session 2: Valorization of food waste**<br>**Chair: Caro Dario, Emine Çokgör** | **09:30 - 10:45** |
| **Comparing the carbon footprint of traditional beef burger with burgers fortified with by-products**<br>D. Caro | 09:30 - 09:45 |
| **Sustainable valorization of seafood waste: enzyme-based chitin extraction as an alternative to chemical processes**<br>I. Kan, A. Morales, L. Sillero and X. Erdocia | 09:45 - 10:00 |
| **Pomegranate Peel Bioplastic: Transforming Food Waste into Eco-Friendly Materials for Product Design**<br>L. Mailat, Delia A. Prisecaru | 10:00 - 10:15 |

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| **Valorisation of watermelon peel into an adsorbent for removal of hexavalent chromium**<br>Mangwandi Chirangano, GartlanCiaran, Khong Justin | 10:15 - 10:30 |
| **Integrated Approach for Sustainable Protein Production: Utilizing Agricultural Waste for Black Soldier Fly Rearing and Feed Applications**<br>A. Jonas-Levi, I. Opatovsky, A. Hurvitz, A. Salomon, R. Gutman, R. Sivan | 10:30 - 10:45 |
| ***Coffee break - Posters viewing*** | ***10:45 - 11:00*** |
| **Session 3: Wastewater management**<br>**Chair: Paraschos Melidis, Güven Didem** | **11:00 - 12:30** |
| **Microalgal treatment of AnMBR Effluent: a low-energy approach to nutrient reduction**<br>E. Politou, A. Makri, D. Matziri, N. Remmas, S. Ntougias and P. Melidis | 11:00 - 11:15 |
| **Circular economy strategy in wastewater treatment: the example of Limassol district local government organisation sewage treatment plant in Moni, Cyprus**<br>Y. Tsouloftas, S. Metaxas, M. Vrionides, P. Marti, V. Konstantinides and G. Panayiotou | 11:15 - 11:30 |
| **Integrating greywater treatment and green façade creation using vertical flow constructed wetlands**<br>E. Stefanatou and M.S. Fountoulakis | 11:30 - 11:45 |
| **An Appraisal for a Sustainable Process Design and Operation for Leachate Treatment**<br>D. Guven, E. Çokgör, G.E. Zengin Balcı, B. Kaya, G. Ozyildiz, D. Soylu, I. Takacs, G. Insel, S. Sözen, and D. Orhon | 11:45 - 12:00 |
| **Removal of non-steroidal anti-inflammatory micropollutants and nitrification in hybrid systems operating at low sludge age**<br>D. Soylu, B. Ciftcioglu Gozuacik, Ş. Yilmaz, G.E.Zengin, İ. Pala-Ozkok, E. Topuz, G. Ozyildiz, D. Guven, G. Insel and E. Çokgör | 12:00 - 12:15 |
| **Quantitative Evaluation of Nitrification Inhibition in Petrochemical Wastewater**<br>AT. Cetinkaya, P. Eryavuz, G. Ozyildiz, D.Güven, N. Artan, E. Çokgör, G. Insel | 12:15 - 12:30 |
| **PLENARY LECTURE: Professor Güçlü Insel**<br>**Novel hybrid nutrient removal process for advanced nutrient removal: experimental based process development**<br>**Chair: Paraschos Melidis, Petros Gikas** | **12:30 - 13:15** |
| ***Lunch break*** | ***13:15 - 14:45*** |

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| **Session 4: Solid waste management and greenhouse gas monitoring**<br>**Chair: Francesca Villa, Güçlü Insel** | **14:45 - 16:30** |
| **Dewatering of landfill leachate by combined flocculation with geotextile filtration**<br>B. Kaya, S. Dogruel, V. Oztug and E. Çokgör | 14:45 - 15:00 |
| **Air Quality Assessment in the Municipality of Pavlos Melas, Thessaloniki**<br>S. Cheristanidis, E. Pitsalidis and D. Melas | 15:00 - 15:15 |
| **The Problem Tree: a strategic tool for priorities' identification, applied to the assessment of operational and design issues of a solid waste treatment facility in Lebanon**<br>F. Villa, A. De Robertis and M. Grosso | 15:15 - 15:30 |
| **Management of household hazardous waste: survey and comparative analysis**<br>M. Markantoni, T. Daras and A. Giannis | 15:30 - 15:45 |
| **Ternary Deep Eutectic Solvent-Mediated Leaching of Valuable Metals from Waste Printed Circuit Boards**<br>A. Alaydaroos, N. Chola, S. Stephen, G.E. Luckachan, G. Xavier, M. Elkadi, E. AlNashef, M. Abi Jaoude | 15:45 - 16:00 |
| **Comparison of source and site level methane emissions measurements at gas installations**<br>N. Tsochatzidis | 16:00 - 16:15 |
| **Preliminary investigation of removal of pharmaceuticals from aqueous solutions by potato peel based biochars produced from hydrothermal conversion and pyrolysis: a comparative study**<br>J.Khong, and C. Mangwandi | 16:15 - 16:30 |
| **PLENARY LECTURE: Professor Paraschos Melidis**<br>**Anaerobic Membrane Bioreactors for Sustainable Municipal Wastewater Treatment**<br>**Chair: Petros Gikas, Jacek Dach** | **16:30 - 17:15** |
| **Session 5: Modeling and optimization in energy and environment**<br>**Chair: Thomas Thomaidis, Vassilis Charitopoulos** | **17:15 - 19:00** |
| **An optimisation approach towards the integration of hydrogen in heat and power decarbonization** | 17:15 - 17:30 |
| M.E. Efthymiadou, V.M. Charitopoulos and L.G. Papageorgiou | |
| **Deciphering the impact of AI's energy demand on Europe's Green Deal**<br>M. Hemmati, V. M Charitopoulos | 17:30 - 17:45 |

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| **Assessment of water-energy-food-ecosystem nexus of sakarya river basin**<br>S. Yaykiran and A. Ekdal | 17:45 - 18:00 |
| **Integrating sustainability into decision support for the transition to resilient business models**<br>I. Mavrogiannis | 18:00 - 18:15 |
| **Development of a decision support system for shallow lakes under the impact of eutrophication and climate change and its application to a hypertrophic lake**<br>A. Ekdal, M. Gürel, C. Gurevin and A. Ertürk | 18:15 - 18:30 |
| **Comparative Assessment of Alternative Waste Management Scenarios for Mixed Municipal Solid Waste: Case study of Cyprus**<br>S. Mai, E.M. Barampouti, D. Malamis, K. Moustakas and M. Loizidou | 18:30 - 18:45 |
| **Policy Pathways for Marine Litter Prevention and Control: Insights from the SeaClear2.0 Project**<br>D. Orthodoxou, X. Loizidou | 18:45 - 19:00 |
| **Gala dinner** | **20:30 - 23:00** |
| **DAY 3 – Wednesday 3 September \| Susteng 2025** | |
| Aristotle University Research Dissemination Center (KEDEA) | |
| **Session 6: Circular economy in waste management**<br>**Chair: Fabio Hernández-Ramos, Abeer Albalawneh** | **09:30 - 10:45** |
| **Deep eutectic solvents and microwave heating for efficient oligosaccharide recovery from apple tree pruning waste**<br>L. Sillero, J. Labidi and A. Morales | 09:30 - 09:45 |
| **From Waste to Value: Pilot-Scale EV Battery Recycling in Armenia**<br>H. Akarmazyan, G. Vardanyan, V. Marukhyan, A. Tadevosyan | 09:45 - 10:00 |
| **Metal leaching from e-waste using phosphonium-based hydrophobic deep eutectic solvent**<br>N. M. Chola, S. Stephen, G. E. Luckachan, G. Xavier, M. Elkadi, I. Alnashef, M. Abi Jaoude | 10:00 - 10:15 |
| **Sustainable Consumption Principles of the Circular Economy: Consumer Preferences and Willingness to Pay for Electric Vehicle (EV) Purchase Options: A Study in Klang Valley, Malaysia**<br>F. Shahudin, R. Ya'cob, L. Yiyang, G. Zihan | 10:15 - 10:30 |
| **From urban pruning to sustainable films: unlocking the value of tree residues**<br>F. Hernández-Ramos, A. Morales, P. de Hoyos-Martínez, J. Pérez-Arce, X. Erdocia, L. Sillero | 10:30 - 10:45 |
| ***Coffee break - Posters viewing*** | ***10:45 - 11:00*** |

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| **PLENARY LECTURE: Professor Jacek Dach**<br>**Biogas and biomethane as a key element of the circular economy and carbon footprint reduction in the products**<br>**Chair: Konstantinos Kakosimos, Petros Gikas** | **11:00 - 11:45** |
| **Session 7: Sustainable agriculture and waste management**<br>**Chair: Patrycja Pochwatka, Konstantinos Tsamoutsoglou** | 11:45 - 13:15 |
| **Traditional and Indigenous Knowledge and Conservation Practices of Forest Food Species in Guinean Forests of West Africa (GFWA) Biodiversity Hotspot**<br>A. E. Assogbadjo, G. Avakoudjo | 11:45 - 12:00 |
| **Optimization of microwave assisted delignification of apple tree pruning using deep eutectic solvents**<br>A. Morales, X. Erdocia, J. Labidi, L. Sillero | 12:00 -12:15 |
| **Application of remote sensing technologies for sustainable forest fire monitoring and management**<br>A. Dudnyk, O. Opryshko, K. Witaszek | 12:15 - 12:30 |
| **Scalable deployment of IoT systems for sustainable precision olive farming in Laconia, greece**<br>G. Panagopoulou, I. Moutsinas, T. Theodosiadis | 12:30 - 12:45 |
| **The application of Revised Theory of Planned Behaviour (RTPB) model to assess the citizens' attitudes and intentions towards e-waste management in the circular economy.** | 12:45 - 13:00 |
| F. Shahudin, R. Ya'cob, L. Yiyang, G. Zihan | |
| **Microplastics an emerging environmental pollutant in agriculture: interaction between microplastics and soil humic substances on an agricultural crop**<br>M. Dimitropoulou, A. Ioannidi, I. Zafeiropoulos, K. Bourikas, M. Papadaki, E. Giannakopoulos | 13:00 - 13:15 |
| ***Lunch break*** | ***13:15 - 14:45*** |
| **PLENARY LECTURE: Professor Konstantinos Kakosimos**<br>**From bench to module scale hydrogen production via artificial and natural light water splitting**<br>**Chair: Petros Gikas, Paraschos Melidis** | **14:45 - 15:30** |
| **Session 8: Sustainable water management and reuse**<br>**Chair: Kupryaniuk Karol, Jakub Kostecki** | **15:30 - 16:15** |
| **Beyond Negative Environmental Results: The Critical Role of Risk Assessment in Legionella Control**<br>A. Papadakis, A. Roditakis, P. Manetakis, N. Gikas, E. Koufakis, K. Tsamoutsoglou, P. Gikas | 15:30 - 15:45 |

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| **Modification of membranes by using the layer by layer technology for the removal of Cr(VI) anions from groundwaters**<br>N. Malouchi | 15:45 - 16:00 |
| **Sensors selection for real-time recovery of textile dyeing wastewater**<br>R. Partal, S. Murat Hocaoglu, M. Kitis, E. Ozturk, E. Simsek Yesil | 16:00 - 16:15 |
| **Session 9: Biosolids management and valorization**<br>**Chair: Patrycja Pochwatka, Jacek Dach** | **16:15 - 18:30** |
| **Conversion of sewage sludge to lipids for biofuels**<br>A. Jonas-Levi, Y. Gerchman, H. Azaizeh | 16:30 - 16:45 |
| **Quantifying european biomass flows and certifying residual biomass valorization: a case from the region of central Macedonia, Greece**<br>A. Karanasiou, S. Skoutida, M. Batsioula, G. Banias, S. Patsios | 16:45 - 17:00 |
| **The role of demand-driven biogas plants in Europe's energy transition: potential for energy system stability and integration with other RES**<br>A. Łukomska, J. Dach | 17:00 - 17:15 |
| **The role of animal biomass in the biogas sector in Poland: current status and potential**<br>P. Pochwatka, A. Kowalczyk-Juśko, A. Mazur, W. Czekała, J. Dach | 17:15 - 17:30 |
| **Influence of the type of straw on the intensity of sewage sludge composting**<br>W. Bojarski, W. Czekała, M. Nowak, P. Sołowiej, K. Kupryaniuk, J. Dach | 17:30 - 17:45 |
| **Spray mode and precursor molarity as key parameters in solution spray pyrolysis of oxygen electrodes for low temperature reversible solid oxide cells (socs)**<br>A. Kotsiolis, E. Roditis, C. Ziazias, N. Nikiforidis, A. Krestou, N. Kiratzis | 17:45 - 18:00 |
| **Optimizing drying kinetics and calorific value assessment of wastewater sludge for enhanced waste-to-energy gasification**<br>L. Tshenyego | 18:00 - 18:15 |
| **Innovative wastewater technologies for the treatment of sewage sludge at overloaded activated sludge plants**<br>K. Tsamoutsoglou, P. Gikas | 18:15 - 18:30 |
| **Session 10: Life cycle assessment**<br>**Chair: Gregoris Panayiotou, Janah Shaya** | **18:30 - 19:15** |
| **Is Life Cycle Assessment essential for sustainability in heritage?**<br>T. Tsoutsos, C. Nikoloudakis | 18:30 - 18:45 |

| | |
|---|---|
| **Advanced Thermolysis of Waste Plastics into Sustainable Aviation Fuel Feedstocks and A Mass-Balance Certified Approach for Waste to Energy Solutions**<br>Aris Gorogias | 18:45 - 19:00 |
| **Sustainable extraction of V and Ti from low-grade V-bearing titanomagnetite deposits**<br>G. Bartzas, D. Vathi, K. Komnitsas | 19:00 - 19:15 |
| **Closing ceremony** | **19:15 - 19:45** |
| **DAY 4 - Thursday 4 September \| Susteng 2025** | |
| **Conference excursion at the capital of ancient Macedonia Aegae, in Vergina, and the grave of Philip II, father of Alexander the Great, and the Byzantine town of Veria** | **09:00 - 17:00** |

## Posters

Aristotle University Research Dissemination Center (KEDEA)

**Bioremendiation of secondary cheese whey effluent by Pseudomonas sp. phDV1**

**E. Pappa, A. Lyratzakis, N.C. Stratigakis, G. Tsiotis**

**Hydrogen-Rich Gas Production From The Steam Gasification Of Olive By-Products With Minimum Carbon Dioxide Emissions**

D. Vamvuka, S. Karvounis, K. Kyriakidis, I. Papakyriakopoulos and A. Strataki

**Optimal wind power investments and bidding strategies in electricity market considering green certificates trading**

M. Kanta, C. Dimitriadis, M. Georgiadis

**Copper recovery from printed circuit boards: Alkaline glycine leaching system**

J. Matado, L.H. Gomes and S.C. Pinho

**Influence of operating parameters on lead hydrometallurgical leaching of lead-acid batteries with NaCl**

L. H. Gomes, A. Lourenço, S. C. Pinho, M. J. J. de S. Ponte, H. de A. Ponte, H. de Santana

**Adsorption of Reactive Red 120 dye by oxidized biochar from palm tree fibers**

P. Haskis, F. Krommida, M. Vlaxou, I. Varampoutis, D. Kyvrikoseos, D. A. Giannakoudakis, I. Ioannidis, I. Pashalidis, P. Mpeza and I. Anastopoulos

**Valorization of industrial waste into silica based adsorbents for water OPPs removal**

G. Silva, O. Freitas, V. Fernandes, F. Gomes

**Assessment of marine fuels stability: a storage perspective**

I. Kosma, L. Chysikou, S. Bezergianni

**Immerse virtual training on critical raw materials: preparing responsible professionals for a sustainable future**

E. Machairas, E. Varouchakis, B. Lottermoser, S. Hajinia Leilabadi

**Analysis of Phospholipid Fatty Acids (PLFAs) as a soil bioindicator: the effect of vineyard abiotic stress on the soil microfauna as a case study**

E. Ieronymaki, M. Drosos, I. Zafeiropoulos, M. Papadaki, E. Giannakopoulos

**The use of coffee grounds as fuel**

P. Sołowiej, W. Bojarski, J. Dach, A. Kowalczyk-Juśko

**Agricultural biogas as a sustainable energy source for non-agricultural regions: the case of Lubuskie Province, Poland**

J. Kostecki, S. Myszograj, E. Płuciennik Koropczuk

**BSF larvae: a sustainable complementary solution for broiler carcass management**
A. Jonas-Levi

**Methane emission during degradation of microplastics in the aquatic environment**

P. Koszelnik, M. Kida, S. Ziembowicz

**Bridging the gap between academic water quality modeling and decision-making: towards usable and trustworthy tools for stakeholders**

A. Gorgoglione, P. Gikas

**Utilization of agricultural by-products and waste biomass for energy purposes**

K. Witaszek, W. Czekała, A. Dudnyk, K. Kupryaniuk, J. Dach

**The influence of substrate extrusion process on the energy and economic efficiency of biogas plant exploitation**

K. Kupryaniuk, K. Witaszek, D. Janczak, W. Czekała, J. Dach

**Biogas yield – theory and practical experience**

A. Kowalczyk-Juśko, M. Byra, P. Pochwatka, A. Mazur, W. Czekała, J. Dach

**On the way to circular economy: valorization of brewery waste for added-value bioproducts from black soldier fly larvae**
J. Reséndiz Luna, V. Caltzontzin Rabell, C. Gutiérrez Antonio, B. Sofia, E. Ieronymaki, E. Giannakopoulos, V. Bekiari, P. Souliou, G. Serifi, S. Argyroudis, I. Zafeiropoulos, G. Karavidas, M. Papadaki
**Integrated microsieving and gasification for energy-neutral municipal wastewater treatment**
K. Tsamoutsoglou, E. Farmakis, P. Gikas
**Optimization of trickling filters operation parametres for the removal of BOD and ammonic nitrogen from municipal wastewater**
E. Gika, I. Chourdakis and P. Gikas

# Session 1: Biochemical engineering and green chemistry

# Anaerobic production of biosurfactants from contaminated soils a waste valorization approach to soil remediation

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***keywords:*** *Biosurfactants, Bioemulsifiers, Soil remediation, Food waste valorization*

## Introduction

Microorganisms capable of degrading hydrocarbons are often producers of biosurfactants (BSs) and bioemulsifiers (BEs), which increase the bioavailability of hydrophobic organic pollutants and enhance their biodegradation. Leveraging this natural metabolic versatility, particularly in hydrocarbon-contaminated soils, offers promising opportunities for the development of sustainable remediation strategies.

This study explored the potential of stimulating the indigenous microbial community in real contaminated soils to produce BSs and BEs under anaerobic conditions, using low-cost, food- and agricultural-derived carbon sources. A circular economy perspective underpins this approach, which aims to valorize waste materials while minimizing the use of synthetic additives. In particular, this study investigated whether biosurfactant and bioemulsifier production can be enhanced under electron-acceptor-limited and mild oxidative stress, with the goal of developing low-toxicity formulations for remediation.

These preliminary experiments were designed as exploratory tests, intended to gather foundational data on biosurfactant productivity, efficacy, and environmental compatibility in real soil systems prior to more extensive process optimization and application studies.

## Materials and methods

Sixty anaerobic microcosms were prepared using a weathered hydrocarbon-contaminated soil (Total Petroleum Hydrocarbon = 4500 mg/kg d.w.) as the microbial inoculum and a microemulsion of waste frying oil and chickpea powder as the main carbon source to investigate the native microbial community's potential for BS and BE biosynthesis under oxygen-deprived and static conditions over a period of nine months. Hydrogen peroxide was added to induce mild oxidative stress and to stimulate enzymatic activity. The experimental design included different concentrations of nitrate and sulfate as electron acceptors (EAs), and salinity as potential regulatory factors for microbial biosynthetic pathways.

All microcosms (250 mL total volume) contained 40 g dried soil and 200 mL amendment solution (Table 1). Methanogenesis was inhibited using 50 mM 2-bromoethanesulfonate to steer microbial metabolism toward alternative anaerobic pathways, which is more conducive to biosurfactant production.

***Table 1***: *Amendment solution*

| | **Concentration** |
|---|---|
| NaCl | 0.0 or 0.5 g/L |
| $MgSO_4$ | 0.1 or 0.5 g/L |
| $KNO_3$ | 5 or 40 mg/L |
| Urea | 0.1% |
| Chickpea Powder | 6.0% |
| Waste Frying Oil | 1.5% |
| $H_2O_2$ 3% | 0.35g/1g TPH |
| 2-Bromoethanesulfonate | 50 mM |

The crude and microfiltered supernatants were analyzed using oil displacement tests and emulsification index (EI24h) assays with various hydrocarbon substrates (fuel oil, gasoline, diesel, and n-hexadecane). The

BS and BE activities were evaluated in terms of surface activity and emulsification stability. Phytotoxicity tests (germination index) were performed using *Zea mays*, *Lepidium sativum*, and *Medicago sativa*.

## Results and Discussion

Oil displacement (Table 2) and emulsification index tests indicated that the biosurfactant and bioemulsifier activity was more frequently observed under mild salinity (NaCl 0.5 g/L), suggesting that appropriate osmotic conditions are beneficial for biosynthesis.

In microcosms amended with high nitrate and sulfate concentrations, more than 40% of oil displacement tests produced a clearing zone ≥1 cm, and emulsification indices above the 50% cutoff were observed in both crude and filtered extracts. These results suggest that even minimally processed biosurfactant-rich mixtures may provide sufficient surface activity to enhance hydrocarbon mobilization, without requiring purification or bioaugmentation.

These findings support the feasibility of biosurfactant production directly within the contaminated matrices, reducing reliance on exogenous chemical surfactants that often pose toxicity and persistence concerns. Moreover, the use of readily available waste materials as substrates makes this approach potentially scalable and compatible with circular-economy principles.

Importantly, this work should be considered as the first exploratory step, with several open questions remaining, including the kinetics of BS/BE production, the identity and stability of active compounds, and their effects on microbial community dynamics, pollutant bioavailability, and plant health.

***Table 2**: Results of oil displacement tests performed with gasoline, diesel oil, mineral and fuel oil, 12 tests for each condition as number of tests with no detected oil displacement (NEG), with oil displacement <1 cm (in diameter) (PART), and oil displacement ≥1 cm (in diameter) (POS).*

| **Test conditions** | **EAs** | **Oil displacement test** | | | | |
|---|---|---|---|---|---|---|
| | | | Gasoline | Diesel Oil | Fuel Oil | Mineral Oil |
| **0.5 g/l NaCl (“saline”)** | **$MgSO_4$ 0.5 g/L + $KNO_3$ 40 mg/L** | NEG (%) | 8.3 | 16.7 | 25.0 | 8.3 |
| | | PART (%) | 33.3 | 25.0 | 33.3 | 16.7 |
| | | POS (%) | 58.3 | 58.3 | 41.7 | 75.0 |
| | **$MgSO_4$ 0.1 g/L + $KNO_3$ 5 mg/L** | NEG (%) | 8.3 | 8.3 | 25.0 | 8.3 |
| | | PART (%) | 0.0 | 25.0 | 25.0 | 8.3 |
| | | POS (%) | 91.7 | 66.7 | 50.0 | 83.3 |
| **No added NaCl (“non saline”)** | **$MgSO_4$ 0.5 g/L + $KNO_3$ 40 mg/L** | NEG (%) | 75.0 | 75.0 | 75.0 | 75.0 |
| | | PART (%) | 16.7 | 8.3 | 0.0 | 0.0 |
| | | POS (%) | 8.3 | 16.7 | 25.0 | 25.0 |
| | **$MgSO_4$ 0.1 g/L + $KNO_3$ 5 mg/L** | NEG (%) | 25.0 | 25.0 | 33.3 | 25.0 |
| | | PART (%) | 0.0 | 8.3 | 33.3 | 0.0 |
| | | POS (%) | 75.0 | 66.7 | 33.3 | 75.0 |

## References

Shekoohiya S., Moussavi G., Naddafi K., (2016), The peroxidase-mediated biodegradation of petroleum hydrocarbons in a H2O2-induced SBR using in-situ production of peroxidase: Biodegradation experiments and bacterial identification, Journal of Hazardous Materials, 313, 170-178.

Moussavi G., Shekoohiya S., Naddafi K., (2017), The accelerated enzymatic biodegradation and COD removal of petroleum hydrocarbons in the SCR using active bacterial biomass capable of in-situ generating peroxidase and biosurfactants, Chemical Engineering Journal, 308, 1081-1089.

# Microalgae-Based Carbon Capture and Bioproduct Synthesis Using Industrial Flue Gas: A Case Study with *Stichococcus* sp.

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***keywords:*** *microalgae cultivation; photo-bioreactors; flue gas utilization; $CO_2$ fixation; bioproduct synthesis.*

## Introduction

The urgent need to mitigate industrial carbon dioxide ($CO_2$) emissions has driven exploration into biologically-based carbon capture technologies. Among these, microalgae have gained prominence due to their rapid growth rates, high photosynthetic efficiency, and capacity to fix $CO_2$ directly from gas streams. Rather than relying solely on chemical or physical capture methods, integrating microalgae into industrial systems offers a biologically driven, sustainable alternative (Goswami et al., 2024).

One of the most compelling applications of microalgal $CO_2$ fixation is the treatment of flue gases emitted by power plants and manufacturing facilities. These emissions, typically rich in $CO_2$ as well as nitrogen and sulfur oxides, are often considered too harsh for biological treatment. However, certain robust microalgal strains have shown the ability not only to survive but also to thrive in these conditions, turning pollutants into biomass with potential commercial applications (Kong et al., 2024).

Beyond environmental benefits, microalgae cultivation offers economic incentives. The harvested biomass can be processed into biofuels, bioplastics, or high-protein animal feed, making the integration of microalgae in carbon capture systems both ecologically and economically attractive (Chen et al., 2023). With continuing innovation in cultivation technologies and photobioreactor design, microalgae may become a cornerstone in the future of industrial carbon management.

## Materials and methods

This study aimed to reduce $CO_2$ emissions from industrial flue gases by cultivating microalgae and converting the resulting biomass into valuable bioproducts. Experiments were conducted at the Lavrio power station in Keratea, Attica, Greece, using two 15-liter closed photobioreactors. *Stichococcus* sp., isolated from Souda Bay, was grown on sandblasted glass tiles to reduce harvesting costs (Makaroglou et al., 2021), with the system housed in a shelter to protect against environmental factors.

Natural gas-derived flue gas was supplied at 0.6 $L\cdot min^{-1}$ as the carbon source. Three lighting regimes (runs) were tested: (i) continuous light, (ii) flashing light at 1,000 Hz, and (iii) continuous light with nitrogen starvation, introduced three days before harvest. LED lighting provided 6,600 lux for the first two conditions, and 3,300 lux under nitrogen starvation to encourage lipid accumulation.

Temperature was maintained at 25 ± 1 °C via air conditioning. The culture medium included artificial seawater and Bold’s Basal Medium, with 35 $g\cdot L^{-1}$ NaCl and 0.75 $g\cdot L^{-1}$ $NaNO_3$. After 26 days, biomass was harvested from the glass tiles and analyzed for dry weight and biochemical content, including lipids, proteins, carbohydrates, and pigments.

## Results and discussion

Throughout the experimental period, *Stichococcus* sp. microalgae demonstrated effective adaptation to the flue gas environment, achieving a $CO_2$ fixation rate of approximately 1.8 kg per kilogram of dry biomass produced. Biomass productivity under the three tested cultivation conditions, continuous illumination, flashing light, and continuous light combined with nitrogen deprivation was recorded as 50.5 $g\cdot m^{-2}$, 47.9 $g\cdot m^{-2}$, and 38.3 $g\cdot m^{-2}$, respectively.

Analysis of the biochemical composition of the harvested biomass (Fig. 1) indicated that high-value bioproducts, comprising carbohydrates, lipids, proteins, and total chlorophyll constituted approximately 80–90% of the total biomass. Among these, carbohydrates represented the dominant fraction, with yields of 24.8 $g\cdot m^{-2}$, 23.4 $g\cdot m^{-2}$, and 11.9 $g\cdot m^{-2}$ under the respective cultivation regimes. Lipid accumulation was notably enhanced under nitrogen starvation and flashing light conditions, with measured values of 6.6 $g\cdot m^{-2}$, 6.8

$g{\cdot}m^{-2}$, and 11.0 $g{\cdot}m^{-2}$, respectively. Protein content was observed at 8.3 $g{\cdot}m^{-2}$, 7.6 $g{\cdot}m^{-2}$, and 6.1 $g{\cdot}m^{-2}$, while total chlorophyll concentrations were calculated as $19.1 \times 10^{-2}$ $g{\cdot}m^{-2}$, $23.0 \times 10^{-2}$ $g{\cdot}m^{-2}$, and $12.0 \times 10^{-2}$ $g{\cdot}m^{-2}$ across the same treatments.

Although the use of flashing light resulted in a modest reduction in overall biomass yield, it was associated with an increase in pigment synthesis. From an energy consumption perspective, continuous lighting required 33.1 kWh over the 26-day cultivation period, whereas the flashing light setup consumed only 25.7 kWh, thereby demonstrating improved energy efficiency and cost-effectiveness in biomass production.

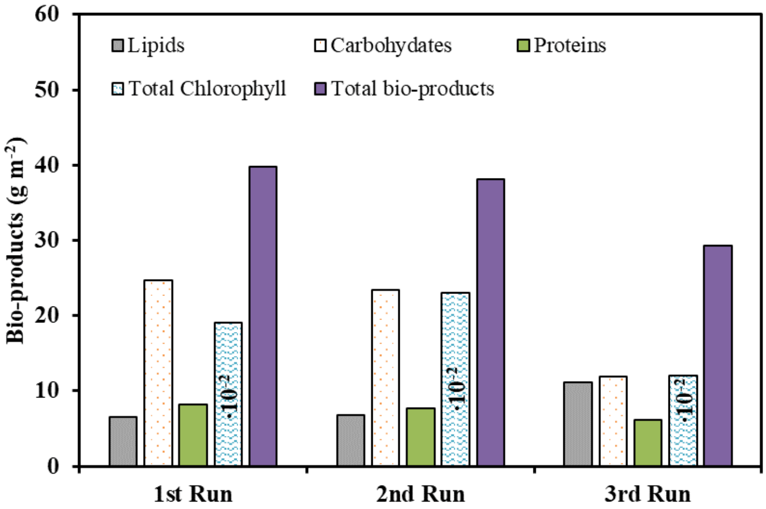

***Figure 1.*** *i) Lipids, ii) Carbohydrates, iii) Proteins, iv) Total chlorophyll, and v) Total bio-products produced by Stichococcus sp. for each experimental run.*

## Conclusions

The experimental results demonstrated that *Stichococcus* sp. can be successfully cultivated utilizing industrial flue gas derived from the combustion of natural gas, underscoring the feasibility of employing microalgae for the mitigation of $CO_2$ emissions prior to their atmospheric release. The generated biomass presents significant potential for downstream conversion into commercially valuable bioproducts. In conclusion, the deployment of large-scale photobioreactor systems for microalgal cultivation represents a promising strategy for lowering atmospheric $CO_2$ concentrations and, consequently, alleviating the impacts of the greenhouse effect.

***Acknowledgements:*** This study was co-financed by the European Regional Development Fund of the EU and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call “Research-Create-Innovate” (project code: T1EDK-02681). Project title: “Bioconversion of $CO_2$ into high-added value bioproducts through sustainable microalgae cultivation processes ($CO_2$-BioProducts)”.

## References

Kong, W., Kong, J., Feng, S., Yang, T., Xu, L., Shen, B., Bi, Y. and Lyu, H., 2024. Cultivation of microalgae–bacteria consortium by waste gas–waste water to achieve $CO_2$ fixation, wastewater purification and bioproducts production. *Biotechnol Biofuels*, 17, 26.

Makaroglou, G., Marakas, H., Fodelianakis, S., Axaopoulou, V. A., Koumi, I., Kalogerakis, N. and Gikas, P., 2021. Optimization of biomass production from *Stichococcous* sp. biofilms coupled to wastewater treatment. *Biochem. Eng. J.*, 169, 107964.

Razzak, S.A., Lucky, R.A., Hossain, M.M. and deLasa, H., 2022. Valorization of Microalgae Biomass to Biofuel Production: A review. *Energy Nexus*, 7, 378, 100139.

Udaypal, Goswami, R.K., Mehariya, S. and Verma P., 2024. Advances in microalgae-based carbon sequestration: Current status and future perspectives. *Environ Res.*, 15, 249, 118397.

# From Lab to Pilot Scale Microalgae-based Photobioreactors: Statistical Optimization of 3rd Generation Biofuel Production

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***Keywords:*** *microalgae; biofuel; photo-bioreactor; $CO_2$; DoE.*

## Introduction

Microalgae are a diverse group of photosynthetic microorganisms that can be found in a variety of aquatic environments, from freshwater lakes to saltwater oceans and even wastewater treatment facilities. These living organisms, which range from unicellular to multicellular forms, have emerged as a promising and sustainable platform for numerous applications. They possess an exceptional ability to efficiently convert solar energy and $CO_2$ into valuable biomass, making them a potential solution to some of the world's most pressing challenges, such as energy security, environmental sustainability, and resource scarcity.

The increasing worldwide demand for sustainable energy sources and the urgency to reduce greenhouse gas (GHG) emissions have directed attention towards biofuels, like biodiesel produced from microalgal lipids, as a promising alternative to fossil fuels. FUELGAE, a research project funded by EU, aims to achieve this via microalgae-based technologies, enabling the conversion of existing production units into advanced 3rd generation (3G) biorefineries, utilizing both biogenic and non-biogenic $CO_2$ sources [1]. By upgrading a 2G bioethanol plant and a conventional steel production plant through an innovative pilot photo-bioreactor (PBR) it provides in-situ cultivation of selected and optimized microalgal species[2]. Specifically, a polysaccharide-producing strain and a lipid-producing strain are employed to capture and convert $CO_2$ emissions from production units directly into microalgal biomass. This biomass is then integrated into both existing and new value chains for liquid biofuel production: polysaccharides are enzymatically hydrolyzed and fermented into bioethanol, while lipids are hydroprocessed into hydrocarbons. Furthermore, the residual microalgal biomass is transformed into biocrude via hydrothermal liquefaction (HTL), offering an additional feedstock for upgrading.

In this study, the Taguchi statistical design of experiments (DoE) is employed to systematically optimize the microalgal bioprocess developed under the FUELGAE project. The objective is to maximize the output responses, i.e. biomass, polysaccharides and lipids concentrations per case. Concurrently, the innovative pilot-scale PBR (Figure 1) and the associated experimental results from the cultivation of the selected microalgal strains are presented, demonstrating the scale-up process implemented within FUELGAE and the efforts undertaken to advance the technology to Technology Readiness Level 5 (TRL 5).

## Materials and methods

Two microalgal strains, i.e. *Stichococcus* sp. and *Chlorella vulgaris* (see Figure 2 for microscope images), previously selected via a screening study[3] and then improved via Adaptive Laboratory Evolution (ALE), were cultivated and used in the present study targeting biomass production, along with adequate accumulation of polysaccharides or lipids. This approach aligns with FUELGAE's two case studies: on-site $CO_2$ capture and conversion within a bioethanol plant (Case Study I) and a steel plant (Case Study II), respectively. The strains are cultivated in a modified BBM nutrient medium using $CO_2$ in excess (at least 10% v/v), as to simulate industrial off gasses.

The selected parameters used as input variables in the DoE include the microalgae strain type, the illumination color and intensity (i.e. cool white, blue and red light at different wavelengths), and the $CO_2$ supply rate. Statistical analysis and regression modelling enable the identification of bioprocess conditions favoring biomass, polysaccharides and/or lipids production.

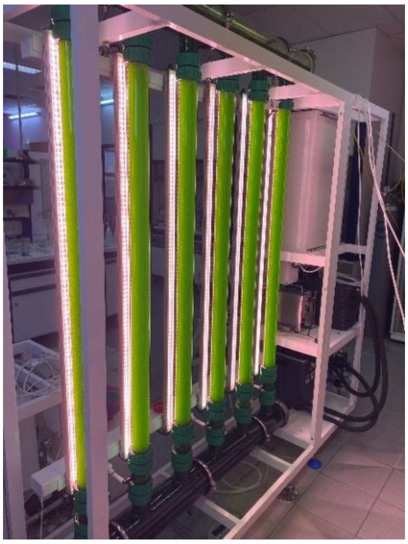

***Figure 1.*** *Pilot-scale tubular airlift photobioreactor installed in CERTH facilities.*

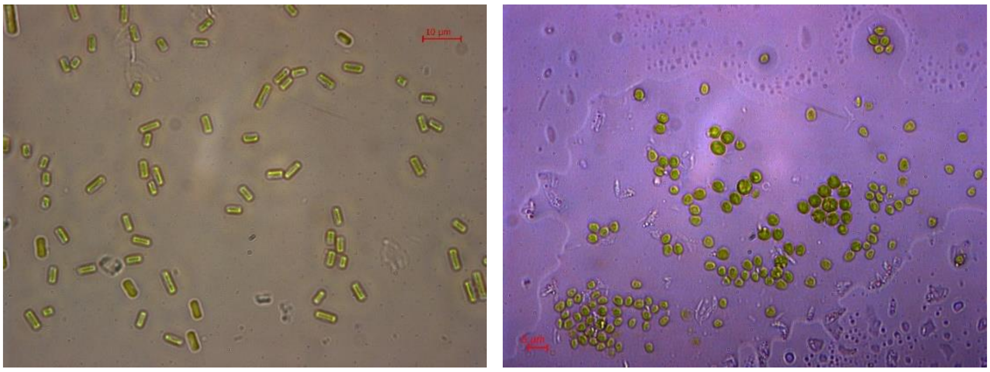

***Figure 2.*** *Optical microscope images of (a) Stichococcus sp. and (b) Chlorella vulgaris cells during cultivation in $CO_2$ excess (10% v/v).*

**Results and discussion**

Analysis of the experimental and DoE results identifies *Stichococcus* sp. as an adequate polysaccharides producer and *Chlorella vulgaris* as an efficient lipids producer for further scaling up their cultures in the pilo-scale tubular air-lift PBR. Subsequently, the scaled-up cultivation results of the selected strains validated the successful scaling-up process.

**Conclusions**

The reported results outline a strategic approach for enhancing specific strains and expanding their cultivation systems to align with industrial demands, establishing microalgae as a key element in the shift toward sustainable biofuel production.

***Acknowledgements:*** This work has been developed in the frame of the FUELGAE research project, funded by the European Union's Horizon Europe research and innovation program under Grant Agreement number 101122151.

**References**

[1] The FUELGAE Project: https://fuelgae.eu/.

[2] Penloglou, G., Pavlou, A., & Kiparissides, C., 2024. Recent advancements in photo-bioreactors for microalgae cultivation: a brief overview, Processes, 12(6), 1104.
[3] Penloglou, G., Pavlou, A., & Kiparissides, C., 2025. Screening Microalgae for Producing Biofuel Precursors from Industrial Off-Gases, Sustainability, 17(7), 2964.

# Willow (*Salix acmophylla* Boiss.) Leaf and Branch Extracts Inhibit *In Vitro* Sporulation of Coccidia (*Eimeria* spp.) from goats

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***keywords:*** *Ethanol extracts; Plant secondary metabolites; Coccidia sporulation; Eimeria sp.; Willow genotypes*

## Introduction

Coccidiosis is a parasitic disease affecting ruminants, primarily caused by *Eimeria* spp., and remains a major challenge in livestock farming due to its economic impact, particularly in young animals. Traditional anticoccidial drugs are increasingly compromised by resistance, drug residues, and rising demand for organic animal products. These limitations prompt the need for alternative, sustainable strategies for disease control. Willows (*Salix* spp.), widespread and diverse members of the *Salicaceae* family, have long been recognized for their secondary metabolites, particularly phenolic compounds and salicylates, which offer a range of pharmacological properties including anti-inflammatory, antioxidant, and antiparasitic activities. While *Salix babylonica* has been studied for its anthelmintic properties, little attention has been given to *Salix acmophylla*, a Middle Eastern species with significant ecological and agricultural potential.

The present study evaluates the potential of ethanolic extracts from leaves and branches of three genotypes of *S. acmophylla*—native to Jordan and Israel—as inhibitors of *Eimeria* sporulation. The study focuses on quantifying the phenolic content, flavonoids, and salicylic acid levels, and assessing their *in vitro* efficacy against coccidia. This work represents a foundational step toward plant-based alternatives to synthetic anticoccidials.

## Materials and methods

Leaves and thin branches were collected from three *S. acmophylla* genotypes grown at the Deir Alla Agricultural Research Centre in Jordan. Dried samples were extracted with 70% ethanol, evaporated, and stored for further analysis. The total phenolic, flavonoid, and salicylic acid contents were quantified using standard spectrophotometric methods.

Oocysts of *Eimeria* spp. were isolated from naturally infected goat faeces and incubated with different extract concentrations (250-5000 mg/L) for 48 hours under aerobic conditions. Sporulation inhibition was assessed microscopically, and results were expressed as percentage inhibition relative to control. Two-way ANOVA and Tukey's HSD test were used for statistical analysis.

## Results and discussion

The yield of leaf extracts (avg. 31.3%) was 2.5 times higher than that of branches. Leaves showed higher salicylic acid content, while branches exhibited significantly higher flavonoid levels. Total phenolic content was comparable across tissues and genotypes (Table 1).

All extracts significantly inhibited *Eimeria* sporulation in a dose-dependent manner. At 750 mg/L, inhibition exceeded 70%, while concentrations of 1250 and 5000 mg/L produced inhibition above 90% (Figure 1). Interestingly, both leaves and branches of all genotypes were comparably effective, despite differences in metabolite profiles.

***Table 1.*** *Selected phytochemical properties and extraction yield of willow leaf and branch genotype.*

| **Willow (*Salix*) Plant Tissue/Genotype** | **Extraction Yield (%) ±2Std** | **TP GAE * (mg)/Extract (g) ±2Std** | **Total Flavonoids Rutin (mg)/Extract (g) ±2Std** | **Salicylic Acid (mg)/Extract (g) ±2Std** |
|---|---|---|---|---|
| **Leaf 3** | 32 ± 0.01 | 83.5±0.98 a | 128 ± 2.31 a | 75.0 ± 1.44 a |
| **Branch 1** | 12 ± 0.00 | 93.0 ± 4.68 a | 210 ± 1.16 a | 40.0 ± 1.83 b*** |

**TP GAE‒total phenols gallic acid equivalent. Means and standard deviation of two experiments, each with three replicates, mean separation in each tissue by Tukey’s HSD test p ≤0.05. *** Different letters indicate significant differences at p ≤0.05.*

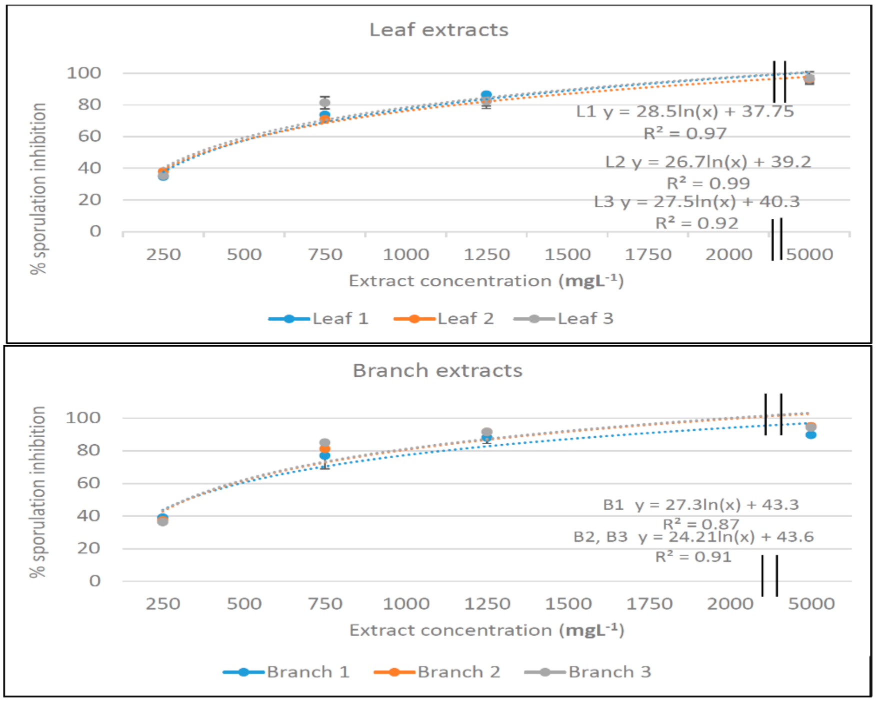

***Figure 1.*** *Percent inhibition of Eimeria sporulation by ethanolic extracts from leaf (**above**) or branch (**below**) tissues from the three genotypes of S. acmophylla. Each data point is the mean of two triplicate experiments. Standard deviation is shown where it is larger than the data point.*

## Conclusions

Ethanolic extracts from leaves and branches of *S. acmophylla* significantly inhibit *Eimeria* sporulation *in vitro*, with over 70% inhibition at 750 mg/L and over 90% at higher concentrations. These results support the use of willow extracts as natural coccidiostats and warrant further *in vivo* evaluation.

***Acknowledgements:*** This research was partially funded by MERC (Middle East Regional Cooperation) Program of USAID, Project #M39-014.

## References

Haj-Zaroubi, M. et al. (2024). *Willow (Salix acmophylla Boiss.) Leaf and Branch Extracts Inhibit In Vitro Sporulation of Coccidia (Eimeria spp.) from Goats*. *Agriculture*, 14, 648.
Rivero-Perez, N. et al. (2019). *Salix babylonica L. as a Natural Anticoccidial Alternative in Growing Rabbits*. *Evid.-Based Complement. Altern. Med.*, 2019, 2107231.
Azaizeh, H. et al. (2013). *Polyphenols from Pistacia lentiscus impair nematode larvae exsheathment*. *Vet. Parasitol.*, 191(1–2), 44–50.

# Optimization of high-added value terpenes recovery from genetically engineered *Saccharomyces cerevisiae* and *Yarrowia lipolytica* strains

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**Keywords:** *Saccharomyces cerevisiae, Yarrowia lipolytica, limonene, squalene, terpene extraction.*

## Introduction

The rapid advancements in metabolic engineering have established microbial fermentation as a promising and sustainable method for the production of high-value secondary metabolites, such as terpenes and terpenoids. These compounds, traditionally derived from plants, are widely used in pharmaceuticals, cosmetics, and the food industry, due to their bioactive properties, including anti-inflammatory, antioxidant, and antimicrobial effects (Tetali et al., 2019). However, their low natural abundance poses significant challenges for their recovery. *Saccharomyces cerevisiae* and *Yarrowia lipolytica* are two widely used yeasts that have been successfully engineered to host terpene biosynthetic pathway for the biotechnological production of limonene, squalene and other terpenes/terpenoids (Manina and Forlani, 2023).

To efficiently extract and recover terpenes/terpenoids from yeast cultures, two-phase fermentation (TPF) systems are commonly employed, especially in the case of production of terpenes/terpenoids with moderate to high volatility. TPF typically involves the use of an organic phase (such as dodecane or isopropyl myristate) layered over the fermentation broth (Ouyang et al., 2019). While current research focuses on the recovery of terpenes/terpenoids from the organic phase, there are limited studies concerning the terpenes/terpenoids extraction from the aqueous and the biomass (i.e. yeast cells) phases.

## Materials and methods

This study focuses on the recovery of the monoterpene limonene and the triterpene squalene from the cultivations of two genetically modified yeast strains: *S. cerevisiae* (EGY48-PER Lim) and *Y. lipolytica* (YLS48-Squ), respectively. Batch fermentations were carried out in flasks, with a 10% v/v isopropyl myristate overlay applied in the case of *S. cerevisiae* (TPF).

For *S. cerevisiae*, the extraction protocol of limonene from all phases (organic, aqueous, biomass) of the TPF culture was studied and optimized. Additionally, the mass distribution of limonene among these phases was investigated, while its production profile was conducted in each phase, throughout a 72h TPF culture of the engineered *S. cerevisiae*.

In the case of squalene, its recovery was studied only from the biomass phase of the *Y. lipolytica* culture, since it is mainly an intracellular metabolite. Specifically, two biomass pretreatment methods were examined, the use of (a) sonication bath and (b) sonication probe. Subsequently, an experimental design was conducted to determine the optimal solvent-to-biomass extraction ratio, and the optimal extraction time for recovering squalene from the yeast biomass.

## Results and discussion

In the first series of experiments concerning the identification of the optimal conditions for extracting limonene from all phases of the *S. cerevisiae* culture, ethyl acetate was found to be the most effective solvent for extracting limonene from the aqueous phase. The optimal aqueous-to-solvent ratio was 1:1 (v/v), with an extraction time of 10 minutes under stirring. Concerning the wet biomass, hexane was determined to be the most suitable solvent, with an optimal biomass-to-solvent ratio of 2:1 (w/v) and an extraction time of 20 minutes using a sonication bath. Under these optimal extraction conditions, the limonene concentration reached 29 mg/L of culture. Limonene was primarily present in the organic phase (95.2% of the total mass), whereas in the aqueous phase and the biomass the limonene mass was much lower, approx. 0.7% and 4.2% of the total mass, respectively (Figure 1).

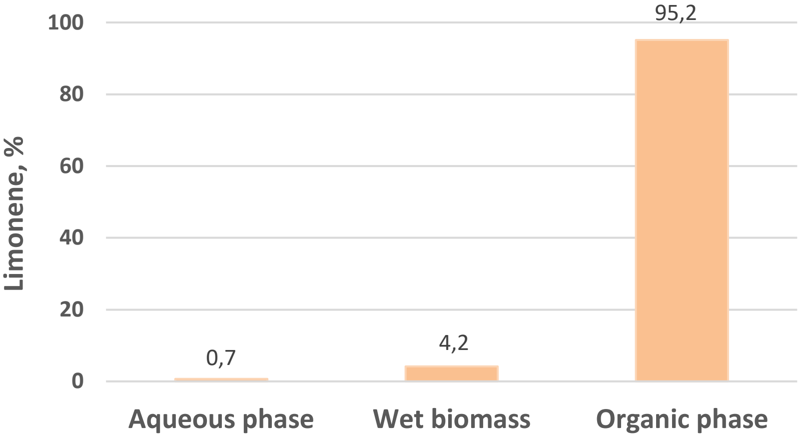

***Figure 1.*** *Mass distribution of limonene across the three phases of the S. cerevisiae culture*

Regarding the cultivation of *Y. lipolytica* strain for squalene production, it was found that, as expected, no squalene was detected in the aqueous phase. Preliminary results from the biomass pretreatment methods showed that using a sonication probe (100 W/g dry biomass) for 1 minute resulted in a higher squalene extraction yield of 0.078mg/g dry biomass, compared to the use of a sonication bath (150 W/g dry biomass), which after 40 minutes resulted in an extraction yield of 0.016mg/g dry biomass. Using experimental design optimization, it was determined that the optimal conditions for extracting squalene from the dry yeast biomass comprise ethyl acetate as the solvent, with a solvent-to-biomass ratio of 10:1 and extraction time of 12.5 minutes under stirring.

## Conclusions

Based on the experimental outcomes, efficient extraction protocols for limonene and squalene from yeast cultures were successfully developed, using ethyl acetate and hexane as key solvents. Further confirmation experiments are scheduled to determine the maximum limonene and squalene recovery. An optimized downstream processing protocol for extracting terpenes from all culture phases is crucial for a biotechnological production process aiming to maximize terpenes recovery.

***Acknowledgements:*** The research project VALORY is implemented in the framework of H.F.R.I call “Basic Research Financing (Horizontal support of all Sciences)” under the National Recovery and Resilience Plan “Greece 2.0” funded by the European Union – NextGenerationEU (H.F.R.I. Project Number: 016559).
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## References

Tetali, S. D., 2019. Terpenes and isoprenoids: a wealth of compounds for global use. *Planta*, 249, 1-8.
Manina, A. S., & Forlani, F., 2023. Biotechnologies in perfume manufacturing: metabolic engineering of terpenoid biosynthesis. *Int. J. Mol. Sci.*, 24(9), 7874-7891.
Ouyang, X., Cha, Y., Li, W., Zhu, C., Zhu, M., Li, S., Zhuo, M., Huang, S., & Li, J., 2019. Stepwise engineering of *Saccharomyces cerevisiae* to produce (+)-valencene and its related sesquiterpenes. *RSC advances*, 9(52), 30171-30181.

# Valorization of Invasive Macroalgae (*Asparagopsis armata and Sargassum spp*.) as Sources of Immune-Enhancing Aquafeed Ingredients: Recovery and In-Vitro Fish Digestibility Assessment

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***keywords:*** *aquafeed; in-vitro fish digestion; invasive macroalgae; phlorotannins; sustainable aquaculture.*

## Introduction

Invasive macroalgae such as *Asparagopsis armata* (red) and *Sargassum spp.* (brown) increasingly impact Mediterranean coasts but contain bioactives (halogenated metabolites, sulfated polysaccharides, phlorotannins, PUFA) relevant for fish health. Prior studies with *Asparagopsis spp.* and brown algal polyphenols indicate antimicrobial, antioxidant, and immunomodulatory activities in fish, supporting their use as functional aquafeed ingredients. This work—conducted as a synergy between the EU funded projects VALIAS (invasive biomass valorization) and FEEDACTIV (functional aquafeeds)—focuses strictly on compound recovery, food-grade formulation, and in-vitro fish digestibility, as a prerequisite to immune-efficacy trials.

## Materials and methods

Biomass of *A. armata* and *Sargassum spp.* was harvested from invaded shores under permits, rinsed, low-temperature air-dried (≤40 °C), and milled (<500 µm). Extraction workflows included: (i) proteins/peptides via aqueous extraction and enzymatic hydrolysis (alcalase; 50 °C; pH 8), (ii) polysaccharides via hot-water extraction (85 °C) and ethanol precipitation, (iii) polyphenols via 70% ethanol maceration, and (iv) lipids via food-grade solvents with GC–MS fatty acid profiling. Characterization included total protein (Kjeldahl), phenolics (Folin–Ciocalteu), sulfated polysaccharides (phenol–sulfuric), and omega-3 PUFA quantification. In-vitro fish digestion was conducted using a two-stage static model adapted for *Sparus aurata*, quantifying bioaccessibility of proteins, phenolics, reducing sugars, and micellarized PUFA.

## Results and discussion

Both *A. armata* and *Sargassum* extracts were rich in immune-relevant compounds: *A. armata* yielded 21.4 ± 1.2% protein, 18.7 ± 0.9% sulfated polysaccharides, and notable halogenated metabolites; Sargassum extracts were high in phlorotannins (46.3 ± 2.1 mg PGE/g) and contained omega-3 PUFA (EPA 2.8%, DHA 1.1% of total FA). In-vitro digestion revealed >65% digestibility for protein hydrolysates, 42–53% bioaccessibility of phenolics, and partial resistance of polysaccharides, suggesting potential prebiotic effects. The choice of these algae is supported by literature demonstrating enhanced innate immune responses in fish fed Asparagopsis and brown algal extracts.

Enhancing the security and sustainability of European aquaculture is best achieved through ecosystem-positive production, where feed and health innovations are coupled with actions that measurably improve marine biodiversity. By valorizing invasive biomass into functional, traceable feed ingredients, farms can reduce reliance on finite fishery resources, lower import risk exposure, and strengthen animal health—while targeted removals of invaders relieve pressure on native communities. This dual approach improves biosecurity and supply-chain robustness (through diversified, locally sourced inputs) and aligns with EU sustainability goals by generating co-benefits: lower feed footprint, healthier stocks, and demonstrable recovery of native species richness and habitat quality.

## Conclusions

This VALIAS–FEEDACTIV study establishes a recover–formulate–digest pipeline for invasive macroalgae-derived ingredients and demonstrates fish-model bioaccessibility, de-risking their progression to immune-endpoint feeding trials in Sparus aurata and Dicentrarchus labrax. By coupling aquafeed innovation with targeted invasive species removals, the approach strengthens both aquaculture sustainability and European marine biodiversity.

***Acknowledgements:*** This study is supported by the European Union's Horizon Europe Framework Programme (HORIZON) under the Marie Skłodowska-Curie grant agreement No 101086261-FEEDACTIV and grant agreement No 101131441-VALIAS.

## References

Kumar, L.R.G., Brown, M.T., Lu, J., 2022. Phlorotannins—bioactivity and extraction perspectives. Marine Drugs, 20, 530; MDPI: Basel, Switzerland.

Ponte, J.M.S., Moreira, A., Pereira, L., 2022. Asparagopsis genus: what we really know. Marine Drugs, 20, 306; MDPI: Basel, Switzerland.

Siddik, M.A.B., Howieson, J., Fotedar, R., 2023. Seaweed metabolites as functional aquafeed modulators. Fishes, 8, 14; MDPI: Basel, Switzerland.

Wang, R., Tian, Q., Song, B., Hu, X., 2021. In-vitro digestion models: critical review for fish. Food Research International, 147, 110505; Elsevier: Amsterdam, The Netherlands.

# Life cycle assessment of systems exploiting microalgae for the wastewater treatment

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**keywords:** *microalgae; life cycle assessment; wastewater; biostimulants; adsorption.*

## Introduction

The attention towards integrating microalgae within wastewater treatments has been recently growing. Microalgae are able both to remove heavy metals and nutrients in wastewater and to sequester $CO_2$. Moreover, the poor-quality growth media makes microalgae cultivation more convenient (Mantovani at al., 2020). Life cycle assessment (LCA) is the appropriate tool to verify these environmental advantages.

## Materials and methods

In this work, two systems exploiting microalgae for wastewater treatment are environmentally assessed. LCA is first applied to a wastewater treatment plant (WWTP) integrating an algal cultivation system (developed by Politecnico di Milano). Furthermore, hybrid materials integrating microalgal biomass with inorganic nanomaterials (developed by the Italian National Research Council-ISSMC) are environmentally assessed.

The LCA is performed with the Environmental Footprint 3.1 method (Fazio et al., 2018). The modelling is performed with primary data integrated by data from the literature and the ecoinvent 3.9.1 database.

### *Microalgae cultivation coupled with a wastewater treatment plant*

The analysis compares a conventional WWTP with the same plant integrated with a microalgal cultivation pond. Data of a pilot-scale algal cultivation system have been scaled, simulating the integration at the full scale. The functional unit (FU) is *the treatment of 1,000 $m^3$ of wastewater*.

In the combined system, described in Crippa et al. (2025), the growth of microalgae is sustained by the nutrients of the liquid fraction of the digestate (sludge is anaerobically digested). The residual algal biomass increases the amount of recovered solid digestate and the biogas production. Biogas is upgraded to methane, with the $CO_2$ used for algal growth. Four valorization routes of the residual algal biomass are examined:

1) Fertilizers - use in agriculture substituting chemical fertilizers.
2) Energy - incineration with energy recovery, replacing energy generated from fossil fuels.
3) Cement - thermal drying and use as an alternative fuel in a cement plant, directly replacing fossil fuels.
4) Biostimulants - production of biostimulants used in agriculture; since biostimulants can favor a higher nutrient-uptake efficiency, the supply of fertilizers can be significantly reduced (Koleška et al., 2017).

### *Hybrid materials for wastewater treatment*

The analyzed system couples microalgal biomasses (Neochloris oleoabundans - NeoC and Phaeodactylum tricornutum - Ptr) with inorganic nanoparticles ($TiO_2$ and $SiO_2$) to produce four types of hybrid reactive granules that combine the adsorption capabilities of microalgae with the photocatalytic activity of nanomaterials: (1) NeoC/$TiO_2$; (2) Ptr/$TiO_2$; (3) NeoC/$TiO_2$NP-$SiO_2$; (4) Ptr/$TiO_2$NP-$SiO_2$.

Microalgae are cultivated, harvested, and combined with inorganic nanomaterials to obtain a colloidal suspension. The colloidal suspension undergoes an atomization with a granulator, followed by a spray freeze-drying, resulting in highly porous dry granules. The system is described in Zanoni et al. (2025).

Since the photocatalytic performance of the hybrid granules is similar to that of activated carbon, the LCA focuses on a representative pollutant removed by adsorption, with FU set as the *adsorption of 1 mg of Cu(II)*.

## Results and discussion

### *Microalgae cultivation coupled with a wastewater treatment plant*

Table 1 reports the results for the four valorization routes. Negative impacts (i.e. benefits for the coupling of microalgae with the WWTP) are limited (3 to 5 categories) when the algal biomass is recovered to produce fertilizers or it is sent to energy recovery or in cement production as an alternative fuel. Differently, with the production and use of biostimulants on crops, benefits are observed in 14 out of the 16 impact categories.

***Table 1.*** *Potential impacts for the four valorization routes of residual microalgal biomass. Green color: the coupling of microalgae and WWTP shows lower impacts than those of the conventional WWTP.*

| **Impact category** | **Unit** | **Valorization route (impact/FU)** | | | |
|---|---|---|---|---|---|
| | | **1) Fertilizers** | **2) Energy** | **3) Cement** | **4) Biostimulants** |
| Acidification (A) | mol $H^+$ eq | 1.94E+00 | 1.95E+00 | 1.94E+00 | 6.03E-01 |
| Climate change (CC) | kg $CO_2$ eq | -4.98E-01 | -3.39E+00 | -8.94E+00 | -2.23E+02 |
| Ecotoxicity - freshwater (ECF) | CTUe | 4.63E+01 | 1.03E+02 | 5.59E+00 | -1.43E+04 |
| Particulate matter (PM) | disease inc. | 1.35E-05 | 1.36E-05 | 1.35E-05 | -2.74E-07 |
| Eutrophication - marine (EM) | kg N eq | 6.02E-02 | 6.25E-02 | 6.01E-02 | -1.19E-01 |
| Eutrophication - freshwater (EF) | kg P eq | 4.32E-04 | 7.65E-04 | 7.87E-04 | -4.30E-02 |
| Eutrophication - terrestrial (ET) | mol N eq | 8.63E+00 | 8.65E+00 | 8.64E+00 | 4.97E+00 |
| Human toxicity - cancer (HTC) | CTUh | 4.82E-09 | 1.80E-07 | -4.97E-09 | -1.67E-07 |
| Human toxicity - non-cancer (HTNC) | CTUh | 1.02E-06 | 2.04E-05 | 2.73E-07 | -1.77E-05 |
| Ionizing radiation (IR) | kBq U-235 eq | 4.36E-01 | 4.84E-01 | 5.94E-01 | -1.27E+01 |
| Land use (LU) | Pt | 6.39E+02 | 6.46E+02 | 6.40E+02 | -6.60E+02 |
| Ozone depletion (OD) | kg CFC11 eq | -7.91E-08 | -1.72E-07 | -8.36E-10 | -5.83E-06 |
| Photochemical ozone formation (POF) | kg NMVOC eq | 2.33E-03 | 3.23E-03 | -6.74E-03 | -6.70E-01 |
| Resource use - fossils (RUF) | MJ | -1.53E+01 | -5.05E+01 | -6.74E+01 | -3.05E+03 |
| Resource use - minerals, metals (RUM) | kg Sb eq | -1.28E-06 | 1.06E-05 | 1.12E-05 | -2.53E-03 |
| Water use (WU) | $m^3$ depriv. | 1.17E+00 | 3.48E+00 | 2.60E+01 | -1.44E+02 |

### *Hybrid materials for wastewater treatment*

Granule (1) NeoC/$TiO_2$ shows the lowest impacts in all categories, with 77-81% impact increases for granule (4), 50-54% for granule (3), and 27% for granule (2). Examining impact contributions of granule (1), electricity consumption (especially for the spray freeze-drying) is the most relevant burden in 15 categories (Figure 1).

The next step of the research will be the comparison of hybrid granules with activated carbon to evaluate the potential benefits of the studied system in the adsorption of pollutants from wastewater.

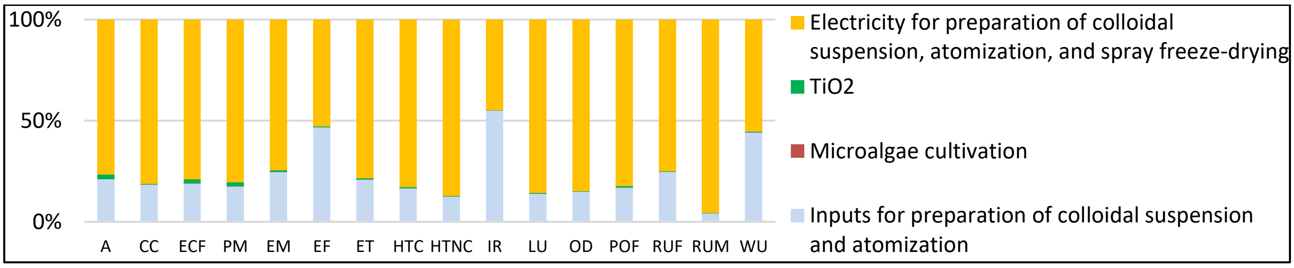

***Figure 1****. Impact contributions for the system (1) NeoC/$TiO_2$; for the impact categories see Table 1.*

### Conclusions

The LCAs showed potential environmental benefits of the assessed solutions, although they are not verified under all conditions (e.g. the choice of the algal niomass recovery route is crucial). Furthermore, LCAs at the lab scale are useful to identify the most relevant burdens, aiming at optimizing the upscaling of processes.

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### References

Crippa, I., Dolci, G., Grosso, M. et al., 2025. Life Cycle Assessment of Microalgal Biomass Valorization from a Wastewater Treatment Process. *Waste Biomass Valor.* 16, 525–541.

Fazio, S., Castellani, V., Sala, S. et al., 2018. Supporting information to the characterisation factors of recommended EF Life Cycle Impact Assessment methods. European Commission, Ispra.

Koleška, I., Hasanagić, D., Todorović, V. et al., 2017. Biostimulant prevents yield loss and reduces oxidative damage in tomato plants grown on reduced NPK nutrition. *J. Plant Interact.* 12(1), 209–218.

Mantovani, M., Marazzi, F., Fornaroli, R. et al., 2020. Outdoor pilot-scale raceway as a microalgae-bacteria sidestream treatment in a WWTP. *Sci. Total Environ*. 710, 135583.

Zanoni, I., Amadori, S., Brigliadori, A. et al., 2025. Hybrid materials for wastewater treatment: synergistic coupling of Neochloris oleoabundans and TiO2 nanoparticles. *Nanoscale Adv*. 7, 3803–3816.

## Efficient mechanochemical synthesis of conjugated porous (macro)molecules via multiple Sonogashira couplings and their energy storage application

R. S. Rao,[1,2] A. Shunnar,[1] B. Pirzada,[1,2] E. Oueis,[1] A. B. Lowe*[1,2] and J. Shaya*[1,2]

# Efficient mechanochemical synthesis of conjugated porous (macro)molecules via multiple Sonogashira couplings and their energy storage application

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***keywords:*** *Sonogashira coupling, Green synthesis, porous polymers, Energy storage, Supercapacitor*

## Introduction

Sonogashira coupling (SC) reactions are pivotal in organic synthesis and materials chemistry, traditionally relying on large solvent volumes, high temperatures, and extended reaction times. Recent efforts have shifted toward greener approaches like mechanochemistry, classified by IUPACas top 10 technologies of the future in chemistry, due to its sustainability and safety benefits. This innovative field leverages high-energy ball milling to facilitate solvent-free SC, enabling the synthesis of porous polymers—advanced materials with large surface areas, tunable porosity, and extensive π-conjugation—offering applications in energy storage, catalysis, and electronics. These conjugated polymeric networks, composed of fused and non-fused aromatic building blocks with heteroatoms and functional groups, benefit from mechanochemical synthesis, which outperforms conventional methods by providing efficient, reproducible pathways to complex structures for high-performance materials in supercapacitors and beyond. These networks exhibit key characteristics such as tunable porosity and building blocks, photophysical stability, large surface area, and extensive conjugation, making them highly versatile for various applications

## Materials and methods

The general SC procedure involved mixing 1 eq. of triethynylbenzene (TEB) with monohalogenated (4.5 eq) or dihalogenated (1.5 eq.) aromatic compounds in the presence of copper sources (5 mol%) and palladium sources (5 mol%), along with 11 eq. of a base. The mixture was placed in a 10 mL milling jar, along with five milling balls (Ø) of different sizes (4, 5, 7 mm), and was subjected to mechanical agitation using a ball mill. The reaction was carried out solvent-free at room temperature under normal air conditions, with the milling instrument set to operate at a speed of 25 Hz for 1 hour. Upon completion of the reaction, the mixture was extracted with dichloromethane (DCM) to separate the organic phase. The organic layer was then treated with anhydrous sodium sulfate ($Na_2SO_4$) to remove residual moisture. After drying, the solvent was evaporated under reduced pressure to obtain a concentrated residue. The crude trimer products were purified by column chromatography and the polymeric network products by Soxhlet extraction. The products were characterized by NMR and FTIR. The electrochemical capacitive performance of synthesized samples was determined by implementing the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge−discharge (GCD) methods in a 1.0 M KOH electrolyte.

## Results and discussion

The present study reports the first successful demonstration of multiple SC *via* a mechanochemical approach within a short reaction time of 60 min under air and ambient conditions using low frequency (25 Hz). The study systematically explores various experimental parameters, including catalytic systems, bases, and milling ball types, to elucidate the optimal conditions for triple SC between TEB and iodobenzene (Figure 1). The scope of the reaction was then evaluated, where substrates with electron-donating, electron-withdrawing, and heteroaromatic groups were coupled successfully to TEB, while also assessing the substitution positions. The optimal catalytic conditions involved $PdCl_2(PPh_3)_2$ and CuI as co-catalysts, with triethylamine as the organobase, and employed mechanochemical activation with low frequency (25 Hz) under normal air conditions. With TEB as the core, ten derivatives incorporating diverse electron-rich and electron-deficient aromatic halides were synthesized, demonstrating the versatility of this protocol. The methodology was extended to the synthesis of conjugated porous macromolecules, which are finding applications in various fields such as energy storage, photocatalysis and electronics. Three representative macromolecules comprising aromatics with different electronic features were synthesized in high yields (71-89%), namely benzene, benzo[d][1,3]dioxole, and benzo[c][1,2,5]thiadiazole. This mechanochemical approach enables a green, solvent-free, and simple route to precisely structured advanced materials.

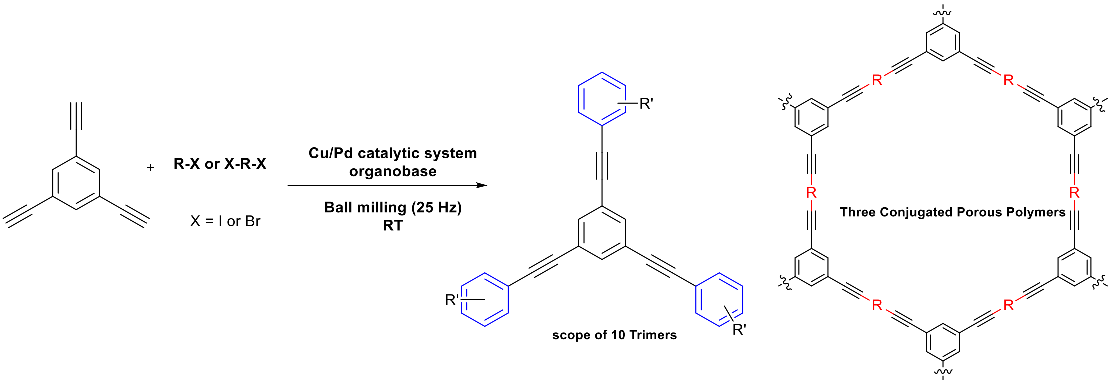

*Figure 1. Multiple SC couplings for the synthesis of trimers and porous macromolecules*

The synthesized polymers were thoroughly characterized to evaluate their potential applications in energy storage. The cyclic voltammetry, electrochemical impedance, and galvanic charge-discharge analysis infer the co-existence of electrochemical double layer capacitance and pseudo-capacitance behaviour. The extended conjugation and the porosity, which is influenced by the type of bridging linker, highlight the scope of the synthesized supramolecules for capacitive energy storage applications. As a result, the polymer bearing benzene rings showed the best performance with a specific capacitance of 64.31 F/g and 4.06 F/g in the open cell and symmetric coin cell configurations, respectively. However, in the coin cell configuration, the polymer bearing benzothiadiazole was found to have the highest specific capacitance of 21.44 F/g but with less stability exhibiting significant potential drop at lower current densities.

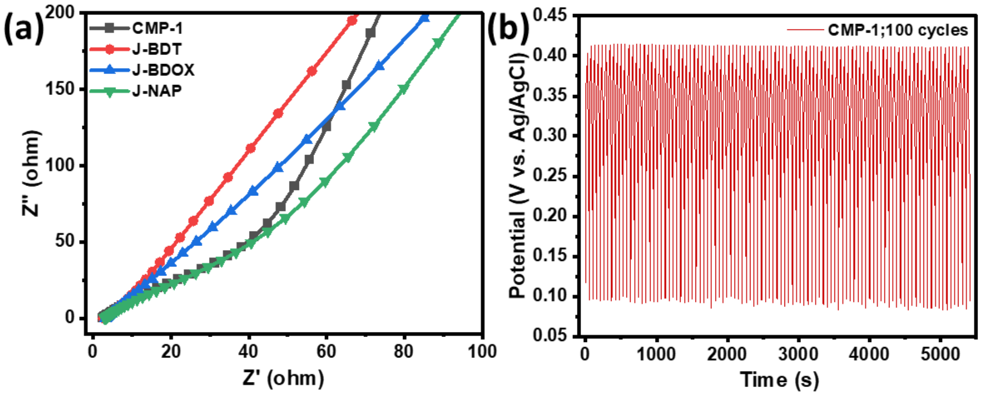

*Figure 2. (a) EIS in the coin cell configuration exhibiting the Nyquist plots. (b) Galvanostatic charge-discharge profile of CMP-1 at 0.8 A/g for 100 cycles exhibiting a nice stability with no evident potential drop.*

## Conclusions

Ball milling has emerged as a powerful, green, and versatile tool in organic synthesis and materials chemistry, offering a sustainable and solvent-free alternative to traditional solution-phase methods. Here, we report the optimization of a triple Sonogashira cross-coupling reaction under room-temperature ball-milling conditions, achieving high yields in short reaction times of 60 min under the optimized catalytic conditions involving PdCl2(PPh3)2 and CuI as co-catalysts, with triethylamine as the organobase, and employed mechanochemical activation with low frequency (25 Hz) under normal air conditions. With TEB as the core, ten derivatives incorporating diverse electron-rich and electron-deficient aromatic halides were synthesized. The methodology was extended to the synthesis of conjugated porous macromolecules. The extended π-conjugation and high surface area led to high capacitance and electrochemical stability, achieving 100 cycles of charge-discharge with no loss in potential over the time range. The as-synthesized symmetric coin cell also exhibited consistent supercapacitor performance, which supports its prospects as a promising electrode for energy storage.

# Session 2: Valorization of food waste

# Comparing the carbon footprint of traditional beef burger with burgers fortified with by-products

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***keywords:** circularity; by-products; carbon footprint; sustainable waste management; recycling.*

## Introduction

Unsustainable management of food waste and losses is responsible for the emission of around 3.3 billion tons of carbon dioxide equivalent annually. The Circular Economy Action Plan in EU countries aims to halve per capita food waste by 2030 supporting the most sustainable management options (EC, 2020). While sending food waste to landfill represents the worst solution in terms of impact on climate change, alternative solutions such as composting can be more efficient for organic waste returning to the soil as fertilizer. However, the European Commission highlights how recycling may be one of the recommended solution for managing food waste. In particular, recycling by-products allows reducing the amount of waste to be disposed and it helps creating a circular economy where waste from food production and consumption is turned into valuable inputs for other processes (Gomez-Garcia et al., 2021).

My presentation will show the effect in terms of carbon footprint estimated by using a Life Cycle Assessment, of replacing an amount of the traditional beef burger with tomato peels and seed. Tomato peels and seed represent two potential by-products of the tomato industry that generally are sent to landfill. Results are discussed in terms of the benefits, in environmental terms, of implementing circular economy practices in the food systems.

## Materials and methods

Both traditional and fortified burgers were prepared. For the traditional burger preparation, ground beef, extra virgin oil, black pepper and meat spices such as salt, were used as ingredients. To prepare the fortified meat products containing tomato peels and seed, the fine powder of dehydrated tomato peels and seeds was added to the basic mixture together with the solvent to previously hydrate the powder such as milk. Both the formulations are reported in Table 1.

***Table 1.** Formulation of traditional and fortified burger with and without tomato peels and seed*

| **Ingredients** | **Traditional burger** | **Fortified burger** |
|---|---|---|
| **Beef** | 976 | 666 |
| **Olive oil** | 16 | 11 |
| **Black pepper** | 2 | 1 |
| **Salt** | 6 | 5 |
| **Tomato peels and seed** | 0 | 122 |
| **Milk** | 0 | 195 |
| **TOTAL** | 1000 | 1000 |

Life Cycle Assessment is a systematic method used to evaluate the environmental impacts of a product, process, or service throughout its entire life cycle. The Functional Unit was defined as 1 kg of burger, and the entire supply chain of all the ingredients in their preparation was considered. Primary and secondary data were used in the Life Cycle Inventory phase. Primary data such as direct data provided by the laboratory of the University of Foggia, were used to analyze the recycling process such as the energy needed for dehydrating and grinding tomato peels and seed. Secondary data from various sources were utilized for each ingredient of the burger. In the Life Cycle Impact Assessment, the analysis was conducted using the "CML-IA baseline v. 3.06" methodology of the SimaPro v. 9.6.0.1 software to assess the potential contributions to the

Global Warming Potential (GWP100, expressed in $kgCO_2eq$), thus providing information about the carbon footprint.

**Results and discussion**

Looking at the impacts per kilogram of beef related burgers, comparing the traditional burger with the fortified one, the reduction of greenhouse gas emission is observed (Fig. 1). In particular the traditional burger records a GWP value of 17.97 $kgCO_2eq$/kg of burger whereas the fortified burger emits 12.7 $kgCO_2eq$/kg of burger. It means that per kg of burger, about 5.2 $kgCO_2eq$ are saved. When looking at the entire food supply chain, the processing of dairy and meat products is recognized as a significant source of energy consumption and associated with high GHG emissions. The amount of extra milk in the fortified burger has a significative impact associated, although it is lower than the saving of emissions due to the decrease of the beef meat with respect to the traditional burger.  Our results are consistent with previous studies identifying beef as a high intensive emission food item. Indeed, bovines, unlike pigs and poultry, release a significant amount of methane from enteric fermentation (Caro et al., 2014) which is saved in the fortified burger.

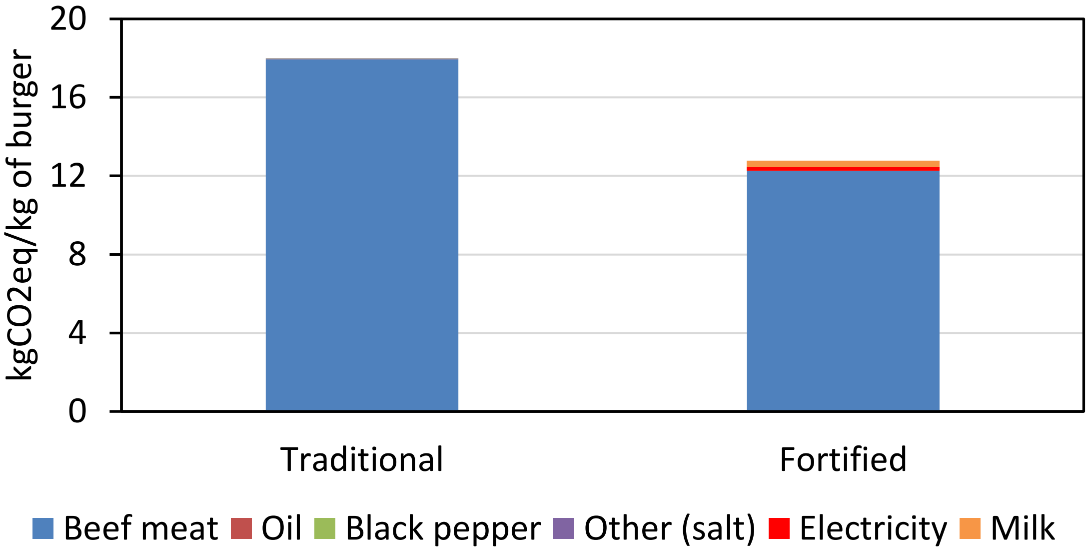

***Figure 1.*** *Global Warming Potential expressed in kg of $CO_2eq$ per kg of burgers (a=beef, b=turkey). Each ingredient and associated impacts are represented by a different color.*

**Conclusions**

The by-products were properly dehydrated and grinded to obtain a fine powder that became an interesting ingredient to enrich the meat burgers. A full Life Cycle Assessment was also carried out to estimate the real benefits in recycling tomato peels and seed, to be used for fortifying a traditional burger. The Life Cycle Assessment has allowed quantifying the environmental savings, using beef with and without tomato peels and seed. The LCA has revealed that recycling by-products with the aim of replacing traditional food is a beneficial option in terms of carbon footprint, above all when high-intensive emissions food items such as beef meat are considered.

**References**

EC, 2020. A new Circular Economy Action Plan: For a cleaner and more competitive Europe. European Commission.

Gomez-Garcìa, R.; Campos, D.A.; Aguilar, C.N.; Madureira, A.R.; Pintado, M. 2021. Valorisation of food agro-industrial by-products: from the past to the present and perspectives. Journal of Environmental Management 299, 113571.

Caro, D., Davis, S.J., Bastianoni, S., Caldeira, K. 2014 Global and regional trends in greenhouse gas emissions from livestock. Climate Change 126:203-216.

# Sustainable Valorization of Seafood Waste: Enzyme-Based Chitin Extraction as an Alternative to Chemical Processes

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***keywords:*** *chitin; enzymes; deproteinization; sea food waste; sustainable extraction.*

## Introduction

Chitin is a highly valuable bio-waste product with numerous applications in various industries. Its abundance, economic value, sustainability and applications make it an important source of renewable materials. Chitin is a long-chain polymer of N-acetylglucosamine, an amide derivative of glucose. It is the second most abundant polysaccharide in nature, behind only cellulose, with an estimated 1 billion tons produced each year in the biosphere. Chitin exists in the shells of arthropods, insects and is also produced by fungi and bacteria and it is biocompatible, biodegradable and non-toxic, making it a promising material for various industries and applications (Elieh-Ali-Komi et al., 2016)

The chitin extraction process typically involves several steps, including demineralization, deproteinization and discoloration, depending on the source material. The most common method for chitin extraction is the chemical method (Islem et al., 2016, Kozma et al., 2022). This method usually requires the use of strong acids and bases, which generate large amounts of hazardous waste that pose significant environmental risks. The choice of the extraction method depends on the source material and the desired properties of the extracted chitin (Islem et al., 2016). While chemical extraction is commonly used in industrial processing, green extraction methods offer potential environmental benefits and are an area of ongoing research and development. These methods utilize techniques such as biological extraction, enzyme-assisted extraction, microwave-assisted extraction and ultrasound-assisted extraction (Islem et al., 2016, Kozma et al., 2022, Mohan et al., 2022). In the enzyme-assisted extraction, results can be different according to the chosen enzymes (Mohan et al., 2022). Proteolytic enzymes like proteases and chitinases have high deproteinization capacity. Despite its potential, enzymatic deproteinization studies remain limited, with a significant knowledge gap regarding whether this method can achieve deproteinization efficiency comparable to conventional chemical treatments while producing chitin of equivalent quality.

In this context, the aim of this work was to compare two different extraction routes for obtaining chitin from seafood waste. Specifically, it aims to evaluate the conventional chemical method against a more sustainable enzymatic approach, in which enzymes are used for the deproteinization of the raw material, enabling chitin recovery.

## Materials and methods

Spider crab shells (*Maja squinado*), sourced from a local restaurant in Donostia-San Sebastián, were washed, dried, and ground (<0.5 mm) prior to chitin extraction. The chemical method (Chitin 1) involved sequential depigmentation (acetone, 48 h), demineralization (2 M HCl, 3 h), deproteinization (2 M NaOH, 24 h), and lipid removal (ethanol, 6 h). For the enzymatic method (Chitin 2), deproteinization was performed using Alcalase® (*Bacillus licheniformis*), followed by the same HCl-based demineralization. Depigmentation and lipid removal were combined into a single ethanol treatment (6 h), and a final mild NaOH step ensured complete protein removal.

Extracted chitin from both methods was characterized via FT-IR, $^{13}$C-NMR, Elemental Analysis, XRD, and TGA to evaluate chemical structure, degree of N-acetylation, crystallinity, and thermal stability.

## Results and discussion

As shown in Table 1 gravimetric analysis revealed a significant difference in chitin yields between chemical method and enzymatic method, primarily due to the distinct deproteinization approaches. The chemical method resulted in a 19.72% chitin yield, while the enzymatic process led to a lower yield of 14.24%. This reduction suggests that the enzymatic-chemical sequence may have removed protein fractions not targeted by the purely chemical method, resulting in lower chitin recovery but potentially higher purity.

***Table 1.*** *Chitin yield obtained from chemical and enzymatic extraction methods.*

| | **Conventional chemical method** | **Enzymatic deproteinization method** |
|---|---|---|
| **Extracted chitin (wt.%)** | 19.72 | 14.24 |

As shown in Figure 1, FT-IR spectra of the purified chitin samples were compared to that of commercial chitin. All spectra exhibited characteristic chitin peaks, including the amide I band (~1652 cm$^{-1}$) and amide II band (~1548 cm$^{-1}$). Minor differences in the 1200–1000 cm$^{-1}$ region, particularly in C–O stretching vibrations, may reflect slight variations in the degree of deacetylation, crystalline structure, or residual impurities. Despite these differences, the overall spectral similarity confirms the effectiveness of the purification process.

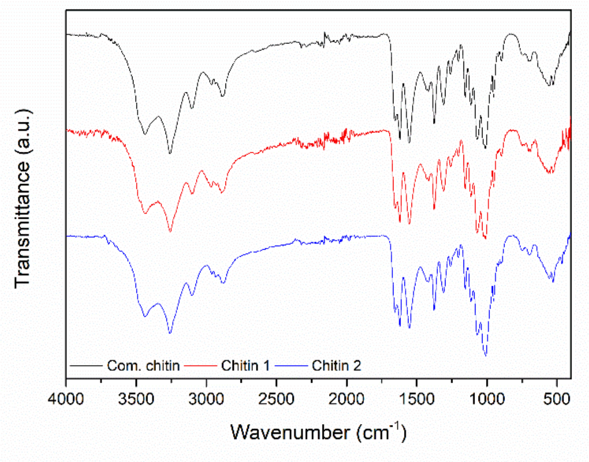

***Figure 1.*** *FT-IR spectra of comercial chitinl (Com. chitin) and the one obtained by conventional cheical method (Chitin 1) and enzymatic deproteninization method (Chitin 2).*

## Conclusions

Chitin obtained through the enzymatic deproteinization method resulted in a high extraction yield. Analytical techniques confirmed the high purity of the extracted biopolymer. Additionally, its potential for application in film and emulsion formulation has been successfully evaluated.

***Acknowledgements:*** This study is supported by the Basque Government (Grant ref. 00001-BIO2023-48 and IT1498-22).

## References

Elieh-Ali-Komi, D. and Hamblin, M.R. 2016. Chitin and Chitosan: Production and Application of Versatile Biomedical Nanomaterials. *Int. J. Adv. Res. (Indore),* 4(3),411-427.

Islem, Y. and Rinaudo, M. 2015. Chitin and chitosan preparation from marine sources. Structure, properties and applications. *Mar. Drugs* 13(3), 1133-1174.

Kozma, M., Acharya, B. and Bissessur, R. 2022. Chitin, chitosan, and nanochitin: extraction, synthesis, and applications. *Polymers* 14(19), 3989.

Mohan, K., et al. 2022. Green and eco-friendly approaches for the extraction of chitin and chitosan: A review. *Carbohydr. Polym.* 287, 119349.

# Pomegranate Peel Bioplastic: Transforming Food Waste into Eco-Friendly Materials for Product Design

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***keywords:*** *pomegranate peel, bioplastics, food waste, product design, circular economy.*

## Introduction

Plastic pollution and food waste stand as two of the most pressing environmental challenges of our time. With global plastic production surpassing 390 million tonnes in 2021—a figure anticipated to double by 2040 under current consumption trends—petroleum-based plastics continue to accumulate in landfills and oceans, inflicting severe and lasting ecological harm. [1] Simultaneously, approximately one-third of global food production is lost or wasted, with fruit and vegetable residues representing a substantial share of this underutilized biomass. [2] Tackling these intertwined issues necessitates the development of innovative, sustainable materials aligned with circular economy principles, transforming waste streams into valuable resources. Bioplastics synthesized from agricultural byproducts emerge as a compelling solution, offering biodegradable alternatives to conventional plastics and addressing critical environmental concerns.

## Materials and methods

Pomegranate peels present significant potential as a raw material, since they are rich in natural polymers (such as pectin and cellulose) and bioactive compounds, making them suitable for conversion into biodegradable films. [3]

The raw material underwent a systematic multi-step preparation process. Fresh pomegranate peels were collected and carefully processed to yield a refined biopolymer feedstock. Initially, the peels were air-dried in a dark, well-ventilated environment over several days, effectively reducing moisture while preserving their bioactive compounds. To achieve complete dehydration, the partially dried peels were subsequently oven-dried at approximately 100 °C for 30 minutes, ensuring the removal of residual moisture without compromising the integrity of the natural polymers. Following dehydration, the inner pith was meticulously removed, isolating the polyphenol-rich outer rind. The rind was then finely ground using a blender, producing a powder that served as the foundational material for bioplastic formulation.

The bioplastic material was developed through a series of experimental iterations, involving the combination of pomegranate peel powder with various natural binders and plasticizers. Initial trials employed glycerol as the sole plasticizer, using powder-to-glycerol ratios such as 50:50 and 70:30. While these formulations produced cohesive films, they exhibited excessive softness and brittleness upon drying, reflecting insufficient mechanical strength. To address this, the formulations were refined to include gelling agents, specifically agar-agar and gelatin. In the optimized composition, pomegranate powder was blended with an equal ratio (50:50) of agar-agar and gelatin dissolved in water, along with a smaller amount of glycerol as a co-plasticizer. The mixtures were heated, thoroughly stirred for uniform dispersion, and cast into flat molds before being cured at room temperature. This improved formulation yielded significantly enhanced materials: the bioplastics dried uniformly within a week, forming solid and rigid samples free of cracks.

## Results and discussion

The pomegranate peel-derived bioplastic demonstrated several promising attributes as a sustainable material. Mechanically, the agar/gelatin-enhanced formulation exhibited sufficient rigidity and strength in dry conditions, coupled with notable impact resistance. Samples withstood drops without cracking, indicating durability suitable for applications like small casings or enclosures. However, the material’s high stiffness limits its flexibility, behaving as a brittle polymer that snaps under excessive force. While advantageous for maintaining shape and structure, this property restricts its use in applications requiring elasticity or impact absorption.

The bioplastic's water and thermal behavior further define its scope of use. It showed moderate resistance to brief water exposure, re-hardening after drying, but is neither waterproof nor suitable for prolonged exposure to moisture or heat, as these conditions cause softening or deformation due to the water-soluble nature of its natural binders. Consequently, it is best suited for dry, low-humidity environments and is unsuitable for high-temperature applications.

Aesthetically, the material's smooth matte finish and warm, natural tint provide a visually appealing quality. This aligns with modern eco-design trends that emphasize materials with a visible organic origin, enhancing its potential for environmentally conscious applications.

A primary advantage of the developed bioplastic lies in its biodegradability. Constructed entirely from bio-based components, the material is anticipated to decompose significantly faster than traditional plastics under natural conditions. Preliminary soil burial tests confirmed this potential, with samples progressively breaking down over several weeks. This characteristic ensures that products made from this bioplastic will not contribute to long-term environmental pollution, seamlessly integrating into composting processes or organic waste streams at the end of their lifecycle. Furthermore, the material satisfies essential functional requirements for low-stress applications while presenting a unique sustainable aesthetic and narrative, aligning with modern environmental priorities.

## Conclusions

The findings of this study hold substantial significance for sustainable materials engineering and circular design. They illustrate how agro-food waste, such as pomegranate peels, can be transformed into a functional material, diverting waste from landfills and reducing dependence on fossil-based resources. The successful formulation and prototyping process exemplifies the practical application of circular economy principles: reclaiming waste as feedstock, processing it through low-energy methods, and producing biodegradable materials. This research establishes a foundation for advancing bio-based materials in design, fostering interdisciplinary collaboration between materials science and product development. By integrating biodegradable, waste-derived materials, designers and engineers can drastically lower the ecological footprint of consumer products while conveying a powerful sustainability narrative. The pomegranate peel bioplastic serves as a compelling example of how functionality and environmental responsibility can converge, marking a meaningful step in the pursuit of innovative solutions to plastic pollution.

## References

[1] UN Environment Programme, "Single-use plastics: A roadmap for sustainability," 2018. [Online]. Available: https://www.unep.org/resources/report/single-use-plastics-roadmap-sustainability

[2] FAO, "Global food losses and food waste – Extent, causes and prevention," 2011. [Online]. Available: https://www.fao.org/3/i2697e/i2697e.pdf

[3] M. R. Sharma et al., "Valorization of pomegranate peel waste into bioactive film for food packaging applications," Foods, vol. 10, no. 3, p. 657, 2021

# Valorisation of watermelon peel into an adsorbent for removal of hexavalent chromium

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***keywords:*** *pharmaceuticals; hydrochars; adsorption; synthetic wastewater; hydrothermal conversion.*

## Introduction

The contamination of water resources by hexavalent chromium (Cr(VI))—a highly toxic and mobile pollutant—remains a critical environmental challenge, particularly in industrial regions where inadequate wastewater treatment exacerbates public health risks (Tumolo et al., 2020). Conventional remediation methods, such as chemical reduction and activated carbon adsorption, are often costly or generate secondary waste. Biochar, a carbon-rich material derived from biomass, offers a sustainable alternative due to its porous structure, functional groups, and potential for waste valorisation (Inyang et al., 2015).

This study explores the synthesis of biochar/silicate composites from watermelon peel (WP), an abundant agricultural waste, to enhance Cr(VI) removal. WP is rich in cellulose, pectin, and oxygenated functional groups, which facilitate metal binding (Wang et al., 2022). Hydrothermal carbonisation (HTC) was employed for biochar production, leveraging its efficiency for high-moisture biomass (Funke & Ziegler, 2010). The composites were characterised to assess the impact of silicate modification on adsorption performance, with a focus on pH dependency, isotherm behaviour, and comparative efficacy against unmodified biochar.

By integrating waste valorisation with water treatment, this research aims to advance low-cost, eco-friendly adsorbents while addressing gaps in composite material performance for heavy metal remediation.

## Materials and methods

To synthesize the silica-biochar composites, sodium silicate ($Na_2SiO_3$) and the previously produced biochar were mixed using a pestle and mortar in different weight ratios of $Na_2SiO_3$ to biochar: 3:1, 5:1, and 7:1. In each mixture, 1 gram of biochar was used. The resulting composites were extruded through a 2 mm sieve to ensure consistent particle size and then allowed to dry.

## Characterisation

The surface area and pore size of the adsorbent particles was analysis using BET. The elemental compositions of the samples were analysed using CHNS analyser. The presence of functional groups in the samples are analysed using FTIR.

## Adsorption experiment

A stock solution of hexavalent chromium (1000 ppm) was prepared using potassium dichromate. Test solutions (10–50 ppm) were prepared by diluting the stock solution. To evaluate the adsorption performance of the composites, 50 mL of chromium solution (adjusted to the target pH) was mixed with 100 mg of adsorbent in a container. The mixture was agitated on a shaker for a predetermined contact time. After agitation, 1 mL aliquots were extracted from each container, and the remaining Cr(VI) concentration was determined spectrophotometrically using previously described method (Wu et al. 2023)

The Cr(VI) removal efficiency was the determined from:

$$R_{eff} = 100\frac{C_o - C_e}{C_o} \tag{1}$$

## Results and discussion

The FTIR spectra of bio-adsorbents S1–S5 are presented in Figure 1. This analysis reveals significant inter-sample differences in surface functional groups, which directly influence their potential for chromium adsorption. Among the samples, S2 exhibited the most intense peaks, particularly in the hydroxyl (~3000–3700 cm$^{-1}$) and carbonyl (~1700 cm$^{-1}$) regions, suggesting a higher density of functional groups available for

Cr(VI) interaction. The C-O stretching vibrations (~1000–1300 cm$^{-1}$) in S2 further indicate the presence of oxygenated functional groups, which can enhance adsorption through electrostatic interactions. In contrast, the silica-modified samples (S3, S4, and S5) displayed weaker FTIR signals, likely due to the dilution of active sites by silicate structures dominating the surface. This observation is supported by adsorption experiments, as the silicate framework may reduce pore accessibility for adsorption. Based on the spectral analysis, S2 is the most promising material for Cr(VI) removal.

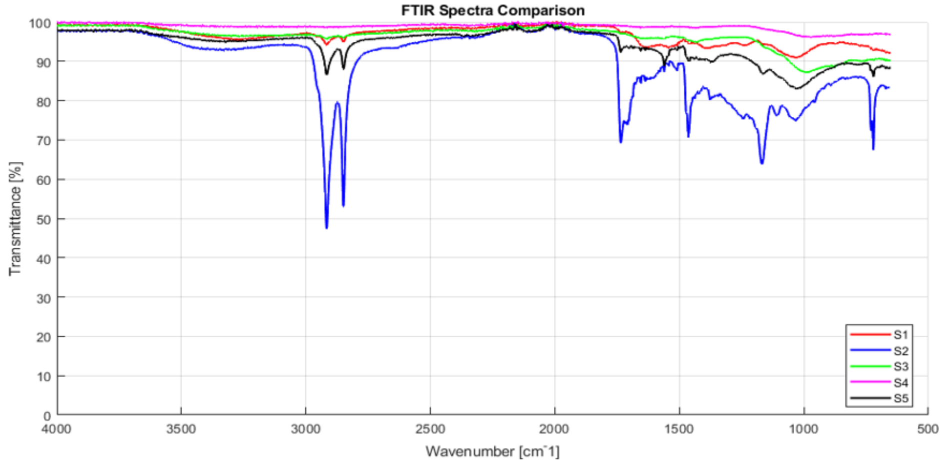

***Figure 1.*** *FTIR spectra for different adsorbent samples.*

The BET analysis results are presented in Table 1, providing insight into the surface characteristics and porosity of the materials. Among the samples yielding valid results, S2 exhibits the highest BET surface area (1.741 m²/g). The Cr(VI) removal efficiencies reported in the final column indicate that incorporating sodium silicate into the composite materials reduces adsorption performance.

***Table 3: BET surfaces area, elemental composition and Cr(VI) removal efficiency at pH of 3 of the samples with different hydro char concentrations.***

| ID: | Hydro Char | Mass % | | | | SA (m$^2$/g) | Pore width (Å) | $R_{eff}$ (%) |
|---|---|---|---|---|---|---|---|---|
| | | C | H | N | O | | | |
| S1 | N/A | 36.64 | 5.72 | 2.45 | 55.19 | - | - | 40 |
| S2 | 1.000 | 41.58 | 7.65 | 1.39 | 49.38 | 1.741 | 60.81 | 58 |
| S3 | 0.250 | 24.42 | 4.12 | 0.73 | 70.73 | 0.634 | 76.14 | 21 |
| S4 | 0.167 | 10.4 | 3.1 | 0.35 | 86.15 | 0.441 | 85.36 | 10 |
| S5 | 0.125 | 10.48 | 3.18 | 0.38 | 85.96 | 0.371 | 68.27 | 16 |

## Conclusions

Biochar produced from hydrothermal conversion of watermelon peels show good potential as an adsorbent for removal of hexavalent chromium. Sodium silicate reduced the removal efficiency of composites.

## References

Funke, A. and Ziegler, F. (2010) ‘Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering’, Biofuels, Bioproducts and Biorefining, 4(2), pp. 160–177. doi:10.1002/bbb.198.

Inyang, M.I. et al. (2015) ‘A review of biochar as a low-cost adsorbent for aqueous heavy metal removal’, Critical Reviews in Environmental Science and Technology, 46(4), pp. 406–433. doi:10.1080/10643389.2015.1096880 .

Wang, Q. et al. (2022) ‘Utilization of low-cost watermelon rind for efficient removal of CD(II) from Aqueous Solutions: Adsorption performance and mechanism elucidation’, Chemical Engineering Journal Advances, 12, p. 100393. doi:10.1016/j.ceja.2022.100393

Wu, J., Annath, H., Chen, H., Mangwandi, C. (2023) Upcycling tea waste particles into magnetic adsorbent materials for removal of Cr(VI) from aqueous solutions Particuology, 80, pp. 115-126. doi: 10.1016/j.partic.2022.11.017

# Integrated Approach for Sustainable Protein Production: Utilizing Agricultural Waste for Black Soldier Fly Rearing and Feed Applications

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***keywords:*** black soldier fly (*Hermetia illucens*), waste-to-insect-based protein, Sustainable aquafeed, Circular economy

## Introduction

This study explores an integrated solution within the framework of circular economy, targeting a small-scale agricultural region such as the Upper Galilee in Israel. The approach leverages local agricultural waste streams to produce high-value alternative protein, thereby closing resource loops and reducing environmental burdens. Central to this strategy is the use of the Black Soldier Fly (*Hermetia illucens*, BSF), whose larvae can efficiently convert diverse organic waste into biomass rich in protein and fat. The resulting BSF meal holds promise as a sustainable protein alternative for aquaculture and potentially for human consumption.

The main objectives of this research were therefore to: (i) characterize the regional agricultural waste resources available for insect rearing; (ii) develop and optimize BSF feeding protocols and protein extraction processes; (iii) evaluate the nutritional performance and feasibility of using BSF meal to partially or fully replace conventional protein sources in rodent and trout diets; and (iv) establish techno-economic models to assess the viability of decentralized BSF production systems in the Galilee.

## Materials and methods

The study encompassed several major research components:

1. Characterization of agricultural waste: A comprehensive survey was conducted to identify and quantify agricultural waste streams in Israel, with a particular emphasis on the Upper Galilee. This effort combined data from Ministry of Agriculture databases with information gathered through interviews with crop advisors, packing house managers, and food processing facility operators. Identified waste streams were further characterized by their nutritional, chemical, and physical properties based on literature data and existing analytical resources.
2. Development of BSF feeding protocols and diet optimization: Data from the waste survey, together with insights from preliminary modeling, were used to formulate feeding protocols for *Hermetia illucens* (Black Soldier Fly, BSF) larvae. Laboratory-scale experiments (1 kg) were carried out to evaluate the effects of various diet compositions on larval growth and biomass yield. Subsequently, medium-scale rearing trials (10 kg) were performed to assess scalability and to conduct preliminary economic feasibility analyses.
3. Protein extraction and meal processing optimization: Parallel to the feeding experiments, processes for extracting and optimizing protein content from BSF larvae at different developmental stages were developed. This included the separation of the larval cuticle and the use of hexane for oil extraction to improve the protein-to-fat ratio in the resulting meal. Protocols were refined to maximize protein quality and yield.
4. Animal feeding trials (rodents and trout): Rodent feeding trials were designed to evaluate the digestibility and nutritional adequacy of BSF meal, both as a partial and complete replacement for conventional protein sources (e.g., casein). Pellets tailored for rodent diets were produced and tested for growth performance and health indicators. In addition, feeding trials were carried out on trout at two growth stages, 16 g (juvenile) and 100 g (fattening), to investigate the feasibility of substituting fishmeal with BSF meal. These trials examined growth rates, feed conversion efficiency, and potential health benefits across both developmental stages.
5. Modeling and economic assessment: A mathematical model was constructed to integrate waste

composition data with BSF growth responses, enabling the formulation of optimized waste-based diets. This model was later enhanced using machine learning techniques (Random Forest) to improve predictive accuracy. Finally, a detailed economic analysis was conducted—including Excel-based sensitivity analyses—to evaluate the viability of establishing BSF facilities that utilize regional agricultural waste, considering various operational scales, automation scenarios, and potential policy incentives.

**Results and discussion**

A comprehensive database was established, cataloging all types of agricultural waste in Israel with particular emphasis on the Galilee region. This database revealed an annual production of approximately 669,964 tons of agricultural waste, which, with appropriate feed blending, has the potential to yield around 23,449 tons of BSF-protein per year. Building on this foundation, a mathematical model was developed to design optimal BSF diets from various waste combinations. This model was later refined using machine learning techniques (Random Forest), achieving prediction accuracy with an MSE of 6.7, thereby enhancing its ability to forecast protein yields.

Feeding protocols based on these formulations were implemented, successfully enabling the production of sufficient quantities of larvae to prepare pellets for both rodent and trout feeding trials. Further optimization efforts demonstrated that the most advantageous BSF meal, characterized by a high protein and low-fat content, was obtained from 6th instar larvae following cuticle separation and hexane oil extraction.

Digestibility experiments in rodents revealed that BSF based meal derived from 5th and 6th instar larvae met essential amino acid requirements suitable for both rodents and humans. However, due to the high fiber content originating from the larval cuticle, these meals could not fully replace dietary protein but were capable of substituting up to 37% of the protein in the diet. Notably, when the cuticle content in the 6th instar meal was reduced, it became possible to completely replace the casein protein found in control diets.

Feeding trials in trout demonstrated that BSF meal could successfully replace up to 100% of fishmeal in small trout diets and approximately 50% in large trout diets, achieving comparable growth performance. Nonetheless, given the current production cost of 1250 NIS per ton of BSF protein, full replacement of fishmeal is not yet economically feasible. Interestingly, trends observed during these trials suggested that BSF meal might offer additional health benefits, such as reduced mortality associated with *Streptococcus* infections, warranting further investigation.

Finally, economic analyses performed through Excel-based sensitivity models indicated that on-farm BSF rearing on local agricultural waste becomes profitable only if farmers proceed beyond larval rearing to actual protein production. With improved automation, efficient spatial organization of the facilities, and optimal time management, such operations could achieve profitability even in the first year. Moreover, reductions in production costs, governmental support, or revenues derived from environmental benefits such as carbon credits would significantly enhance the attractiveness and feasibility of this venture.

**Conclusions**

This study provides a foundation for small-scale agricultural industries based on regional waste utilization, requiring local cooperation and public investment. It offers a path to reduce environmental impacts and, as costs decrease, could eventually replace fishmeal in trout farming and serve as an alternative protein for humans. All datasets, economic models, and protocols are publicly available.

***Acknowledgements:*** This study was supported by the Chief Scientist of the Israel Ministry of Agriculture and Rural Development.

# Session 3: Wastewater management

# "Microalgal Treatment of AnMBR Effluent: A Low-Energy Approach to Nutrient Reduction"

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***keywords:*** *AnMBR; microalgae bioreactors; nutrient reduction; low energy consumption; circular economy*

## Introduction

Anaerobic membrane bioreactors (AnMBRs) are gaining interest in the treatment of municipal wastewater as an alternative to conventional systems due to their ability to produce high-quality effluent while simultaneously recovering energy through methane production (Ozgun et al., 2013). Despite their advantages, such as the effective removal of suspended solids and pathogens (Azis et al., 2017), and the generation of an effluent with extremely low levels of biodegradable organic matter, AnMBRs yield effluent with elevated concentrations of nutrients, particularly nitrogen and phosphorus. These nutrients must be further treated prior to discharge or reuse, as their presence can lead to environmental issues such as eutrophication.

In a typical AnMBR system treating municipal wastewater, effluent may contain orthophosphate concentrations of approximately 5–7 mg/L, total nitrogen (TN) levels ranging from 50 to 70 mg/L, and COD and $BOD_5$ concentrations of 10–25 mg/L and 2–5 mg/L, respectively. These concentrations, especially of nutrients, exceed common environmental discharge standards and pose a significant threat to aquatic ecosystems if released without additional treatment (Kanafin et al., 2021).

Microalgae-based treatment systems have shown considerable potential as a sustainable post-treatment solution for nutrient-rich effluents. Microalgae possess the capacity to assimilate inorganic nitrogen and phosphorus directly from wastewater, incorporating them into their biomass. This biological uptake not only reduces the nutrient load but also produces valuable algal biomass, which can be utilized for biofuel production, fertilizers, animal feed, or even biogas enhancement through recycling into the anaerobic digester (Ruiz-Martinez et al., 2012).

## Materials and methods

When employed for AnMBR effluent post-treatment, microalgae are typically cultivated in photobioreactors or open ponds under controlled light and temperature conditions. The low $BOD_5$ and COD levels of the AnMBR effluent create an ideal environment for algal growth, minimizing competition from heterotrophic bacteria and reducing oxygen demand. Moreover, the clarity of the effluent enhances light penetration, which is essential for efficient photosynthesis.
For this study, two bioreactors with working volume of 1000 mL were operated under controlled light (4800 lumen) and temperature conditions (25°C). One reactor was supplied with a synthetic nutrient substrate, while the other received the effluent from an AnMBR system as the growth substrate. The degradation of organic content, nitrogen, and phosphorus was investigated, along with the growth performance of microalgae.

## Results and discussion

The reduction of orthophosphate ($P\text{-}PO_4^{3-}$), ammonium ($N\text{-}NH_4^+$), was achieved under semi-continuous cultivation conditions in the bioreactors. The respective removal efficiencies were 80% for $P–PO_4^{3-}$, and 65% for $NH_4^+$. Additionally, the dry biomass concentration of microalgae increased by 406.7% over the course of the study (ca 3 months), indicating substantial growth under the given operational conditions.

## Conclusions

The findings of this study indicate that microalgae are effective in reducing nutrient concentrations—particularly nitrogen and phosphorus—in the effluent of anaerobic membrane bioreactors (AnMBRs). The nutrient-rich composition of the AnMBR effluent provided favorable conditions for microalgal growth, highlighting its potential as a suitable medium for post-treatment applications. In addition to nutrient removal, the system facilitates the generation of valuable algal biomass. Overall, microalgae-based post-treatment systems represent a sustainable and energy-efficient approach for improving the quality of AnMBR effluents.

## References

Azis, K., Vardalachakis, C., Ntougias, S., Melidis, P., 2017. Microbiological and physicochemical evaluation of the effluent quality in a membrane bioreactor system to meet the legislative limits for wastewater reuse. Water Sci. Technol. 76, 1796–1804. https://doi.org/10.2166/wst.2017.364

Kanafin, Y.N., Kanafina, D., Malamis, S., Katsou, E., Inglezakis, V.J., Poulopoulos, S.G., Arkhangelsky, E., 2021. Anaerobic Membrane Bioreactors for Municipal Wastewater Treatment: A Literature Review. Membranes 11, 967. https://doi.org/10.3390/membranes11120967

Ozgun, H., Dereli, R.K., Ersahin, M.E., Kinaci, C., Spanjers, H., van Lier, J.B., 2013. A review of anaerobic membrane bioreactors for municipal wastewater treatment: Integration options, limitations and expectations. Sep. Purif. Technol. 118, 89–104. https://doi.org/10.1016/j.seppur.2013.06.036

Ruiz-Martinez, A., Martin Garcia, N., Romero, I., Seco, A., Ferrer, J., 2012. Microalgae cultivation in wastewater: Nutrient removal from anaerobic membrane bioreactor effluent. Bioresour. Technol., Advances in Biological Waste Treatment and Bioconversion Technologies 126, 247–253. https://doi.org/10.1016/j.biortech.2012.09.022

# Circular economy strategy in wastewater treatment: The example of Limassol District Local Government Organisation Sewage Treatment Plant in Moni, Cyprus

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***keywords:*** *Limassol, sewage, biological treatment plants, circular economy*

The implementation of a circular economy strategy within wastewater treatment systems has emerged as a critical approach for enhancing sustainability and resource efficiency. In this work a comprehensive analysis of the circular economy framework applied to the Limassol District Local Government Organisation Sewage Treatment Plant (STP) in Moni, Cyprus is presented together with their plans for the future.

By focusing on this case study, we explore the integration of innovative technologies and processes that promote the recovery and reuse of resources, such as energy and water within the STP. The study highlights the current operational practices, challenges encountered, and the measures undertaken to transition towards a more sustainable operational model. Additionally, the possibility of applying new technologies in view of achieving nutrients extract from wastewater is examined as part of a future action plan.

The findings underscore the potential for enhanced resilience in local governance and the promotion of sustainable urban development through the adoption of circular economy principles in wastewater management. Overall, this work contributes to the growing body of knowledge on best practices and innovative solutions for sustainable wastewater treatment in the context of circular economy initiatives. The findings suggest that establishing a circular economy within wastewater treatment can serve as a model for other municipalities striving for environmental sustainability and resilience in the face of growing water scarcity challenges in Cyprus and the broader Eastern Mediterranean region.

# Integrating Greywater Treatment and Green Façade Creation Using Vertical Flow Constructed Wetlands

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***keywords:*** *ornamental plants; wastewater; organic matter; porous media; vegetation*

## Introduction

By 2050, 68% of the global population will live in urban areas, with the Mediterranean Basin experiencing rapid urbanization driven by environmental changes, tourism, and migration (UN, 2018). This growth will increase water demand, wastewater generation, and exacerbate the urban heat island effect (Rehan et al., 2016). Nature-based solutions (NBS), such as greywater recycling through low-energy constructed wetlands, offer sustainable strategies for water reuse and urban cooling (Boyjoo et al., 2013). In this context, the present study examines the integration of greywater treatment into vertical green systems as a cost-effective solution. By combining ornamental climbing plants with constructed wetlands, it is possible to develop green façades that serve as on-site greywater treatment systems. These façades use greywater to meet the plants' irrigation needs while producing reclaimed water for non-potable indoor and outdoor uses.

## Materials and methods

Eight vertical flow constructed wetlands (VFCWs) were installed at the University of the Aegean, Lesvos island, Greece. Synthetic light greywater was prepared and dosed every four hours, while three plant species, *Trachelospermum jasminoides*, *Lonicera japonica*, and *Callistemon laevis,* were tested alongside unplanted controls. The VFCWs consisted of sand or vermiculite media in layered systems and operated over two years. Plant growth, chlorophyll content, evapotranspiration, hydraulic conductivity, and removal of physicochemical pollutants, surfactants, pathogens, and organic matter were monitored.

## Results and discussion

All ornamental and climbing plants adapted well to the VFCWs, showing no visible stress symptoms despite receiving approximately 203 mm of greywater per day over a period of one and a half years (Figure 1). Statistical analysis revealed that systems with sand substrate achieved significantly higher removal rates ($p < 0.05$) for turbidity, TSS, and COD compared to those with vermiculite, across all three plant species as well as the unplanted controls.

***Figure 1.*** *Examined VFCWs after two years of operation receiving greywater. From left to right: T. jasminoides; L. japonica; C. laevis*

Moreover, $BOD_5$ removal rates were significantly higher in *Lonicera japonica* and *Callistemon laevis* systems with sand substrate (94 ± 8 % and 91 ± 7 %, respectively) compared to vermiculite (84 ± 12 % and 80 ± 15 %). The mean removal percentage of anionic surfactants in the examined VFCWs ranged from 82 % to 99 %. Statistical analysis showed that all three plant species had significantly higher daily evapotranspiration values ($p < 0.05$) than the corresponding unplanted systems, regardless of substrate type. Additionally, all planted systems with sand exhibited significantly higher hydraulic conductivities ($p < 0.05$) compared to the unvegetated controls. After two years of operation, hydraulic conductivity decreased by 16 % in VFCWs planted with *Trachelospermum jasminoides*, whereas the unplanted sand-filled system showed a 64 % reduction.

## Conclusions

The aim of this study was to evaluate the performance of VFCWs in treating greywater after two years of operation. Results showed that sand-based systems outperformed those with vermiculite across all studied parameters. Over the two-year period, removal rates for most parameters were significantly higher in sand systems, with some improvements also observed in vermiculite systems. Notably, *Trachelospermum jasminoides* and *Lonicera japonica* in sand substrates outperformed their unplanted counterparts in turbidity and TSS removal, highlighting the beneficial role of plants. Planted sand systems also exhibited significantly higher hydraulic conductivity compared to unplanted ones, indicating reduced clogging. Although planted sand systems experienced greater water loss, *Callistemon laevis* showed significantly lower losses than the other two species. Overall, VFCWs planted with ornamental climbing plants not only enhance the aesthetic appeal of constructed wetlands for greywater treatment but also improve system performance.

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## References

Boyjoo, Y., Pareecj, V.K., Ang, M. 2013. A review of greywater characteristics and treatment processes. Water Sci Technol. 67, 1403-1424.

Rehan, R.M., 2016. Cool city as a sustainable example of heat island management case study of the coolest city in the world. HBRC J. 12, 191–204.

U.N. 2018. World Water Assessment Programme/UN-Water The United Nations World Water Development Report 2018: Nature-based Solutions for Water UNESCO, Paris

# An Appraisal for a Sustainable Process Design and Operation for Leachate Treatment

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***keywords:*** *landfill; plant-wide simulation; membrane systems; process design; operation.*

## Introduction

Treatment of landfill leachate has long been a challenge due to its distinct characteristics when compared to the municipal wastewater, with its complex nature containing recalcitrant organics, metals, and xenobiotics as well as high concentrations of organic matter and ammonia. Biological processes are often preferred for carbon and nitrogen removal. However, biological treatment alone fails to satisfy the discharge standards and therefore are mostly coupled with membrane separation technologies. (Teng et al., 2021). Treatment of landfill leachate is an energy-intensive process as the high organic matter and nitrogen content of landfill leachate, resulting a high operational cost for biological processes as well as for membrane operations. Therefore, it is important to have a thorough understanding of the composition, variations, and degradation characteristics of landfill leachate for a sustainable design and to implement effective treatment methods.

This study aims to bring an evaluation on alternative design and operational conditions for treatment of landfill leachate with simulations for the different scenarios which can provide a guidance for an efficient and sustainable design and operation of LLTPs.

## Materials and methods

The landfill site is located in Istanbul, Turkey, and has been in operation since 2008 with a capacity to of 2500 $m^3.day^{-1}$. The carousel type bioreactor for biological nitrogen removal is operated as a pre-denitrification system with extremely high internal recirculation. After biological processes, an Ultrafiltration (UF) membrane for solids separation and a Nanofiltration (NF) for color, odor, hardness and inert COD removal, were installed. COD fractions, bioprocess kinetics were determined previously (Doğruel et al., 2023, Güven et al., 2025). Simulation studies were carried out with the Sumo22.1 program of Dynamita company. A whole plant model (Sumo2) was used to simulate the effluent quality (COD, TN, TP). The LLTP was introduced to Sumo22 program with the configuration illustrated in Figure. 1. Operational scenarios were tested for different dissolved oxygen concentrations (DO), recirculation rate (RR) and sludge retention time (SRT) and temperature (T).

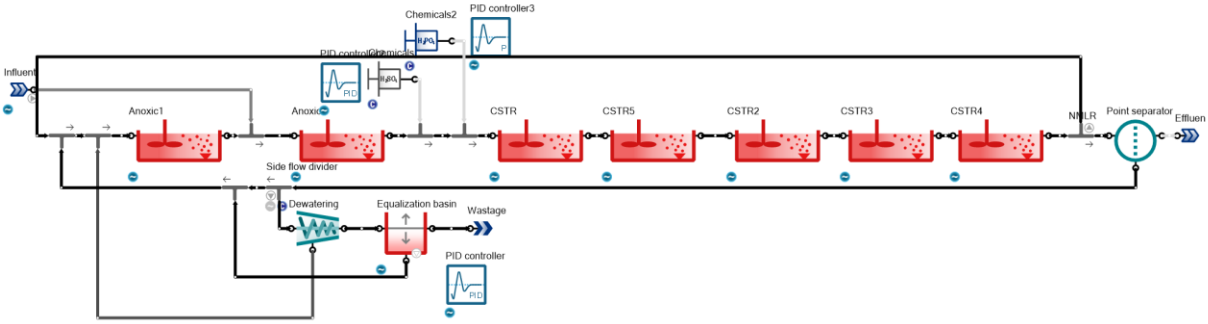

***Figure 1.*** *LLTP configuration in SUMO v. 22.1.*

## Results and discussion

Bioprocess kinetics were determined through a series of batch respirometric tests and resolved with model studies. Figure 2 presents the OUR profiles obtained from respirometric analyses with raw leachate.

Leachate treatment plant data, belonging for about a year, were used in the simulations considering the biomass concentration, sludge disposal, temperature, pH, pollution loads and air supply. Aerobic Ammonia Oxidizing Bacteria (AOB), Nitrite Oxidizing Bacteria (NOB), Ordinary Heterotrophic Organisms (OHO) and Carbon Storing Organisms (CASTO) were taken into consideration and related parameters were previously estimated (Güven et al., 2025).

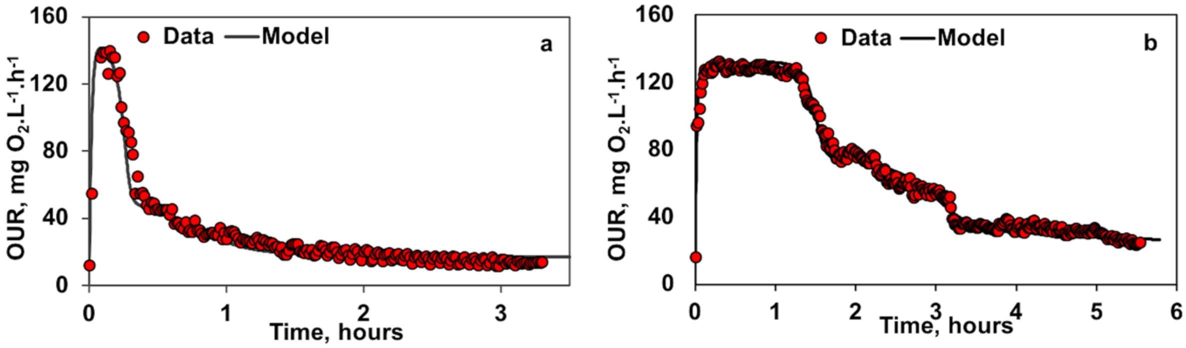

***Figure 2.*** *OUR profiles obtained from respirometric analyses with raw leachate; (a) 25°C, (b) 35°C.*

Several dynamic simulations were carried out for different air supply modes, recirculation ratios, temperature and SRT values to achieve a cost-efficient process design and operation. Simulation results were evaluated in comparison to existing plant operational conditions. The two major parameters that are correlated with the nitrogen removal: aeration regime/oxygen concentration in the reactor, and the temperature increase. Contribution of MLSS dynamics and COD load can be taken into account, as well.

## Conclusions

The COD fractionation of leachate is very important for the selection, design and operation of leachate treatment. Biodegradation kinetics of organic matter directly influences the efficiency of denitrification as well as the carbon storage metabolism.

A very high biomass concentration is required for an efficient nitrogen removal. The temperature and oxygen supply in the reactor are the other important factors which determine the nitrogen content in the effluent.

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## References

Teng, C., Zhou, K., Peng, C., Chen, W., 2021. Characterization and treatment of landfill leachate: A review. *Water Res*. 203, 117525. https://doi.org/10.1016/j.watres.2021.117525.

Doğruel, S., Kaya, B., Soylu, D., Çokgör, E., Baran, A., Sözen, S., Orhon, D., 2023. Analysis of particle size distribution of organic carbon for landfill leachate—implications for sustainable treatment. *J. Chem. Technol. Biotechnol.* 98, 2981–2991. https://doi.org/10.1002/jctb.7503.

Güven, D., Çokgör, E., Zengin, G.E., Kaya, B., Ozyildiz, G., Soylu, D., Çoker, F., Yağcı, N., Insel, G., Takacs, I., Sözen, S., Orhon, D. Unveiling the bioprocess kinetics of leachate treatment through plant-wide dynamic simulation supported by experimental validation, *Waste Manag.,* Under review.

# Removal of Non-Steroidal Anti-Inflammatory Micropollutants and Nitrification in Hybrid Systems Operating at Low Sludge Age

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***keywords:*** *moving bed biofilm reactors; wastewater; biological treatment; nitrification.*

## Introduction

Hybrid systems, which have become an interesting alternative in wastewater treatment, are also included in many studies in micropollutant removal studies (Godzieba et al., 2022; Ødegaard et al., 2014). Moving bed biofilm reactors (MBBR) are one of the most preferred processes among hybrid systems that combine the advantages of activated sludge and biofilm processes and eliminate the disadvantages of these systems.

In this context, laboratory-scale sequential batch hybrid reactors were operated for the removal of diclofenac, ibuprofen, naproxen, ketoprofen, indomethacin and mefenamic acid, which were selected among the non-steroidal anti-inflammatory drugs (NSAIDs). NSAIDs are the most commonly detected drug groups in wastewater treatment plants, based on the concentration levels determined in samples taken from an advanced biological wastewater treatment plant located in Istanbul. Thus, it was aimed to see the effect of both the aerobic treatability and the performance of the hybrid reactors in nutrient removal and micropollutant removal in case of long-term feeding of micropollutants to the hybrid reactor.

## Materials and methods

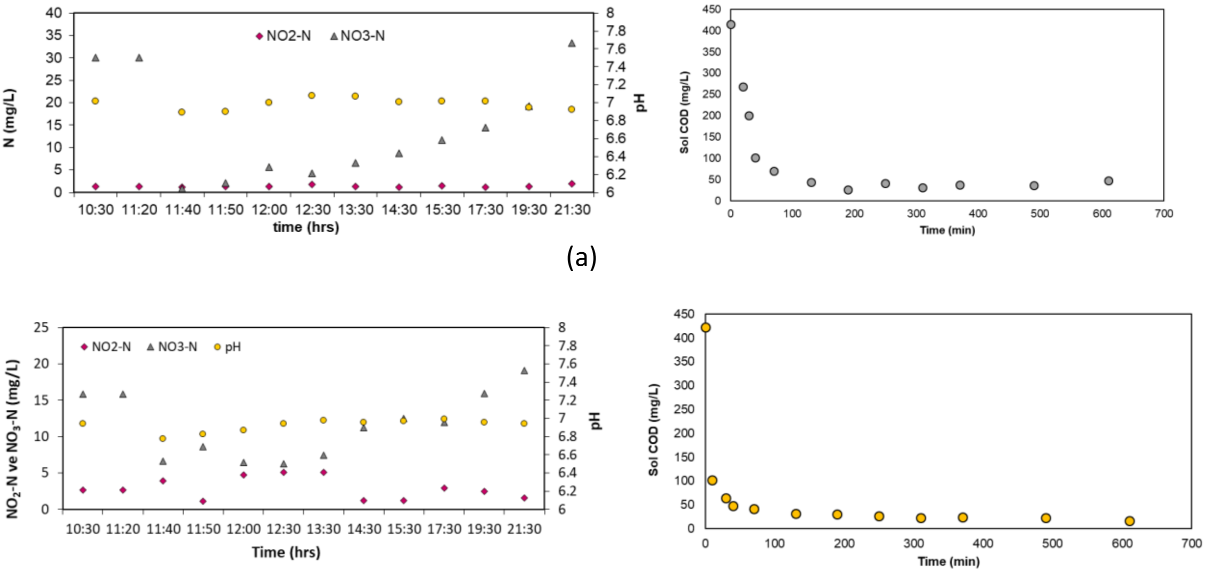
In the operation of the reactors, the cycle time was determined as 12 hours for two cycles per day. During each cycle, the reaction phase was stirred continuously under aerobic conditions for 630 minutes. Feeding was done within the first 30 minutes of the reaction phase. At the end of the reaction phase, before the settling phase started, excess sludge was withdrawn from the system while the reactor was in mixing stage. When the reaction phase was completely finished, settling phase, which was set as 60 minutes, started. At the end of this period, the supernatant was discharged, which was set for 20 minutes. After discharging the supernatant, 8 L of working volume was decreased to initial reactor volume of 4 L at the end of the cycle.

Micropollutant measurements were performed by Liquid Chromatograph-Tandem Mass Spectroscopy (LC/MS-MS), which provides high precision separation and analytical level selectivity. Since the selected micropollutants are expected to be at ng/L levels in most of the samples to be measured in this study and the measurement sensitivity of the LC-MS/MS instrument alone is insufficient for these levels, solid phase extraction (SPE) was performed by applying a pretreatment prior to measurement and the samples were concentrated. In addition, pH, suspended solids (TSS), volatile suspended solids (VSS), dissolved COD, ammonium, nitrite and nitrate parameters were monitored regularly throughout the operation of the reactors to monitor reactor performance.

Two reactors, a control hybrid reactor and a micro-pollutant hybrid reactor were operated for 360 and 167 days, respectively with a sludge age of 5 days. The NSAIDs concentrations added to the micro-pollutant reactor through the feed were set as 10 μg/L for ibuprofen and naproxen and 1 μg/L for diclofenac, ketoprofen, indomethacin and mefenamic acid to reflect the micropollutant concentrations observed in domestic wastewater.

## Results and discussion

The addition of micro-pollutants with anti-inflammatory properties increased the values of SS and VSS in the hybrid reactor and there was also an increase in the amount of solid matter deposited on the carriers. While COD concentrations in the effluent of the hybrid reactors did not show a significant difference, a slight increase in COD removal rate was observed after the addition of NSAIDs. In both the control hybrid reactor and the micro-pollutant hybrid reactor, nitrification was not fully achieved, ammonia accumulation was observed (**Figure 1**). With these evaluations, it was observed that NSAIDs had no chronic inhibition effect on the biodegradation of organic matter in the hybrid reactor and on the biomass in the nitrification process. In micropollutant measurements, removal efficiencies above 90% were obtained for naproxen, mefenamic acid and indomethacin. Diclofenac, ibuprofen and ketoprofen showed lower removal efficiencies. When the results were compared with the reported studies, it was observed that the hybrid reactor showed a better removal efficiency performance at low sludge age and partial nitrification compared to activated sludge reactors at higher sludge ages.



(a)

(b)

***Figure 1.*** *pH, ammonia, nitrate, nitrite nitrogen and COD values in (a) control (b) micropollutant added hybrid systems.*

## Conclusions

Assessment of the NSAIDs removal in hybrid systems revealed that long term exposure to micro-pollutants did not have chronic inhibition effect on carbon removal as well as nitrification processes. Moreover, partial nitrification could be achieved at a sludge of 5 days in hybrid systems which could be only achieved at higher sludge ages in conventional systems. These findings indicate that integration of conventional systems with hybrid systems is a promising approach both for removal of micro-pollutants and nutrients.

***Acknowledgements:*** This study was supported by TÜBİTAK 1001 Project No: 117Y087 and ITU BAP Project No: MYL-2020-42694. We would like to express our deepest condolences for our beloved friend and colleague Prof. Didem Okutman Tas, whose exquisite work in this study is deeply appreciated. Without her precious contribution, this study would not have been possible. Her absence is a grave loss for our academia, but her dedication to science and her students will continue to inspire us all. May she rest in peace.

## References

Godzieba M., Zubrowska-Sudol M., Walczak J., Ciesielski S., 2022. Development of microbial communities in biofilm and activated sludge in a hybrid reactor. Scientific Reports 12(1):12558.

Ødegaard H., Christensson M., Sørensen K., 2014. Hybrid systems. In: Jenkins D, Wanner J. Activated Sludge - 100 years and counting. IWA Publishing, London, UK.

# Quantitative Evaluation of Nitrification Inhibition in Petrochemical Wastewater

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***Keywords:** nitrogen removal, nitrification; growth kinetics, BTEX.*

## Introduction

Measurement of nitrification kinetics in petrochemical wastewater are critical for evaluating the performance and viability of biological nitrogen removal processes in industrial wastewater treatment. The petrochemical industry generates large volumes of complex effluents characterized by high chemical oxygen demand (COD), variable pH, elevated TDS, and the presence of various inhibitory compounds (Eryavuz, 2003). These characteristics pose significant challenges to conventional biological treatment processes, particularly nitrification, which is sensitive to a wide range of environmental and chemical stressors (Dold, 1989).

Petrochemical wastewater typically exhibits a high organic load, with COD values ranging from 2,000 to over 10,000 mg/L and TKN ranging from 50-700 mgN/L depending on the specific production processes and the degree of process integration. The wastewater composition varies widely and includes hydrocarbons, solvents, surfactants, phenolic compounds, and suspended solids. Among the most critical contaminants for biological treatment are the BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), which are common in petrochemical effluents. These monoaromatic hydrocarbons are highly toxic to nitrifying bacteria, particularly the ammonia-oxidizing bacteria (AOB), and can significantly inhibit the rate of nitrification even at low concentrations (e.g., <10 mg/L for benzene).

The inhibitory effects of BTEX and similar xenobiotics are due to their hydrophobicity and their ability to disrupt microbial cell membranes and enzyme systems. These compounds are not only acutely toxic but also persistent, especially under aerobic conditions, where their biodegradation may be slow or incomplete. Their presence necessitates either advanced pretreatment methods or process adaptations, such as bioaugmentation or use of specialized microbial consortia, to maintain effective nitrification.

## Materials and methods

The net growth rate is obtained by subtracting the decay rate from the maximum growth rate of nitrifying bacteria. An insufficiently selected aerobic volume can cause a municipal wastewater treatment plant to fail in nitrogen removal. The net growth rate (can be measured under laboratory conditions, and experimental results can be obtained within 5–20 days when acclimated activated sludge is used. The effluent of the wastewater treatment plant is aerated until a constant temperature is reached in a water-jacketed aerobic reactor. Then, a low concentration of biomass (100-150 mg/L) is added, followed by an appropriate ammonium source, such as $NH_4Cl$. At least two samples are taken per day to monitor oxidized nitrogen over time. In batch reactors, the initial nitrogen concentration is adjusted to approximately 20 mg N/L. Bicarbonate were added at the beginning of the experiment to provide sufficient alkalinity (Melcer et al., 2003).

## Results and discussion

The table below summarizes the nitrification kinetics determined under different experimental conditions in this study for the petrochemical industry. In Figure 1, simulation profiles representing microbial growth was fitted to the experimental $NO_x$ data, and the calibration was performed using the Simplex Algorithm in MS Microsoft Excel. The results show that the net growth rate ($\mu_A$-$b_A$) is approximately 40% of that typically observed in municipal wastewater (Tchobanoglous et al., 2003; Melcer et al., 2003) applications. This suggests that inhibitory substances present in industrial wastewater may have a suppressive effect on nitrification kinetics.

***Table 1.*** *Simulation results for nitrification kinetics*

| Parameter | Unit | Sample 1 | Sample 2 | Municipal WW |
|---|---|---|---|---|
| **Growth Rate, $\mu_A$** | day$^{-1}$ | 0.37 | 0.36 | 0.90 |
| **Decay Rate, $b_A$** | day$^{-1}$ | 0.10 | 0.10 | 0.17 |

The aerobic sludge age determination should be considered according to the actual measurements carried out for petrochemical wastewaters. The design rules utilized for municipal wastewater in this case will not be applicable for refineries. This study will also investigate the COD fractionation within the context of appropriate process configuration for nitrogen removal from refinery wastewaters.

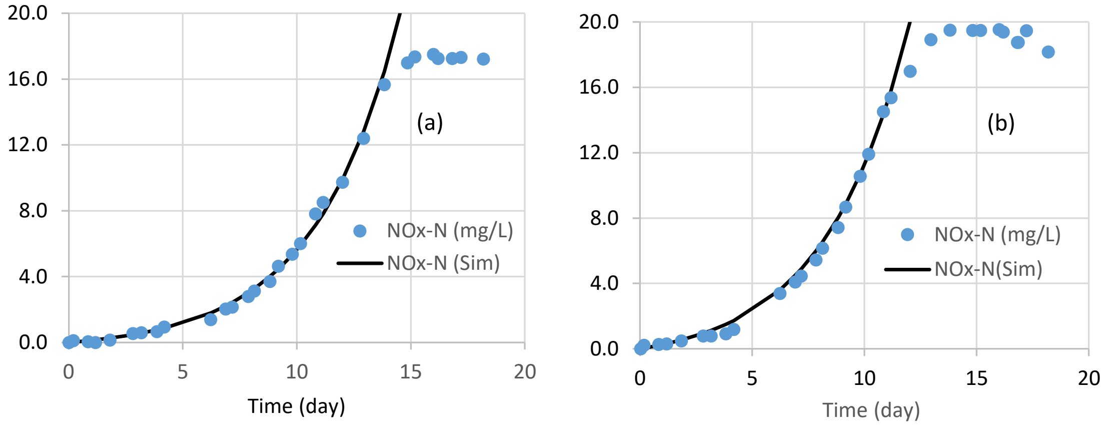

***Figure 1.*** *Batch experimental and simulated NO$_x$ profiles for petrochemical wastewater (2 sets of experiment)*

## Conclusions

Accurate nitrification rate measurements and COD fractionation analysis are essential for designing and optimizing biological treatment systems capable of withstanding the specific challenges posed by petrochemical effluents. To enhance nitrification in petrochemical wastewater treatment, integrated approaches are increasingly being explored, such as combining physical-chemical pretreatment (e.g., air stripping, adsorption, or ozonation) with biological treatment in sequencing batch reactors (SBRs), membrane bioreactors (MBRs), or moving bed biofilm reactors (MBBRs) to guarantee the stability of nitrification process.

## References

Dold PL. 1989. Current practice for treatment of petroleum refinery for wastewater and toxics removal, Water Poll. Res. Jour., 24(3), 363-390.

Eryavuz P. 2003. Organic carbon and nitrogen removal in petrol refinery wastewaters, MSc thesis, ITU Environmental Engineering Deptaerment, Istanbul, Türkiye.

Melcer H., Dold P., Jones R.M., Takács I., Stensel H.D., Wilson A.W., Sun P., Bury S. 2003. Methods for wastewater characterization in activated sludge modeling. Technical Report, Water Environment Research Federation, Alexandria, USA.

Tchobanoglous G., Burton F. and Stensel D. 2003. Metcalf and Eddy: Wastewater Engineering, Treatment and Reuse, 4th ed.; McGraw Hill: New York, NY, USA.

# Session 4: Solid waste management and greenhouse gas monitoring

# Dewatering of Landfill Leachate by Combined Flocculation with Geotextile Filtration

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***keywords:*** *geomembrane; filtration; solids; leachate; waste.*

## Introduction

Geotextile filtration is an effective method for dewatering contaminated sediments with high water content. It offers advantages such as rapid disposal of large waste volumes, ease of construction, and convenient placement, and has quickly become the preferred in-situ technique in recent years (Khachan et al., 2017; Stoltz et al., 2019).

The aim of this study was to dewater the landfill leachate and biogas waste in the waste pond located in a municipal Solid Waste Landfill in Türkiye by using a geotextile tube and to carry out experimental studies to determine the most suitable conditions for the removal of the solid part with the geotextile tube and the solid content in the liquid phase formed after dewatering by using a geotextile tube is less than 2%.

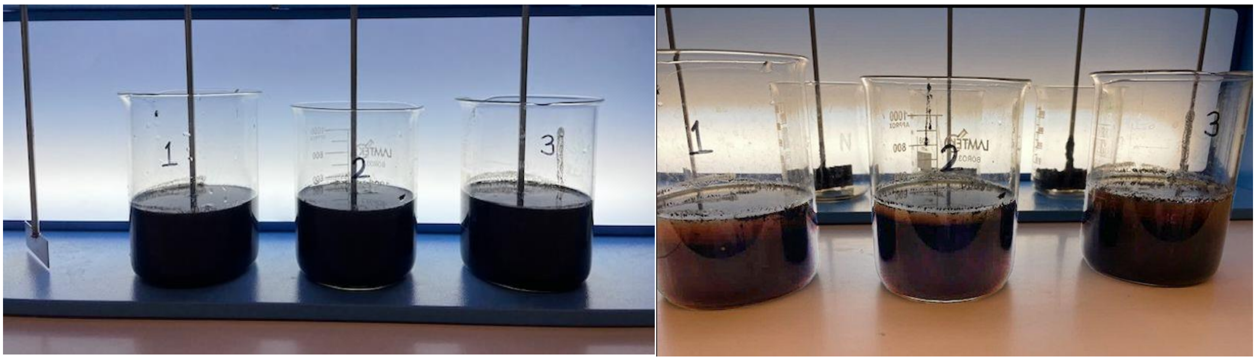
## Materials and methods

There different cationic polymers were used in the experimental studies. Studies were carried out using a jar tester (Velp Scientifica FC6S) without pH adjustment. In the experiments, polymer addition was followed by rapid mixing at 120 rpm for 2 minutes and flocculation at 60 rpm for 15 minutes and settling for 30 minutes, respectively. The geotextile tube used in the studies is ACETube brand and has a tensile strength of 100x100 kN/m and a pore size of 0.425 mm.

## Results and discussion

This study included the characterization of samples collected at different times and depths, focusing on solids content, dewaterability, solid-liquid separation using geotextile tubes following polymer addition, and recommendations for the most suitable operating conditions. The average total solids and volatile solids values of the sample taken from the waste pond were measured as 6.19% and 3.41%, respectively. The pH value was 8.53.

Experimental studies were carried out using three different dosages of cationic polymer ranging from 0.1-0.2 g/500 mL (**Figure 1**). In all sets, it was found that the high solids content was retained on the geotextile tube (12 - 15%) (**Figure 2**). After filtering with geotextile tube, it was observed that the concentration of the SS in the underlying liquid phase was in the range of 1210-1600 mg /L and the COD concentration was in the range of 3325 - 3400 mg/L for all experimental sets examined (**Table 1**).



***(a)*** ***(b)***

**Figure 1.** Flocculation experiments with cationic polymer(a) Before mixing (b) End of experiment

**Figure 2.** After filtration with geotextile tube

**Table 1.** Suspended solids and COD values after filtration with geotextile tube

| Cationic polymer amount | SS | COD |
|---|---|---|
| (g) | (mg/L) | |
| 0.10 | 1210 | 3350 |
| 0.15 | 1325 | 3400 |
| 0.20 | 1600 | 3325 |

## Conclusions

Solid and liquid phase separation was successfully achieved by cationic polymer flocculation using geotextile tube with cost effective approach and very promising for practical applications.

## References

Khachan M.M., Bhatia S.K, 2017. The efficacy and use of small centrifuge for evaluating geotextile tube dewatering performance, Geotext. Geomembr. 45(4): 280–293.

Stoltz G., Delmas P., Barral C., 2019. Comparison of the behaviour of various geotextiles used in the filtration of clayey sludge: an experimental study, Geotext. Geomembr. 47(2): 230–242.

# Air Quality Assessment in the Municipality of Pavlos Melas, Thessaloniki

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**Keywords:** *Air Pollution, Particulate Matter, Spatial Distribution*

The Municipality of Pavlos Melas, located in the metropolitan area of Thessaloniki, carried out an extensive air quality assessment through the installation of 14 monitoring stations in representative locations. The network was designed to capture both background conditions and localized pollution, offering insights into spatial variability and temporal fluctuations of key pollutants.

The evaluation was conducted in accordance with the European and World Health Organization (WHO) guidelines. These frameworks define exceedances as daily PM10 concentrations above 50 µg/m$^3$ for more than 35 days per year, annual PM2.5 averages exceeding 25 µg/m$^3$, hourly $NO_2$ levels greater than 200 µg/m$^3$ on more than 18 occasions per year, and hourly $O_3$ concentrations surpassing the 180 µg/m$^3$ information threshold.

Results showed that particulate matter, particularly PM10, is the dominant air quality concern in the municipality. Several stations recorded frequent daily exceedances of the 50 µg/m$^3$ limit, with evidence that in some locations the annual allowance of 35 days was exceeded. PM2.5 levels were also notable, with annual averages in certain stations approaching or slightly surpassing the WHO guideline value. Seasonal differences were apparent, with higher concentrations during winter, coinciding with residential heating activities and unfavorable meteorological conditions that restrict pollutant dispersion.

Ozone exhibited a different behavior, with systematic exceedances of the 180 µg/m$^3$ threshold observed at certain monitoring sites. These patterns reflected the influence of photochemical activity and regional atmospheric transport, typical of the Thessaloniki basin during warmer months. Nitrogen dioxide concentrations were generally lower and less problematic, though in areas with dense traffic, short-term peaks approached the hourly limit, underlining the localized effect of vehicular emissions.

The spatial distribution of pollutants across Pavlos Melas was uneven. Stations situated near busy roads, construction areas, or densely populated districts reported consistently higher particulate matter concentrations. By contrast, stations located in suburban areas or at schools away from main traffic arteries often reflected cleaner background conditions. This intra-municipal heterogeneity demonstrates that exposure levels vary significantly within short distances, emphasizing the importance of dense monitoring networks in urban settings.

Although the deployed sensors are not equivalent to reference-grade instruments, they provided reliable indications of trends, exceedances, and episodic events. The classification of “multiple” exceedances in several locations strongly suggests regular breaches of established thresholds, while “possible” exceedances highlight cases where measurement periods or data coverage were insufficient for full verification. Despite these limitations, the dataset effectively captured the variability and magnitude of pollution across the municipality.

Overall, the assessment revealed that Pavlos Melas is characterized by both clean-air zones and pollution hotspots. Areas of low pollution provide a valuable reference for evaluating background air quality, while hotspots highlight the influence of local emission sources and meteorological factors. The recurring exceedances of PM10, PM2.5, and ozone indicate that air quality remains a significant issue for the municipality, with direct implications for population exposure and health risks.

The findings contribute to a more detailed understanding of urban air quality dynamics in Mediterranean environments. They underscore the complexity of pollutant behavior at the municipal scale, shaped by a combination of traffic density, residential heating, atmospheric transport, and local topography. This complexity necessitates continuous monitoring in order to capture both long-term averages and short-term pollution episodes.

# The Problem Tree: a strategic tool for priorities' identification, applied to the assessment of operational and design issues of a solid waste treatment facility in Lebanon

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***keywords:*** *problem tree, compost, optimization, waste treatment, low-income countries.*

## Introduction

Solid waste management is still an issue, especially in low and middle-income countries. The case of Lebanon is particularly interesting: in the past two decades, many investments have been done by the European Union and other international actors to target this problem, without reaching a satisfying solution, as highlighted by the waste crisis of 2015; moreover, Lebanon is also suffering from land degradation, which makes every effort towards organic waste valorisation extremely important. The present research (performed in 2018 within a development cooperation project) is focused on the improvement of an existing solid waste treatment plant, providing a method for the identification of problems and the prioritisation of interventions, with special attention to compost production.

## Materials and methods

The Ain Baal Solid Waste Treatment Facility (SWTF) was built in 2009 to serve 63 municipalities within the Governorate of Sour by treating 150 t/d of MSW. The facility is composed of a mechanical treatment area, where the mixed waste is divided into several streams: the organic waste is biologically stabilized, while the non-organic waste is separated manually to extract the recyclables. Since its construction, the facility has never been able to cope with the expected amount of waste and was consequently revamped in 2018. Moreover, the stabilized organic waste did not have the minimum quality characteristics requested to be used as compost, since it originates from mixed MSW.

The Project Cycle Management (PCM) was used to identify a strategy for the improvement of the situation. The problem tree for Ain Baal SWTF Operation and management was created to highlight cause-effect relationships and share them in an effective way with the key local stakeholders. The identification of problems was carried out during a three months' period of on-site investigation. Data was collected through interviews with key stakeholders, and field surveys and observations done on a daily basis. Biological and characterization analyses were also done for a better understanding of the process.

## Results and discussion

More than fifty issues were identified, ordered to create the problem tree, and gathered in seven major threads. Therefore, a solution tree was created and general objectives were identified: 1) reduction of odours; 2) improvement of the quality of the compost; 3) implementation of a proper system for leachate treatment; 4) clear description of the operation and management for the SWMF; 5) increase of the market for the output materials. Specific objectives were identified, together with expected results, actions, investment and priority.

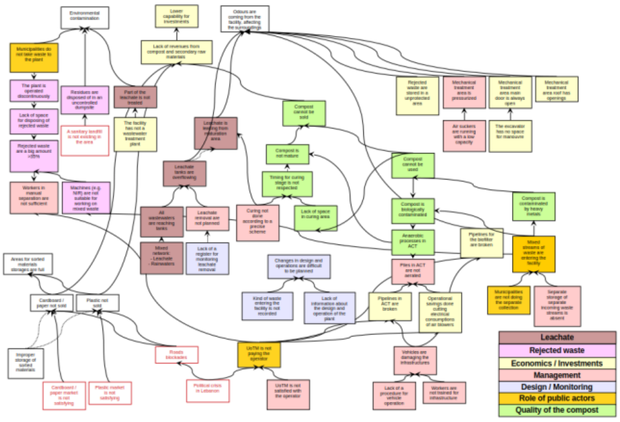

***Figure 1.*** *The Problem Tree for Ain Baal SWTF*

***Table 1.*** *General and specific objectives, actions, tipologies of investment and priorities, an example*

| General / specific objectives | Actions | Tipology of investment | Priority |
|---|---|---|---|
| *General objective: Odours coming from the facility shall be reduced* | | | |
| *Specific objective:*<br>Exhausted air from ACT and curing area is correctly treated by Biofilter 1 | Damages to pipelines for the Biofilter 1 have been clearly identified | Maintenance / low investment | **Urgent** |
| | Air flows in pipelines have been tested | Maintenance / low investment | Medium |

## Conclusions

The application of the problem tree made possible a clear understanding of cause-effect chains, identifying the source of each problem and not its most evident consequences. As an example, the low quality of compost was addressed in the past through expensive technical interventions, while the main reason had to be found literally "at the source" (organic waste originated from MSW and not from segregated food waste). Within the study, 42 actions were identified, and five actions out of 6 targeted as "urgent" required low-cost interventions, making an upgrade of the facility more accessible and feasible.

In the opinion of the authors, the use of PCM, and more specifically of the problem tree, widely used in project design, can be extended to technical cases. This approach allows the prioritization of interventions and can be fundamental, especially in contexts where the lack of resources poses a limit to possible actions, and every effort is needed to avoid pointless investments.

***Acknowledgements:*** This study is supported by the Italian Development Cooperation Agency (AICS) within the project "Gestione Integrata delle Risorse Naturali nell'Unione delle Municipalità di Tiro" (AID 2016/337/000090/3).

## References

ISWA, 2016. Technical guidance on the operation of organic waste treatment plants, *International Solid Waste Association*

European Commission, 2004. Project Cycle Management Guidelines. *Aid Delivery Methods*

Villa, F., De Robertis, A., 2020. Proposals for Ain Baal Mechanical Biological Treatment facility.

# Management of Household Hazardous Waste: Survey and Comparative Analysis

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***keywords:*** *Hazardous household waste; Waste management; Public perception, Socio-economic factors; Sustainable practices.*

## Abstract

The increasing generation of household hazardous waste (HHW) poses significant environmental and public health burden globally. Effective management strategies are crucial for minimizing HHW impact and promoting sustainable practices. This study investigates current trends of HHW management and demonstrates an analysis to identify key factors of public awareness in recycling initiatives. The research employs a comprehensive survey methodology to gather data on public perceptions, attitudes, and behaviors concerning HHW. The analysis focuses on identifying demographic and socio-economic variables that correlate with recycling practices and awareness of HHW risks. Findings indicate that income plays a role in recycling habits, though the relationship is not always precise. For instance, a p-value of 0.054 suggests a borderline dependency between income and the perception of certain reasons hindering recycling and the Phi coefficient of 0.177 indicates a weak correlation. Specifically, respondents within €10,001–€30,000 income range are more likely to report being deterred from recycling owing to specific reasons, whereas no participant in the >€70,001 income range considers this a deterrent for HHW recycling. Furthermore, the study explores the perceived importance of establishing "green collection points" for HHW. However, a direct correlation between income and the perceived significance of green collection points cannot be definitively established due to a high percentage (46.7%) of the expected frequencies cells (cross table in the $\chi^2$ independence test) being less than 5 , exceeding the acceptable threshold of 20%. This limitation highlights the complexity of analyzing such correlations and suggests the need for alternative statistical approaches or a larger, more diverse dataset. Overall, this research sheds light on the multifaceted nature of HHW management, emphasizing the importance of understanding public attitudes and socio-economic factors to design effective recycling campaigns and infrastructure. The findings underscore the need for targeted interventions and educational programs to enhance public engagement and promote responsible HHW disposal. Future research should focus on exploring these complex relationships further and developing more robust analytical frameworks.

# Ternary Deep Eutectic Solvent-Mediated Leaching of Valuable Metals from Waste Printed Circuit Boards

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***keywords:*** *e-waste, metal leaching, printed circuit board, type III deep eutectic solvent.*

## Introduction

The growing volume of discarded consumer electronics challenges sustainable development and poses significant environmental burdens by threatening ecosystems and human health. Printed circuit boards (PCBs) are core components of waste electronic equipment (e-waste), with complex chemical composition and undisputed environmental release hazards. Many elements found in PCBs (e.g. gold, silver, copper, nickel, zinc, and tin) are derived from finite natural resources and are regarded as essential drivers for the contemporary clean energy and digital economy transitions. Therefore, discarded PCBs present valuable opportunities for urban mining for their diverse and sizeable content in technologically critical minerals [1].

Traditional techniques for the recovery of minerals from waste PCBs rely on thermal treatment (pyrometallurgy) and chemical treatment (hydrometallurgy) [1]. Available processing methods challenge the establishment of cost-efficient and environmentally conscious e-waste management strategies due to high energy requirements, secondary toxic waste generation, use of harsh leaching agents, and reliance on multistage separation processes for selective resource recovery. With the advent of neoteric solvents, eutectic liquids and deep eutectic solvents (DESs) have gained increasing attention as processing and extraction media in solvometallurgy. Their undemanding preparation from widely available organic and inorganic precursors, customizable physical properties (e.g. pH, viscosity, density, conductivity), and chemical functionality (e.g. acid-base, redox, and chelating character) have paved the way for the rational design of benign and selective metal leaching agents [2].

In this study, a common type-III binary DES, consisting of choline chloride (ChCl) as hydrogen bond acceptor (HBA) and oxalic acid (OA) as hydrogen bond donor (HBD) is physico-chemically tailored with the addition of ethylene glycol (EG) as second HBD, at ChCl:OA:EG molar compositions of (1:1:x), where x= 0, 0.25, 0.5, 0.75, and 1. The effect of EG loading on the density, viscosity, and pH of the reported DESs is examined. Control and optimal DES compositions were further used in leaching studies. The effects of incubation temperature, sample mass loading, processing time under static conditions, on the selective leaching of valuable metals from pulverized waste PCBs are studied and correlated with the physicochemical properties of the DESs. The efficiency, selectivity, and mechanism of leaching are elucidated via qualitative and quantitative analytical spectroscopy and separation techniques. A phase-separation-induced selective recovery of a metal salt from a leachate with a sacrificial role of the DES in the leaching medium is explored.

## Materials and methods

ChCl (98%), OA (99%), and EG (99.8%) were mixed at appropriate molar ratios at 60 °C, using magnetic stirring, until a clear and transparent liquid was formed. The DES density, viscosity and pH were measured at room temperature. Structural analysis was performed by using complementary FTIR, $^{1}$H/$^{13}$C NMR, and GC/MS analyses. Discarded mobile phone PCBs were crushed at 25,000 rpm forming particles below 3 mm in size. The resulting powder was sieved into different batches falling in the size ranges of [500 µm-3 mm] (batch 1), [250-500 µm[ (batch 2), [125-250 µm[ (batch 3), [60-125 µm[ (batch 4), and < 60 µm (batch 5). The leaching studies were performed in a temperature range of 25-60 °C for 72 h, under static conditions. The sample-to-DES loading was examined at 50, 75, and 100 mg/mL.

For qualitative and quantitative analysis, 100 mg of different batches of PCB powders were digested in

1 mL aqua regia and diluted tenfold with deionized water for further analysis of their source metal content and elemental distribution. All DES leachates were centrifuged, and 100 mg aliquots were digested with 1 mL ultrapure aqueous $HNO_3$ (70%). The metal ion content in the digested source solutions and sample liquors was determined by ICP-MS. FTIR, SEM-EDX, and XRD were performed on the selectively recovered solid product to assess the purity, morphology, elemental composition, and phase structure.

## Results and discussion

Increasing the EG content in the ternary DES reduced the density, viscosity, and acid character at room temperature relative to the binary system (Fig.1a-c). FTIR and NMR studies revealed that the EG addition disrupted the hydrogen bonding environment between ChCl and OA. Green-yellow leachates were formed under static leaching (Fig.1d), irrespective of the DES composition or operating conditions. ICP-MS demonstrated that Cu and Sn were selectively leached from the PCBs using the equimolar DES composition, and the leaching efficiency and yield increased with the incubation temperature (Fig.1 e,f). DESs deficient in EG achieved lower leaching yields, with leachates solidifying at incubation temperatures above 50 °C, indicating reduced liquor solvation efficiency. The presence of EG plays a critical role in stabilizing the liquor above 50 °C. The green-yellow leachates formed with the equimolar system suggest the presence of copper and tin chloride complexes. SEM-EDX of the green solid product revealed rod-like morphology with a co-presence of Cu and Cl as major elements and no Sn, indicating selective Cu recovery.

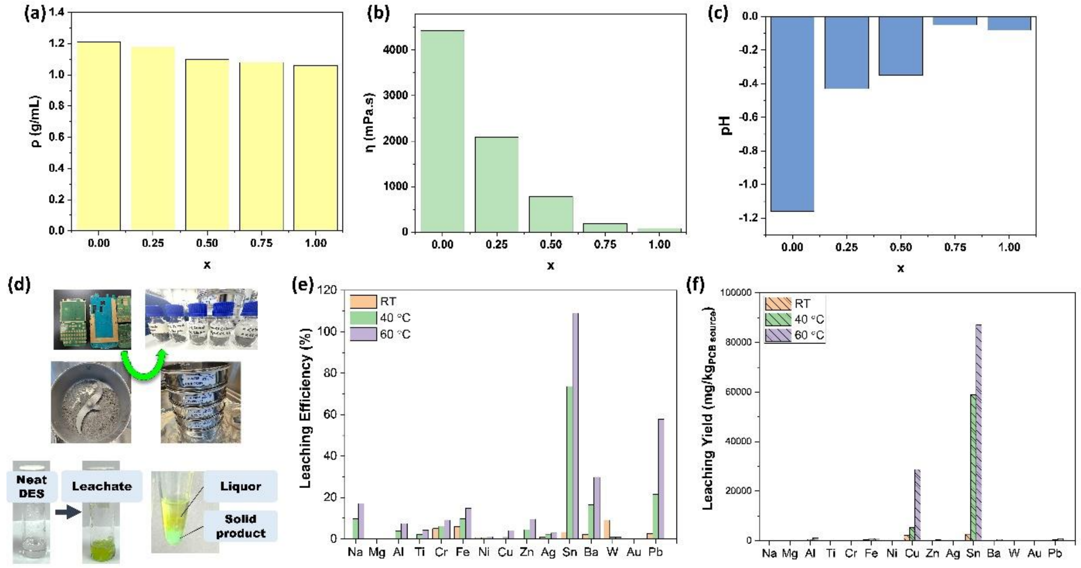

***Figure 1.*** *Estimated (a) density, (b) viscosity, (c) pH of ChCl:OA:EG (1:1:x) DES with different EG fractions at 20 (±2) °C. (d) digital photos of source PCBs before/after pulverization and sieving; change in DES color before/after static leaching; phase-separated green product from leaching liquor. Effect of incubation temperature on leaching (e) efficiency and (a) yield at 50 mg/mL PCB powder (batch 2) loading.*

## Conclusions

A ternary DES consisting of equimolar ChCl:OA:EG demonstrated the lowest room temperature viscosity while maintaining an acidic character compared to EG-deficient DES compositions. The optimal DES demonstrated selective Cu and Sn leaching from pulverized waste PCBs, with leaching yields increasing with the incubation temperature up to 60 °C. Copper could be selectively recovered as a chloride salt.

***Acknowledgments:*** This study is supported by the KU research and innovation grant RIG-2023-019.

## References

[1] Baldé, C.P., Kuehr, R., Yamamoto, T., McDonald, R., D'Angelo, E., Althaf, S., Bel, G., Deubzer, O., Fernandez-Cubillo, E., Forti, V. and Gray, V., 2024. *Global e-waste monitor 2024*, ed. 2 November 2024.

[2] Anuoluwapo, E.O., and Potgieter, J.H., 2025. Sustainable leaching of metals from waste printed circuit boards using efficient carboxylic acid-based deep eutectic solvents. *Sep. Purif. Technol.*, 374, 133712.

# Comparison of Source and Site level methane emissions measurements at gas installations

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***keywords:*** *methane emissions; gas installation; gas network; greenhouse gases*

## Introduction

Methane is the main component of natural gas and one of the most important contributors to climate change. Methane is responsible for around 30% of the rise in global temperatures since the industrial revolution. Its concentration in the atmosphere continues to rise rapidly, in large part from anthropogenic sources. Gas operators worldwide are carrying out intensive programs on the quantification of the total methane emissions in their activities and are designing mitigation measures for methane emissions [1].
This paper presents and compares Source and Site-level measurements on methane emissions at DESFA's gas installations. The differences between the two methods are reported to improve methane emissions understanding.

## Materials and methods

Methane emissions are divided into three macro categories [2]: Fugitive emissions, Vented emissions and emissions from Incomplete Combustion. Emissions measurements at gas installations may be performed at Source-level (Figure 1) for any individual component [3] or at Site-level (Figure 2) using Drones or other techniques. Results of measurements using these two different methodologies are compared in terms of their Uncertainty. Valuable considerations are made to improve the emissions understanding.

***Figure 1.*** *Source-level methane emissions measurements (LDAR survey)*

***Figure 2.*** *Site-level methane emissions measurements using Drones*

## Results and discussion

Site-level methane emissions measurements are conducted independently of the Source-level surveys at various gas installations of DESFA SA. Among sources of discrepancy between the sum of Source-level and Site-level measurements are different operating conditions at the time of measurements, different leaking population due to repairs or new leaks, weather conditions, limitations of emissions detection techniques.

## Conclusions

The object of this paper is the comparison of Source-level (bottom-up) with Site-level (top-down) methane emissions measurements implemented at various gas installations of DESFA SA.

Source and Site-level methane emissions detection methodologies are very different, making their comparison a challenging task. Site-level measurements with Drone flights provide a quick estimate, but they are not able to precisely locate the Source of the emissions.

## References

[1] Tsochatzidi, A. and Tsochatzidis, N.A. Best practices to reduce methane emissions at gas transmission networks. A literature review and case studies. *Green Energy Sustain.* 2023;3(2):0003. https://doi.org/10.47248/ges2303020003

[2] Marcogaz, 2019. WG_ME-485, Assessment of methane emissions for gas Transmission and Distribution system operators.

[3] EN15446:2008 Fugitive and diffuse emissions of common concern to industry sectors - Measurement of fugitive emission of vapours generating from equipment and piping leaks. CEN, January 2008.

# Preliminary investigation of removal of pharmaceuticals from aqueous solutions by potato peel based biochars produced from hydrothermal conversion and pyrolysis: a comparative study

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***keywords:*** *pharmaceuticals; biochars; adsorption; synthetic wastewater; pyrolysis.*

## Introduction

The removal of pharmaceuticals such as carbamazepine from wastewater effluents prior to discharge into natural water bodies is critically important due to its environmental persistence, documented ecotoxicity, and broader implications for ecosystem and human health. Carbamazepine exhibits high resistance to degradation in conventional wastewater treatment processes, resulting in its widespread detection in global aquatic environments (Patel et al. 2019). This persistence facilitates bioaccumulation and chronic exposure, causing significant harm to aquatic organisms. Studies confirm sublethal effects, including endocrine disruption, reproductive impairment, altered behaviour, and reduced viability in fish, invertebrates, and algae (Fent, Weston, and Caminada 2006). Although carbamazepine itself is not an antibiotic, pharmaceutical effluents frequently contain genuine antibiotics alongside other bioactive compounds. The discharge of antibiotics into waterways is a major driver of antimicrobial resistance (AMR), selecting for resistant bacteria and enabling the proliferation of antibiotic resistance genes (ARGs) in environmental microbial communities – posing a substantial threat to public health (Bengtsson-Palme and Larsson 2016).

Furthermore, carbamazepine recurrently contaminates drinking water sources due to inadequate removal, presenting potential chronic exposure risks to humans; however, the full health implications necessitate further research (aus der Beek et al. 2015). The precautionary principle mandates proactive removal, reflected in regulatory frameworks such as the EU Water Framework Directive, which includes carbamazepine on its "Watch List" due to environmental concerns (European Commission, 2020). Effective elimination requires advanced treatment technologies, including ozonation, activated carbon adsorption, or membrane filtration. Failure to remove such persistent pharmaceuticals risks irreversible ecological damage, exacerbates the global AMR crisis linked to antibiotic residues (UNEP, 2023; WHO, 2015), and compromises water security.

Recent studies have explored biochar-based adsorbents for carbamazepine (CBZ) removal. Algae-derived NaOH-activated biochar demonstrated a high adsorption capacity (118.4 mg/g), primarily through H-bonding (Zhang et al., 2023). A polypyrrole/graphene oxide/palm seed biochar nanocomposite achieved >97% CBZ removal via π-π interactions and electrostatic attraction (Pandiyarajan et al., 2023). Activated charcoals exhibited variable CBZ adsorption capacities (4.46–14.49 mg/g), with higher activation temperatures enhancing performance (Stoykova et al., 2013). Pine sawdust biochar, initially used for heavy metal adsorption, removed >80% of CBZ through combined adsorption and photodegradation (Yukhymchuk et al., 2024). These findings underscore the potential of biochar-based materials for sustainable pharmaceutical removal.

In the current study, biochar adsorbents were synthesised using hydrothermal conversion and conventional pyrolysis. The performance of these biochars for pharmaceutical pollutant adsorption was evaluated using carbamazepine as a model contaminant.

## Materials and methods

### Preparation of the potato peel adsorbent via Pyrolysis

Biochar samples were produced from dried potato peel powder using potassium hydroxide as an activation agent, under different conditions of reaction time and KOH ratios keeping the reaction temperature at 400 °C. Pyrolysis reaction time was either 2 or 4 hours, whilst the KOH/ biomass ratio was either 1:1 or 2:1. The samples produced by pyrolysis are names using the convention PYR-X-Yhrs, where X represent the parts of KOH by mass and YY represents pyrolysis reaction time for instance, a sample produced with a feedstock with KOH : biomass ratio of 2:1 and reaction time of 2 hours would be named PYR-2-2hrs.

### Preparation of the potato peel adsorbent via Hydrothermal Cracking

Hydrochar was produced in an autoclave reactor vessel from dried potato peel powder with distilled water. During the hydrothermal conversion the reaction temperature was kept constant at 200°C while varying the reaction time (1 or 25 hours) and weight /volume ratios of the biomass to distilled water (1:1 or 1:5).

### Adsorption study

50 ppm aqueous solution of carbamazepine were produced from 1000 ppm stock solution by dilution and pH adjusted to 6 using HCl and NaOH. 10 ml of the CBZ solution were transferred into a 4 20 ml glass vials followed by addition of 10 mg of each of the adsorbent. The vials were put on a shaker at room temperature and contact time was 24 hours. After 24 hours the concentration of CBZ remaining solution was determined using UV-VIS spectrophotometer at wavelength. The removal efficiency and CBZ uptake of the adsorbent were determined.

## Results and discussion

Figure 1 (a) and (b) show the CBZ removal efficiencies and CBZ uptake or samples produced through hydrothermal conversion. The removal efficiencies of between 73 and 89.5 % were achieved. The CBZ uptake of the samples was between 36 and 45 mg/g. Figure 1 (c) and (d) show the CBZ removal efficiencies and CBZ uptake or samples produced through pyrolysis respectively. The removal efficiencies of between 55 and 100 % were achieved. The CBZ uptake of the samples was between 27 and 50 mg/g.

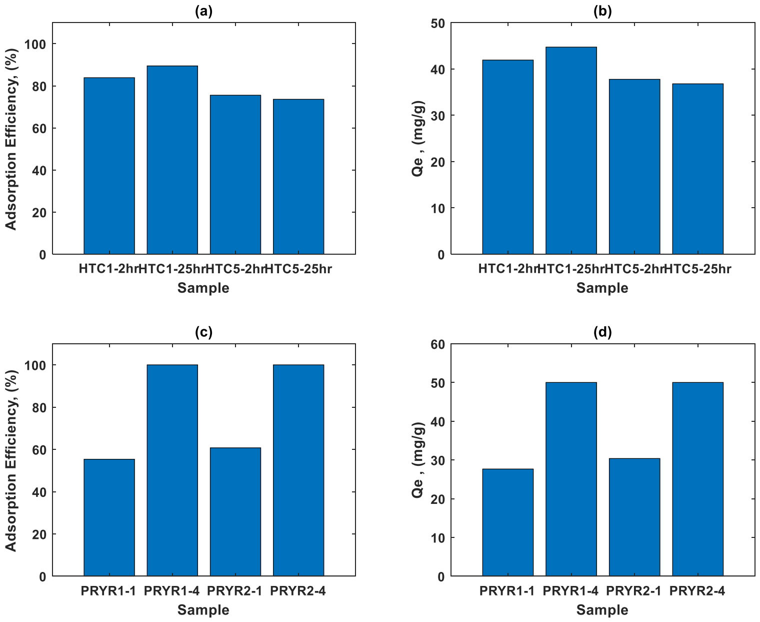

***Figure 1.*** *(a) and (b) Adsorption efficiencies and CBZ uptake of hydrothermal conversion biochar(c) and (d) Adsorption efficiencies and CBZ uptake of pyrolysis potato peel biochars.*

## Conclusions

The potato peel based biochars produced from both methods show good potential for use as adsorbents for pharmaceutical remediation. However more work has to be done in terms of optimization of both process to improve the performance of adsorbents.

## References

aus der Beek, Tim, Frank-Andreas Weber, Axel Bergmann, Silke Hickmann, Ina Ebert, Arne Hein, and Anette Küster. 2015. 'Pharmaceuticals in the environment—Global occurrences and perspectives', *Environmental Toxicology and Chemistry*, 35: 823-35.

Bengtsson-Palme, J., and D. G. Larsson. 2016. 'Concentrations of antibiotics predicted to select for resistant bacteria: Proposed limits for environmental regulation', *Environ Int*, 86: 140-9.

Fent, Karl, Anna A. Weston, and Daniel Caminada. 2006. 'Ecotoxicology of human pharmaceuticals', *Aquatic Toxicology*, 76: 122-59.

Patel, Manvendra, Rahul Kumar, Kamal Kishor, Todd Mlsna, Charles U. Pittman, Jr., and Dinesh Mohan. 2019. 'Pharmaceuticals of Emerging Concern in Aquatic Systems: Chemistry, Occurrence, Effects, and Removal Methods', *Chemical Reviews*, 119: 3510-673.

# Session 5: Modeling and optimization in energy and environment

# An optimisation approach towards the integration of hydrogen in heat and power decarbonisation

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***keywords:*** *Decarbonisation; Net-Zero; Hydrogen Integration; Infrastructure Planning; Optimisation.*

## Introduction

The combustion of fossil fuels is the main contributor to rising greenhouse gas concentrations in the atmosphere, which in turn drives global warming. To mitigate the harmful impacts of climate change, there is an increasing imperative to pursue Net-Zero emissions and explore low-carbon alternatives. The UK became the first major economy to legally commit to achieving net-zero carbon emissions by 2050, publishing a comprehensive strategy outlining policies for a decarbonised economy Achieving this goal necessitates major changes in the energy sector, particularly the decarbonisation of heating and electricity, which contribute 21% and 10% of the UK's carbon emissions, respectively (Department for Energy Secuirity & Net-Zero, 2025). Therefore, cutting $CO_2$ emissions from buildings is essential to meet climate targets. This involves phasing out natural gas boilers, with key decarbonisation strategies including the electrification of heating and the use of hydrogen-based systems (HM Government, 2021a). In this regard, hydrogen plays a critical role in lowering the environmental impact of energy systems, either by replacing natural gas directly or by serving as an energy carrier for renewable energy sources.

Over the past decade, energy system models focused on heat decarbonisation have gained significant attention in academic research. Many studies have employed mathematical modelling to assess the effects of heat sector electrification across various case studies (Lizana et al, 2023; Charitopoulos et al. 2023). Additionally, the shift toward a hydrogen-based heating infrastructure has been explored through optimisation-based approaches (Sunny et al., 2021; Efthymiadou et al., 2024, Efthymiadou et al. 2025). Nevertheless, analysing the energy system as a whole is crucial for a comprehensive understanding and to inform strategic decisions about the future energy mix (Ran et al., 2022; Bounitsis et al., 2024).

## Materials and methods

In this study, we introduce a spatially detailed, multi-period Mixed Integer Linear Programming (MILP) framework designed to support infrastructure planning for achieving Net-Zero emissions in the heat and power sectors. Great Britain is divided in 13 regions, aligned with local gas distribution zones. Thus, spatial resolution is incorporated in heat and power demand as well as renewable availability. Moreover, a multi-scale temporal resolution is adopted, combining decadal time steps for long-term planning with representative days within each period to capture operational variability. Each representative day is modelled at hourly resolution to accurately reflect fluctuations in energy demand and resource availability.

The mathematical framework accounts for both hydrogen-based and electrification pathways, jointly optimising investment and operational decisions to generate insights into the performance of future energy systems. Given the high spatial and temporal resolution and the broad range of technologies included, the model faces considerable computational complexity. To manage this, we apply advanced decomposition and clustering methods that maintain solution quality while improving computational efficiency.

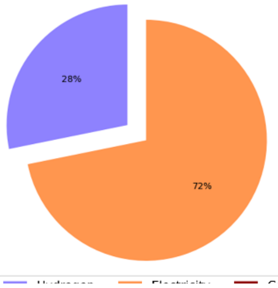

***Figure 3:*** *Heat mix in 2050*

## Results and discussion

A case study is presented to illustrate the applicability of the model for planning heat and power infrastructure in the UK from 2030 to 2050. By leveraging real-world gas consumption data, we conduct a detailed assessment of the optimal role of hydrogen and identify strategic investment priorities across domestic, commercial, and industrial heating sectors aiming to clarify the potential of hydrogen in a decarbonised energy system.

The role of hydrogen in the energy mix becomes increasingly significant over time. Figure 1 illustrates the projected heat mix in 2050, where hydrogen accounts for approximately 28% of total heat supply. Hydrogen production capacity grows from 22 GW in 2030 to 107 GW by 2050, with the majority of infrastructure investments concentrated in northern and eastern England. The predominant production technologies are reforming-based, particularly steam methane reforming and autothermal reforming coupled with carbon capture and storage (CCS) while an additional 8 GW of biomass gasification with CCS is also deployed.

To enable this transition, dedicated hydrogen and $CO_2$ pipeline networks are developed. Figure 2 depicts the hydrogen transmission infrastructure in 2050, which connects most regions across Great Britain, facilitating interregional hydrogen flow. Similarly, $CO_2$ pipelines are deployed to link major emission sources with storage sites, with three reservoirs located in the North Sea and Irish Sea identified for long-term $CO_2$ sequestration. These developments are essential to support the widespread deployment of low-carbon hydrogen technologies and ensure the viability of a decarbonised energy system.

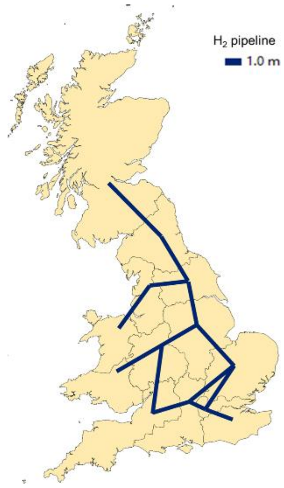

***Figure 2:*** *Hydrogen pipelines in 2050*

## Conclusions

A multi-period optimisation model with detailed spatio-temporal resolution is developed to capture electricity and hydrogen production, storage, and transmission, along with $CO_2$ transport and storage. Low-carbon hydrogen, mainly from reforming or biomass gasification with CCS, plays a crucial role in decarbonising heat and power. Overall, the model provides key insights for long-term energy policy planning.

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## References

Bounitsis, G. L., Charitopoulos, V. M., 2024. The value of ammonia towards integrated power and heat system decarbonisation. *Sustain. Energy Fuels*, 8, 2914–2940.

Charitopoulos, V. M., Fajardy, M., Chyong, C. K., Reiner, D. M., 2023. The impact of 100% electrification of domestic heat in Great Britain. *iScience*, 26, 108239.

Department for Energy Security & Net-Zero, 2025. 2024 UK greenhouse gas emissions, provisional figures. https://assets.publishing.service.gov.uk/media/67e4060df356a2dc0e39b4cd/2024-provisional-greenhouse-gas-emissions-statistics-statistical-release.pdf

Efthymiadou, M. E., Charitopoulos, V. M., Papageorgiou, L. G., 2024. Optimal hydrogen infrastructure planning for heat decarbonisation. *Chem. Eng. Res. Des.*, 204, 121–136.

Efthymiadou, M. E., Charitopoulos, V. M., Papageorgiou, L. G., 2025. Optimization approach for hydrogen infrastructure planning under uncertainty. *Ind. Eng. Chem. Res.*, 64, 7431–7451.

HM Government, 2021a. Heat and buildings strategy. https://assets.publishing.service.gov.uk/media/61d450eb8fa8f54c14eb14e4/6.7408_BEIS_Clean_Heat_Heat___Buildings_Strategy_Stage_2_v5_WEB.pdf

HM Government, 2021b. Net zero strategy: Build back greener. https://www.gov.uk/government/publications/net-zero-strategy

Lizana, J., Halloran, C. E,, Wheeler, S., Amghar, N., Renaldi, R., Killendahl, M., Perez-Maqueda, L. A., McCulloch, M., Chacartegui, R., 2023. A national data-based energy modelling to identify optimal heat storage capacity to support heating electrification. *Energy*, 262, 125298.

Ran, L., Mao, Y., Yuan, T., Li, G., 2022. Low-carbon transition pathway planning of regional power systems with electricity-hydrogen synergy. *Energies*, 15, 8764.

Sunny, N., Mac Dowell, N., Shah, N., 2020. What is needed to deliver carbon-neutral heat using hydrogen and CCS. *Energy Environ. Sci*., 13, 4204–4224.

# Deciphering the impact of AI's energy demand on Europe's Green Deal

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***Keywords:*** *Artificial intelligence (AI), AI energy impact; Energy systems planning; Net-zero; Decarbonization.*

## Introduction

The European Union's increasing deployment of AI factories relies heavily on the rapid expansion of large, energy-intensive data centers. This surge in electricity demand is placing mounting pressure on the EU's power grid and could significantly delay the achievement of its 2050 net-zero target [1]. In 2024, European data centers consumed an estimated 96 TWh of electricity, representing approximately 3% of total demand. This figure is projected to rise to 168 TWh by 2030 and 236 TWh by 2035, a nearly 150-fold increase of the current consumption [2]. Although estimates vary, recent analyses by ICIS and the IEA consistently identify data centers as one of the fastest-growing electricity-consuming sectors, with demand expected to exceed that of electric vehicles and building heating by 2030 [3].

EU's approval of the AI Gigafactories plan in February 2025, comprising multiple sites across Europe, could significantly influence the spatial dynamics of long-term grid development. This raises a critical question that how will AI Factories will impact EU's Green Deal? To address this, we develop a comprehensive optimisation-based framework to assess the effects of AI-driven electricity demand on Europe's long-term power system development, while ensuring alignment with emission reduction targets through 2050.

## Materials and methods

This research aims to investigate the impact of AI-driven electricity demand under multiple scenarios on the spatial and temporal dynamics of power grid development across the EU. To this end, a long-term generation and transmission expansion planning model has been developed, as a Mixed-Integer Linear Programming (MILP) problem with an annual resolution [4]. For calibration purposes, the latest Ten-Year Network Development Planning (TYNDP) projections are used as a reference pathway [5], enabling a comparative assessment of how AI-driven demand growth may alter or delay planned grid development trajectories across Europe.

The proposed optimization model aims to minimize the total system cost, including investment costs for generation and transmission, fixed and variable operating costs, fuel cost, carbon emissions costs, and the cost of unserved energy [6]. To capture the potential impact of AI demand, four scenarios are considered as presented in Table 1.

***Table 1.*** *Forecasted AI demand for different scenarios in TWh*

| Year | IEA | ICIS | McKinsey | Ambitious |
|---|---|---|---|---|
| **2040** | 212 | 466 | 1625 | 2242 |
| **2050** | 357 | 1033 | 3251 | 4851 |

## Results and discussion

Table 2 presents the total installed generation capacity under all AI demand scenarios, compared to the TYNDP projections for 2040 and 2050. Under the conservative scenario, approximately 68 GW of additional capacity is required by the end of 2050, while in the ambitious scenario, this figure rises to 1,461 GW.

To assess the impact of AI-driven demand on energy planning, the total installed capacity of key technologies is compared against the base case in Figure 1. This figure indicates that the planned rate of gas technology phase-out — a central target in 2050 energy planning — declines across all AI scenarios, which may serve as a warning sign. As expected, the additional demand is primarily met by solar and wind across scenarios. However, the increase in nuclear is particularly notable in the McKinsey and Ambitious scenarios.

***Table 2.*** *Total installed capacity results for 2040 and 2050*

| Year | Total Installed Capacity (GW) | | | | |
|---|---|---|---|---|---|
| | Without AI | With AI | | | |
| | | IEA | ICIS | McKinsey | Ambitious |
| **2040** | 3,400 | 3,472 | 3,498 | 3,765 | 4,825 |
| **2050** | 4,041 | 4,109 | 4,227 | 4,626 | 5,502 |

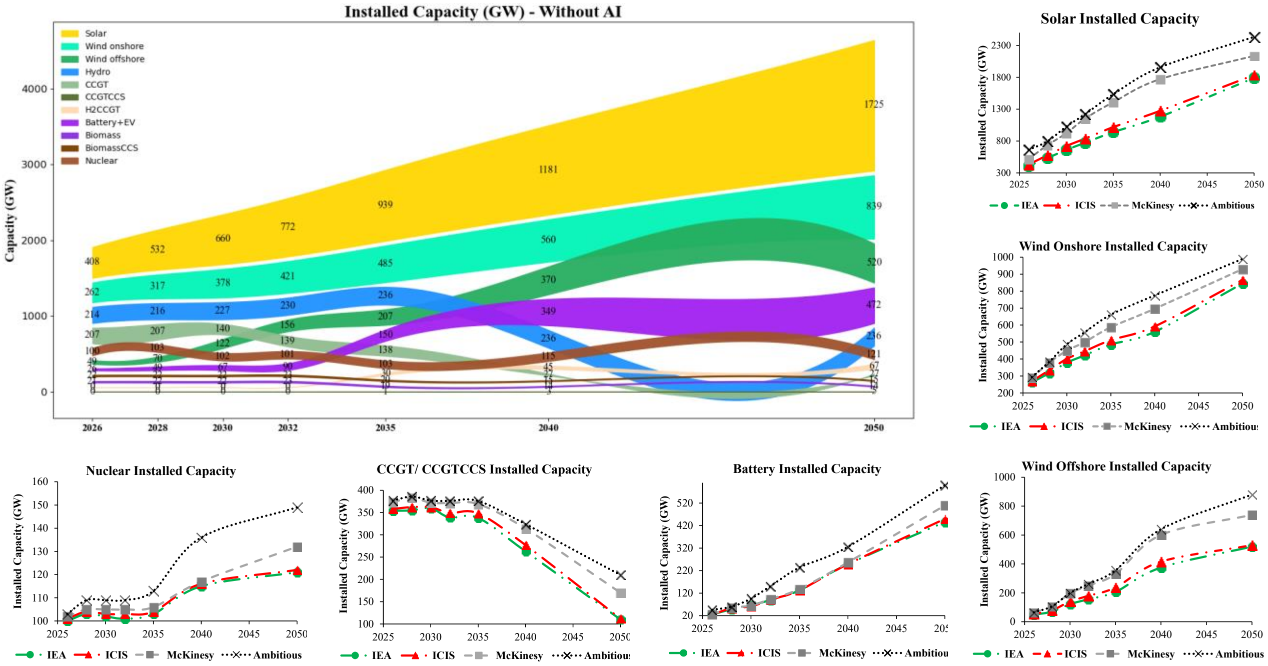

***Figure 1.*** *Comparison of total installed capacity of key technologies by 2050 under different scenarios.*

## Conclusions

The EU's 2050 net-zero goals may be threatened by the fast growth of AI industries, which is becoming a significant contributor in Europe's power use. This study shows that major capacity shortages might appear as early as 2032 if present grid growth plans are not modified. Meeting high-growth AI scenarios would require an additional 1344 GW of renewable energy (solar, wind on/offshore), 135 GW of H2CGT and CCGT-CCS, and 28 GW of nuclear. Additionally, cross-border power interchange would need to expand by 35%. These results demonstrate urgently long-term energy planning must incorporate AI-driven demand estimates in order to protect the green deal.

***Acknowledgements:*** Financial support from the Engineering & Physical Sciences Research Council (EPSRC) under the projects EP/T022930/1 and EP/V051008/1, is gratefully acknowledged.

## References

[1] V. M. Charitopoulos, M. Fajardy, C. K. Chyong, and D. M. Reiner, “The impact of 100% electrification of domestic heat in Great Britain,” *Iscience,* vol. 26, no. 11, 2023.

[2] H. T. Alastair Green, Jesse Noffsinger, Pankaj Sachdeva, *How data centers and the energy sector can sate AI’s hunger for power*, 2024.

[3] B. P. Ali Candlin, Sarah Brown, Lauren Orso, Claire Kaelin and, and I. Urbańska, *Grids for data centres: ambitious grid planning can win Europe’s AI race*, 2025.

[4] X. Zhou, M. E. Efthymiadou, L. G. Papageorgiou, and V. M. Charitopoulos, “Data-driven robust optimisation of hydrogen infrastructure planning under demand uncertainty using a hybrid decomposition method,” *Applied Energy,* vol. 376, pp. 124222, 2024.

[5] ENTSO-E, *Ten-Year Network Development Plan 2022 (TYNDP 2022)*, 2024.

[6] N. E. Koltsaklis, A. S. Dagoumas, G. M. Kopanos, E. N. Pistikopoulos, and M. C. Georgiadis, “A spatial multi-period long-term energy planning model: a case study of the Greek power system,” *Applied Energy,* vol. 115, pp. 456-482, 2014.

# Assessment of Water-Energy-Food-Ecosystem Nexus of Sakarya River Basin

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**keywords:** *sustainable development; water-energy-food- ecosystem nexus; integrated water resources management; SUWO; multi-objective optimization*

## Introduction

Water, energy, food, and ecosystems represent essential and interdependent systems that together constitute the water–energy–food–ecosystem (WEF-E) nexus. Effective and sustainable management of these resources is essential to address the increasing demands of a growing global population (Bazilian et al., 2011). Population growth, climate change, and economic development have exacerbated stress on water resources, highlighting the need for integrated and optimized management strategies (Vörösmarty et al., 2000). Conventional approaches to water resources management frequently prioritize singular objectives, which can result in inefficiencies and intersectoral conflicts among energy production, agriculture, and environmental conservation (Loucks and van Beek, 2017). Integrated Water Resources Management (IWRM), in alignment with the WEF-E nexus, provides a systems-oriented and multi-objective framework for effectively addressing these complex interdependencies (Grigg, 2019).

In this study a new simulation-optimization framework, which was designed for supporting IWRM in complex, multi-objective contexts across river basins, is introduced. The developed tool was applied to a river basin for the investigation of WEF-E nexus.

## Materials and methods

Sustainable Water Optimization Tool (SUWO), which was developed by Yaykiran and Ekdal (2025), was used for Water – Energy – Food – Ecosystem Nexus assessment in this study. SUWO is an open-source simulation-optimization framework that is based on Python for the management of water-resources at basin-scale. SUWO employs multi-objective genetic algorithms (MOGA), such as Non-dominated Sorting Genetic Algorithm II (NSGA-II) and NSGA-III, for generating Pareto-optimal solutions and enabling trade-off analysis among water uses, which includes simulations of reservoir operations, hydro-energy production, irrigation, and flow regulation. SUWO conducts scenario analysis for evaluating management, climate, and environmental scenarios. It also can carry out multi-criteria decision making (MCDM) analysis to address complex problems with competing objectives, helping decision-makers find compromise solutions.

Sakarya River Basin (SRB) in Türkiye was selected as the study area, that is rapidly developing under water infrastructure development, hydroelectric power plants (HEPPs), and irrigation expansion pressures. The basin has a drainage area of 58,160 km$^2$, which corresponds approximately to 7% of Türkiye's total land. Major land-use in the basin is agriculture with 53% of the basin area, where forests/semi-natural areas are the second highest land-use type with 44%, and the remaining part of the basin is occupied with artificial surfaces. The water demand for irrigation and domestic use was estimated as 2034 hm$^3$ and 689 hm$^3$, respectively. 13 different scenarios, including management scenarios, hydrological conditions and environment management classes, were developed and applied to the study area for the optimization of water allocation. Following this step, the SUWO-SRB model results were compared based on the energy, irrigation and ecosystem objectives. This comparison was conducted to elucidate the intricate interdependencies within the WEF-E nexus, with a focus on identifying trade-offs and synergies among alternative water management strategies.

## Results and discussion

The optimization results of four management scenarios, and for different hydrological conditions and environment management classes are presented in Table 1 considering hydropower generation, irrigation supply ratio and ecological deviation.

***Table 1.*** *Optimization results for the SUWO-SRB model*

| Scenario | | Hydropower generation (GWh) | Irrigation supply ratio | Ecological deviation |
|---|---|---|---|---|
| Management scenarios (NSGA-II)[1] | Balanced allocation | 1836 | 0.96 | 0.13 |
| | Maximizing energy | 1909 | 0.87 | 0.14 |
| | Sustainable irrigation | 1749 | 1.00 | 0.08 |
| | Eco-centric approach | 1795 | 0.92 | 0.07 |
| Management scenarios (NSGA-III)[2] | Balanced allocation | 1846 | 0.96 | 0.11 |
| | Maximizing energy | 1887 | 0.89 | 0.13 |
| | Sustainable irrigation | 1794 | 0.99 | 0.08 |
| | Eco-centric approach | 1781 | 0.93 | 0.08 |
| Hydrological conditions[3] | Normal year | 1839 | 0.99 | 0.12 |
| | Wet year | 2196 | 1.09 | 0.49 |
| | Dry year | 1272 | 0.86 | 0.14 |
| Environment Management Classes[4] | A: Natural | 1882 | 0.90 | 0.08 |
| | B: Slightly modified | 1846 | 0.96 | 0.11 |
| | C: Moderately modified | 1793 | 1.00 | 0.49 |
| | D: Largely modified | 1786 | 1.04 | 1.39 |
| | E: Seriously modified | 1788 | 1.05 | 2.97 |
| | F: Critically modified | 1763 | 1.06 | 5.46 |

[1]Normal year, EMC-B; [2]Normal year, EMC-B; [3]EMC-B, NSGA-II, Balanced Allocation; [4]Normal year, NSGA-II, Balanced Allocation.

Different management scenarios yielded varying outcomes across the WEF-E nexus. The “Maximizing Energy” scenario, resulted in the highest hydropower generation but reduced the average irrigation supply ratio compared to the “Sustainable Irrigation” scenario. The “Eco-Centric Approach” improved environmental performance but with mixed effects on hydropower and irrigation. Notably, both NSGA-II and NSGA-III exhibited similar trends across these scenarios, despite slight differences in their results.

Hydrological conditions significantly influenced system performance. Wet conditions led to a substantial increase in hydropower generation and an increased irrigation supply ratio. However, this also resulted in the highest ecological deviation, indicating potential adverse impacts on the ecosystem. In contrast, dry conditions caused a significant reduction in hydropower generation and a decrease in the irrigation supply ratio, highlighting the vulnerability of these sectors to water scarcity.

A clear trend of increasing ecological deviation is observed as EMCs progress from EMC-A to EMC-F, demonstrating a strong negative correlation between ecosystem health and human intervention. Conversely, the irrigation supply ratio exhibits a positive correlation with EMCs. However, hydropower generation follows a negative correlation highlighting a trade-off between energy production and ecological preservation.

## Conclusions

Application of SUWO to the SRB demonstrates the framework’s capacity to generate diverse and balanced management strategies under competing demands. Although SUWO is a newly developed and still-evolving tool, a general comparison with existing models can be made based on its core characteristics and intended functionalities. Future development of SUWO will prioritize enhancing its performance, usability, and applicability across diverse basin contexts to better support integrated WEF-E management.

## References

Bazilian, M.; Rogner, H.; Howells, M.; Hermann, S.; Arent, D.; Gielen, D.; Steduto, P.; Mueller, A.; Komor, P.; Tol, R.S.; et al., 2011. Considering the water, energy and food nexus: Towards a resource-sufficient and resilient future. *Energy Policy*, 39, 7896–7906.

Grigg, N.S., 2019. IWRM and the nexus approach: Versatile concepts for water resources education. *J. Contemp. Water Res. Educ.*, 166, 24–34.

Loucks, D.P. and van Beek, E., 2017. *Water Resource Systems Planning and Management*; Springer International Publishing: Cham, Switzerland.

Vörösmarty, C.J., Green, P., Salisbury, J. and Lammers, R.B., 2000. Global water resources: Vulnerability from climate change and population growth. *Sci. New Ser.*, 289, 284–288.

Yaykiran, S. and Ekdal, A., 2025. Sustainable water optimization tool (SUWO): An optimization framework for the water-energy-food-ecosytem nexus. *Water*, 17, 1280

# Development of a Decision Support System for Shallow Lakes Under the Impact of Eutrophication and Climate Change and Its Application to a Hypertrophic Lake

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**keywords:** *shallow lakes; eutrophication; hypertrophy; decision making.*

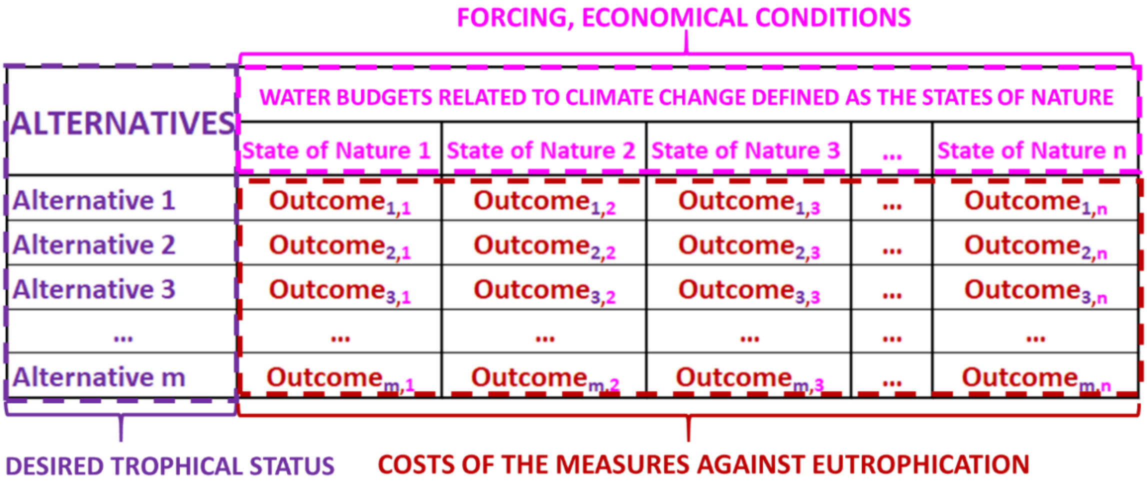
## Introduction

In this paper, a decision support system that is designed for shallow lakes under the impact of eutrophication and climate change is presented together with its application to a hypertrophic lake (Manyas Lake) that is located in the northwestern part of the Republic of Türkiye and is under the threat of aging in the following decades due to the cultural eutrophication. Climate change is considered as another treat adding to eutrophication. The lake that is an important breeding area for many bird species as well as one of the major resting area for migratory birds is under the impact of mainly diffuse emission sources of nutrient and is classified as hypertrophic according to the countries water quality regulations reaching an average TSI of 78 according to the Regulations of Republic of Türkiye given in the full paper.

## Materials and methods

As by any conventional decision support system (DSS), the DSS in this study is designed to provide the decision alternatives for the decision maker, who is defined as a group of relatively high-ranked bureaucrats who would formulate the suggestion for setting targets towards higher levels in the administrations eventually reaching the level of policy makers. Therefore, the decision problem in this study is defined as "aiming feasible and sustainable trophic status of an arbitrary shallow lake under the impact of cultural eutrophication and climate change".

Considering the relatively scarce financial resources allocated to solve environmental problems, the cost minimization of environmental measures is considered as the objective and the environmental quality is considered as the constraint that must be fulfilled for any acceptable decision. The output of the DSS is the so-called pay-off matrix as given in Figure 1, where each outcome is cost minimized group of diffuse nutrients pollution countermeasures using operation research methods.



| ALTERNATIVES | WATER BUDGETS RELATED TO CLIMATE CHANGE DEFINED AS THE STATES OF NATURE | | | | |
|---|---|---|---|---|---|
| | State of Nature 1 | State of Nature 2 | State of Nature 3 | ... | State of Nature n |
| Alternative 1 | Outcome$_{1,1}$ | Outcome$_{1,2}$ | Outcome$_{1,3}$ | ... | Outcome$_{1,n}$ |
| Alternative 2 | Outcome$_{2,1}$ | Outcome$_{2,2}$ | Outcome$_{2,3}$ | ... | Outcome$_{2,n}$ |
| Alternative 3 | Outcome$_{3,1}$ | Outcome$_{3,2}$ | Outcome$_{3,3}$ | ... | Outcome$_{3,n}$ |
| ... | ... | ... | ... | ... | ... |
| Alternative m | Outcome$_{m,1}$ | Outcome$_{m,2}$ | Outcome$_{m,3}$ | ... | Outcome$_{m,n}$ |

***Figure 1.*** *The pay-off matrix as the output of DSS.*

Following the operation research approach the DSS aims the minimization of initial investments and continuous annual expenses defining the total annual cost as the objective function and utilizes the trophic status and related water quality as the main constraints, defining the Carlson trophic state index (TSI) (Carlson, 1977) as the constraint function along with the basic design parameters for pollution countermeasures as the decision variables. The infrastructure calculating the values of the objective function is based on the algorithmic sizing of the engineering structures reducing the nutrient loads into the lake and using the unit costs of non-negligible cost items and macroeconomic parameters such as the discount rates, whereas the value of the constraint function is calculated using a mass-balance model with total nitrogen, total phosphorus, chlorophyll-A and detrital organic carbon as the state variables and Secchi disc depth as the derived variable. The non-linear nature of response of both, the objective and the constraint functions to decision variables necessitated the utilization of the non-linear mathematical programming to solve the operation research-based minimization problem to form the pay-off matrix illustrated in Figure 1.

As stated in the introduction, the case study area on which the decision support system was applied is a shallow lake classified as hypertrophic by the latest updated “Regulation of Surface Water Quality” published in the Official Gazette of the Republic of Türkiye, Number: 32091. The outflows from the lake related to water budgets for different climate scenarios as defined by the states of nature in the pay-off matrix (Figure 1) using the outputs of a previous study (Öztürk et al., 2013), where all the hydrological processes were calculated for different climate scenarios to construct water budgets of Manyas Lake.

## Results and discussion

The main results of this study are the successful development of the DSS and its successful application on the decision problem of aiming feasible and sustainable trophic status of the case study area based on Carlson trophic status index (TSI). The outputs of the DSS were used to develop the cost curves for phosphorus and nitrogen reduction. Because the lake was phosphorus limited the system designs were focused on phosphorus control, where the nitrogen control efficiency was a secondary result depending on phosphorus control efficiency, eventually reaching an estimated phosphorus and nitrogen reduction of 76% and 63% respectively. According to these nutrient load reductions expected Carson TSI value of 63-64 with an annual cost of 42 million of Euros are expected.

## Conclusions

The main conclusion is that even though the related lake will stay eutrophic, the probability of a hypertrophic state can at least be reduced drastically. Setting a target TSI range of 63-64 can be recommended. This range is still eutrophic; however, it corresponds to a much higher ecological state compared to TSI 78 keeping in mind that the TSI value is based on logarithms meaning that each unit increase occurs by an exponential increase of relevant nutrient and chlorophyll concentrations. Further details are given in the full paper and will be presented in the conference.

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## References

Carlson R.E., 1977. A trophic state index for lakes. *Limnol Oceanogr.* 22, 361–369. https://doi.org/10.4319/lo.1977.22.2.0361

Ozturk, I., Gurel, M., Erturk, A. 2013. Effects of Climate Change on Water Resources in Turkey, Proceedings of *AASSA Regional Workshop on Sustainable Development of Asian Countries, Water Resources and Biodiversity Under Climate Change*, Compilation by D.M. Bezmaternykh, D.N.Troshkin, Institute for Water and Environmental Problems, Siberian Branch of the Russian Academy of Sciences (IWEP SB RAS), August 19-23, 2013, Barnaul, Russia.

# Comparative Assessment of Alternative Waste Management Scenarios for Mixed Municipal Solid Waste: Case study of Cyprus

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***keywords:** Municipal Solid Waste; Anaerobic Digestion; Mechanical-Biological Treatment; RDF/SRF; Waste-to-Energy*

## Introduction

Sustainable management of municipal solid waste (MSW) is a key priority for regions aiming to meet the European Union's circular economy targets. Cyprus, as an island state with limited landfill capacity and increasing waste generation, is under pressure to upgrade its waste infrastructure. This study focuses on the Integrated Waste Management Facility (IWMF) in Koshi, which serves the districts of Larnaca, Famagusta, and since 2018, Nicosia. The facility currently handles over 260,000 tonnes of waste annually, with the majority being mixed MSW.

The main objective of this study is to evaluate alternative technological scenarios for the future operation of the Koshi IWMF, assessing their performance in terms of material recovery, energy production, environmental impact, and economic feasibility. The scenarios were designed in line with the national Municipal Waste Management Strategy (2021–2027) and the targets for 2025 and 2030.

## Materials and methods

Six technological scenarios were developed, combining mechanical sorting, aerobic composting, anaerobic digestion (AD), biodrying, thermal drying, and thermal treatment (incineration). Each scenario assumes separate collection of recyclables and biowaste, with projected quantities based on national strategic estimates for 2025: 170,449 t/y of mixed waste, 75,755 t/y of source-separated biowaste, and 35,281 t/y of other recyclable streams.

Mass balances were calculated for each scenario using established yield assumptions: 43% of mixed waste as RDF, 35% as biodegradable organics, and 12% recoverable recyclables. Biogas yield from AD was assumed at 180 $m^3$/tonne of biowaste, with combined heat and power (CHP) generation at 2 kWh/$m^3$ (electric) and 4 kWh/$m^3$ (thermal). Compost yield was estimated at 50% of incoming biowaste.

Capital (CAPEX) and operational (OPEX) costs were estimated using data from EU benchmarks and previous studies. Environmental performance was evaluated based on landfill diversion, energy recovery, and the amount of products requiring market outlets (e.g., RDF, SRF, compost).

## Results and discussion

Scenario I represents the baseline approach, involving mechanical sorting, aerobic processes - composting, and RDF export to industry. Scenario II introduces AD for biowaste with CHP, but retains RDF export. Scenario III and IV integrate thermal treatment (incineration) for RDF/SRF onsite, with III using aerobic composting and IV using AD. Scenarios V and VI employ thermal drying instead of biodrying for improved RDF quality.

Among the alternatives, Scenario V (mechanical sorting + composting + thermal drying + incineration) emerged as the most balanced in terms of landfill diversion (6%), energy production (494 GWh/year), and operational cost. Scenario II demonstrated strong environmental performance through biogas generation but required higher investment and showed dependency on off-site RDF handling.

By normalizing the quantitative values of each criterion (score 1-worst to 10-best), the overall score of the alternative technological scenarios is obtained. The overall score of each scenario is calculated as the sum of the individual scores without the use of weighting factors.

***Table 4***.*Normalized criteria scoring of alternative technological scenarios*

| Criteria<br>Scenarios | Quantity of products to find a market | Quantity of products for disposal (SRF, RDF) in industries or landfills | Energy | % Landfill disposal | CAPEX | OPEX | TOTAL |
|---|---|---|---|---|---|---|---|
| **I Composting of organic waste/ Mechanical sorting of mixed waste + Biodrying + Disposal of RDF / SRF in energy-intensive industries** | 10 | 1 | 0 | 1 | 10 | 10 | **32** |
| **II Anaerobic Digestion of organic waste / Mechanical sorting of mixed waste + Biodrying + Disposal of RDF / SRF in energy-intensive industries** | 8.83 | 1 | 0.55 | 1 | 7.74 | 6.02 | **25.15** |
| **III Composting of organic waste / Mechanical sorting of mixed waste + Biodrying + Disposal of RDF / SRF in a thermal treatment unit within the Koshi IWMF** | 10 | 10 | 3.55 | 10 | 3.26 | 4.98 | **41.78** |
| **IV Anaerobic Digestion of organic waste / Mechanical sorting of mixed waste + Biodrying + Disposal of RDF / SRF in a thermal treatment unit within the Koshi IWMF** | 8.83 | 10 | 3.55 | 10 | 1 | 1 | **34.38** |
| **V Composting of organic waste / Mechanical sorting of mixed waste + Thermal drying + Disposal of RDF / SRF in a thermal treatment unit within the Koshi IWMF** | 10 | 10 | 10 | 10 | 4.23 | 5.74 | **49.97** |
| **VI Anaerobic Digestion of organic waste / Mechanical sorting of mixed waste + Thermal drying + Disposal of RDF / SRF in a thermal treatment unit within the Koshi IWMF** | 8.83 | 10 | 10 | 10 | 1.35 | 1.62 | **41.80** |

According to the table above, it appears that the prevailing scenario for the upgrade of the OEDA Koshi facilities is Scenario V which includes:

- **composting** of organics separated at source by utilizing the existing infrastructure,
- **mechanical sorting** of mixed waste and other recyclables separated at source for the recovery of materials (with a small expansion of the existing unit) and
- **installation of a thermal treatment unit** for the production of renewable energy by utilizing the excess thermal energy for drying the organic fraction.

Scenario III follows, which envisages the installation of a thermal treatment unit without the use of thermal energy and the installation of a biodrying unit for the production of SRF.

It should be noted that even if the ambitious targets for source separation—particularly of organic waste—set by the 2021–2027 waste management strategy are not fully achieved, Scenario VI (which ranked similarly to Scenario III) retains operational flexibility to handle increased volumes of mixed waste. Specifically, the installed composting unit can be repurposed for biodrying processes to produce Solid Recovered Fuel (SRF), which can be directly sent for thermal treatment.

The comparison of scenarios shows that while incineration-based solutions deliver higher energy outputs and landfill reduction, their success depends on stable energy markets and emission control compliance. In contrast, biological routes (composting, AD) offer modular, lower-risk options but require robust end-use strategies for compost and digestate.

## Conclusions

The integrated assessment reveals that a hybrid approach combining biological treatment for source-separated organics and thermal valorisation of high-calorific residuals provides the most resilient and sustainable waste management pathway for Cyprus. Scenario V, in particular, leverages existing infrastructure while aligning with EU recovery and landfill targets. Its flexibility allows adaptation to future fluctuations in waste composition or policy changes.

The findings support the need for targeted investment in thermal treatment infrastructure and enhanced source separation to reduce reliance on landfilling. Future work should include sensitivity analysis for market outlets of RDF/compost and potential integration of carbon capture technologies.

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# Policy Pathways for Marine Litter Prevention and Control: Insights from the SeaClear2.0 Project

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***keywords:*** *marine litter; policy analysis; pollution prevention; innovation; Mediterranean.*

## Introduction

Our oceans contain roughly 25 million tonnes of plastic waste. Over 90% of all marine litter is located on the seafloor, making it difficult and expensive to collect. While plastic pollution affects all waters across Europe, the Mediterranean is the most affected sea due to its semi-enclosed basin and the intense human activities taking place on the surrounding coastal areas. There is no one-size-fits-all approach to addressing marine litter. Concerted actions, combining legislation, technology and socio-economic tools are required to ensure that there is a paradigm shift in the way materials that end up as marine litter are produced, consumed and managed at the end of their life, and that "legacy" marine pollution is addressed.

The SeaClear2.0 project (www.seaclear2.eu) is developing an integrated approach to address the full cycle of marine litter in a way that will help meet the objectives of the European Union's Mission to restore, protect and preserve the health of our oceans, seas and water by 2030. This approach includes the development of an autonomous team of robots that can detect and collect seabed and floating litter, and the development of recommendations for policy interventions that can help prevent and minimise marine litter as well as support technologies and innovations to restore affected areas and mitigate the impact of marine litter.

This paper presents an analysis of the policy framework that affects seabed marine litter (sources, prevention, collection, reuse/recycling) and relevant clean-up operations/technologies and identifies gaps, barriers, opportunities, synergies and coherence problems, both legal and institutional, at the EU and international level. It also makes recommendations that can help close regulatory gaps and loopholes, and take more concerted action to prevent and mitigate marine litter pollution.

## Materials and methods

The policy analysis was conducted using a desk-study approach, analysing policies that can affect marine litter as well as policies influencing the development, uptake, and commercialization of the SeaClear2.0 innovations. A systematic approach was employed to identify, review, and analyse relevant policies (Figure 1). Initially, a broad spectrum of policies was identified, with a particular emphasis on those implemented at the European Union (EU) and international levels. To identify potential policies of relevance, keywords relevant to marine litter and technology were compiled. These keywords included 'EU policy', 'EU law', 'waste', 'packaging', 'marine litter', 'plastics', 'artificial intelligence', and 'drones', as well as combinations of these words.

***Figure 1.*** *The method used for the policy analysis.*

The identified policies were subsequently screened based on their stated aims and objectives, and those deemed irrelevant to the focus areas were excluded from further consideration. For the remaining policies, the analysis sought to determine their potential to impact the generation of marine litter or the development, deployment, and commercialisation of systems such as SeaClear2.0. Specifically, the evaluation addressed how these policies could influence these areas positively or negatively and identified any barriers or opportunities they might present. A literature review, exploring themes of policy relevance and effectiveness, supplements the analysis.

## Results and discussion

European policies that are relevant to marine litter, European policies that are relevant to the technical and/or commercial aspects of the innovations developed within the SeaClear2.0 project, and international policies relevant to marine litter were reviewed and analysed. The results demonstrate that the European and international policy framework on the issue of marine litter is comprehensive and evolving. Key policy recommendations stemming from the work fall within three broad categories: (i) design and prevention, (ii) waste management, (iii) marine litter, and (iv) technological innovation.

Design and prevention recommendations include (i) strengthening the focus on prevention, (ii) mandating the eco-design for plastics and polymers, (iii) accelerating the phase-out of harmful additives in plastics, (iv) expanding the bans on the destruction of unsold goods included in the Eco-design Regulation to include plastic-intensive product groups, (v) closing loopholes in the Single Use Plastics Directive and expanding its scope so that it is not limited to only plastic single-use products, (vi) mandating the reporting on the consumption of very lightweight plastic bags and heavyweight plastic bags and exploring relevant reduction targets, and (vii) supporting small and medium enterprises in adopting digital product passports.

Policy recommendations on waste management focus on (i) supporting a levelled circular economy approach across Europe by helping underperforming countries through capacity-building and financial support, (ii) addressing difficult-to-recycle plastics through investments in chemical recycling technologies, (iii) incentivizing investments in Europe’s recycling infrastructure, (iv) curbing cigarette butt pollution as this remains an important problem which is unlikely to be resolved through extended producer responsibility alone, and (v) optimizing the management of ship-generated waste.

The recommendations that specifically address marine litter, with a focus on seabed litter, are: (i) improving data collection, sharing and interoperability through standardized data collection and sharing mechanisms as well as open-access, harmonized databases, (ii) mandating seabed litter monitoring and removal in European legislation, such as the Marine Strategy Framework Directive, and (iii) tackling abandoned, lost or discarded fishing gear through the provision of appropriate and free-of-charge disposal facilities, investment in technologies and mechanisms for locating and removing lost gear, and research into fit-for-purpose alternative materials.

Finally, in terms of technological innovation two main policy recommendations emerge: (i) harmonizing cross-border regulation for autonomous marine technologies to facilitate innovation, cross-border collaboration and the widespread adoption of these technologies, and (ii) enabling SMEs and start-ups to scale innovative marine solutions through dedicated funding mechanisms and simplified regulatory pathways for testing and deployment.

## Conclusions

Marine litter, particularly on the seafloor, remains a persistent and under-addressed challenge in European waters, requiring coordinated policy, innovation, and investment. While the EU has developed a comprehensive set of strategies and regulations, gaps in implementation, harmonisation, and enforcement limit their full effectiveness. Furthermore, real uptake of technological innovations to address marine litter, such as those developed by SeaClear2.0, depends on enabling policies, consistent funding mechanisms, and regulatory alignment across Member States. To ensure lasting impact, these efforts must be supported by inclusive, co-developed policy processes that translate ambition into action and empower both innovators and communities to be part of the solution. This paper has presented an initial set of policy recommendations towards this end, which will be discussed and validated through a high-level policy roundtable before being published in a White Paper.

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# Session 6: Circular economy in waste management

# Deep Eutectic Solvents and Microwave Heating for Efficient Oligosaccharide Recovery from Apple Tree Pruning Waste

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**keywords:** *oligosaccharides; deep eutectic solvent; apple tree pruning: biorefinery; autohydrolysis*

## Introduction

In 2024, global apple production reached 84.3 million metric tons (USADA, 2024), with a significant portion processed into products such as juice, cider, and dried goods. The Basque Country, known for its strong cider-making tradition, hosts over 100 cider houses. This industry generates not only direct waste from cider production but also large amounts of lignocellulosic waste from apple tree pruning. This pruning residue, rich in cellulose, lignin, and hemicelluloses, presents a valuable opportunity for biorefinery applications. However, its decentralized generation and the small scale of producers complicate its valorization. Oligosaccharides extracted from such biomass have shown antioxidant and prebiotic properties, making them attractive for their use in food and packaging industries. Among extraction methods, autohydrolysis stands out for its environmental friendliness, though improvements in energy efficiency are still needed.

To address these challenges, recent research has focused on using deep eutectic solvents (DESs) and process intensification techniques like microwave treatment. DESs, composed of hydrogen bond donors and acceptors, offer advantages such as low vapor pressure, chemical stability, and tunable solubility, making them promising green alternatives to water. Recent studies have confirmed the ability of these solvents to fractionate lignocellulosic biomass (Baraka et al. 2025). Microwaves, on the other hand, enhance biomass fractionation by promoting cell disruption, enabling faster and potentially more efficient oligosaccharide extraction. Studies have shown that microwave-assisted processes can achieve similar or better yields in significantly shorter times, supporting their growing use in sustainable biorefinery strategies (Dávila et al. 2021).

This work aimed to optimize oligosaccharide extraction from apple pruning waste. A conventional autohydrolysis served as a reference, followed by microwave-assisted treatments at varying times. Finally, water was replaced with DES in the microwave reactor to enhance yields.

## Materials and methods

A local farmer in the Basque Country kindly supplied the apple tree pruning residues in the winter of 2024. Before being used, the raw material was dried in darkness, ground and sieved to obtain a particle size <5 mm.

The autohydrolysis was firstly conducted in a conventional way using a steel reactor (1.5 L stainless steel 5100 Parr reactor with a 4848 Parr controller), and secondly by intensifying the process via microwaves (MILESTONE flexiWAVE). For conventional autohydrolysis, previously optimized conditions for the same feedstock were used, more specifically a solid-liquid ratio (SLR) of 1:10, 180 °C and 30 min (García eta l. 2017). An attempt was then made to replicate the conditions in the microwave reactor. In this case, the SLR and the temperature (180 °C) were maintained, but the reaction time was lowered to avoid burning the raw material, studying the microwave-assisted autohydrolysis at 5, 12.5 and 20 min. The microwave power was set at 500 W for this work.

In order to minimize the impact of the process to obtain oligosaccharides, the use of choline chloride:lactic acid (ChCl:LA) DES as solvent for the microwave-assisted autohydrolysis process was studied. In this work, the influence of the time (5, 12.5 and 20 min) in the process was studied and the SLR (1:10), the employed

DES (ChCl:LA 1:10), and the reaction temperature (80 °C, set on the basis of previous experiments) were fixed.

Once the reaction time had finished, the solid and liquid phases were separated by filtration. The liquid phase or autohydrolysis liquor, which contained the solubilized products of the hemicellulosic fraction, was characterized, while the solid phase was washed with water and stored at 4 °C. The autohydrolysis liquor was subjected to a post-hydrolysis step using 4% sulfuric acid as described by Dávila et al. (2017) to determine the oligosaccharide content in the autohydrolysis liquors. Quantification of the produced monosaccharides and acetic acid was also carried out by HPLC.

## Results and discussion

Conventional autohydrolysis in the reactor at 180 °C yielded an oligosaccharide amount of 3.42 g oligosaccharide (OS)/L, while the amount of monosaccharides obtained was 3 times more. Applying the process parameters in a microwave reactor, lower oligosaccharide values were obtained than in the conventional reactor (between 0.16 and 1.5 g OS/L, for the 5 min and 20 min, respectively). The amount of monosaccharides was similar to that obtained in the conventional reactor for the times of 20 and 12.5 min (10.8 and 10.13 g monosaccharide (MS), respectively), while it was lower when studying 5 min (8.84 g MS/L).

To favor oligosaccharide over monosaccharide extraction, the microwave reactor temperature was lowered to reduce process severity. When autohydrolysis was performed in the microwave reactor at 80 °C, a significant reduction in monosaccharide content was observed, with values ranging from 2.04 to 6.07 g MS/L for reaction times between 5 and 20 min. Regarding oligosaccharides, using a 20 min reaction time yielded a concentration similar to that obtained in the conventional reactor at 180 °C (3.15 g OS/L).

Finally, to further improve the results, the use of ChCl:LA as a solvent for extraction was investigated. In this study, the amount of monosaccharides obtained was significantly reduced, with values between 0.07 and 2.57 g MS/L, while the oligosaccharide content exceeded 10 g OS/L at 12.5 and 20 minutes. Since the oligosaccharide yields at 12.5 and 20 min were similar (10.6 and 10.9 g OS/L, respectively), it is considered that the maximum oligosaccharide yield is already achieved at 12.5 minutes, clearly surpassing the values obtained with the conventional method.

## Conclusions

Microwave-assisted autohydrolysis with ChCl:LA at 80 °C significantly reduced monosaccharide formation and improved oligosaccharide selectivity compared to conventional conditions, yielding over 10 g/L of oligosaccharides at 12.5 min with minimal monosaccharide content.

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## References

Baraka, F., Langari, M.M., Beitia, I., Dávila, I., Labidi, J., Morales, A., Sillero, L., 2025. Enhancing lignocellulosic biomass pretreatment with choline chloride-based deep eutectic solvents. J. Environ. Chem. Eng. 13, 117087.

Dávila, I., Gullón, P., Andrés, M.A., Labidi, J., 2017. Coproduction of lignin and glucose from vine shoots by eco-friendly strategies : Toward the development of an integrated biorefinery. Bioresour. Technol. 244, 328–337.

Dávila, I., Gullón, P., Labidi, J., 2021. Influence of the heating mechanism during the aqueous processing of vine shoots for the obtaining of hemicellulosic oligosaccharides. Waste Manag. 120, 146–155.

García, A., Spigno, G., Labidi, J., 2017. Antioxidant and biocide behaviour of lignin fractions from apple tree pruning residues. Ind. Crops Prod. 104, 242–252.

USDA, United States Department of Agriculture, Foreign Agricultural Service. Available at: https://www.fas.usda.gov/data/production/commodity/0574000.

# From Waste to Value: Pilot-Scale EV Battery Recycling in Armenia

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***keywords:*** *Lithium-ion batteries; EV battery recycling; Critical raw materials (CRM); Armenia*

## Introduction

The transition to electromobility is accelerating globally, driven by the urgent need to decarbonize transport. However, it brings a new environmental and resource challenge: the end-of-life management of lithium-ion batteries (LIBs). These batteries, widely used in electric vehicles (EVs), contain critical raw materials (CRMs) such as lithium, cobalt, nickel, and manganese. As demand for EVs grows, the accumulation of spent LIBs is becoming a significant waste stream with both environmental and strategic implications. Armenia, a country currently in the early stages of e-mobility adoption, is projected to generate up to 500 tons of EV battery waste annually by 2028–2029, based on import trends and vehicle lifespan modeling. This research offers a timely opportunity to establish a localized, sustainable recycling system rooted in hydrometallurgical recovery.

## Materials and methods

This study presents a pilot-scale hydrometallurgical process developed at the National Polytechnic University of Armenia, designed for the treatment of up to 850 kg/day of black mass extracted from spent LIBs.

The process consists of mechanical pretreatment, vacuum drying, sulfuric acid leaching (with $H_2O_2$ as oxidant), solid-liquid separation, selective solvent extraction for Co/Ni, and crystallization for Li recovery as $Li_2CO_3$. Reactor volumes, dosing strategies, and filtration systems were selected based on lab-scale kinetics and scaled using solid-to-liquid ratio optimization (1:3 w/v) and residence time calibration. Energy and water balances were also modeled to assess the feasibility of 24-hour batch operation.

***Table 1.*** *Key Calculation Results for Pilot-Scale Li-ion Battery Recycling (850 kg/day Black Mass)*

| Parameter | Value | Notes |
|---|---|---|
| **Black Mass Input (per day)** | 850 kg | From shredded LIBs |
| **Moisture Content (pre-drying)** | ~10–15% | Removed in vacuum drying step (~85–130 kg $H_2O$) |
| **Liquid-to-solid Ratio (Leaching)** | 3:1 (v/w) | Total leaching solution: ~2,550 L/day |
| **Sulfuric Acid Consumption** | ~530 L/day (98% $H_2SO_4$) | Adjusted for neutralization and leaching stoichiometry |
| **Hydrogen Peroxide ($H_2O_2$)** | ~85–100 L/day (30% w/w) | Oxidant for Co/Ni/Mn |
| **Leaching Efficiency** | Li: 90+%, Co: 95%, Ni: 85% | Under $T = 80°C$, $pH < 2$, 4–6 h residence time |
| **Crystallized $Li_2CO_3$ (product)** | ~95–110 kg/day | ~11–13% Li content in black mass, >99.5% purity |
| **Co/Ni Electrolyzer Output** | Co: ~40–50 kg/day, Ni: ~50–60 kg/day | After SX + electrowinning |

| | | |
|---|---|---|
| **Water Consumption** | ~3,700 L/day | Including dilution, cooling, washing; ~925 m³/year |
| **Estimated Energy Use** | ~1,200–1,600 kWh/day | Including shredding, drying, leaching, pumps, SX, electrolysis |

**Results and discussion**

Experimental trials demonstrated metal recovery efficiencies of over 90% for lithium, 95% for cobalt, and 85% for nickel, under optimized leaching conditions (T = 80 °C, pH < 2, 4–6 h residence time). The recovered lithium carbonate reached battery-grade purity (>99.5%) after single-stage crystallization. Water and reagent reuse strategies reduced freshwater demand to <4 m³/day for full-scale operation. The integration of a modular electrowinning cell for Co/Ni further improved purity and enabled downstream re-use in cathode precursor production. Economically, the projected 500 t/year waste stream in Armenia could sustain a localized plant with minimal import dependence, offering a 5 year payback period under current CRM prices. Beyond the technical process, this work highlights the strategic importance of urban mining — a modern approach that views waste streams as secondary resource reserves. In resource-constrained regions like Armenia, where geological mining of lithium or cobalt is not currently viable, urban mining provides a powerful complement. Reclaiming critical elements from post-consumer batteries reduces external dependency, supports EU-aligned circular economy goals, and positions Armenia as a regional actor in CRM supply resilience.

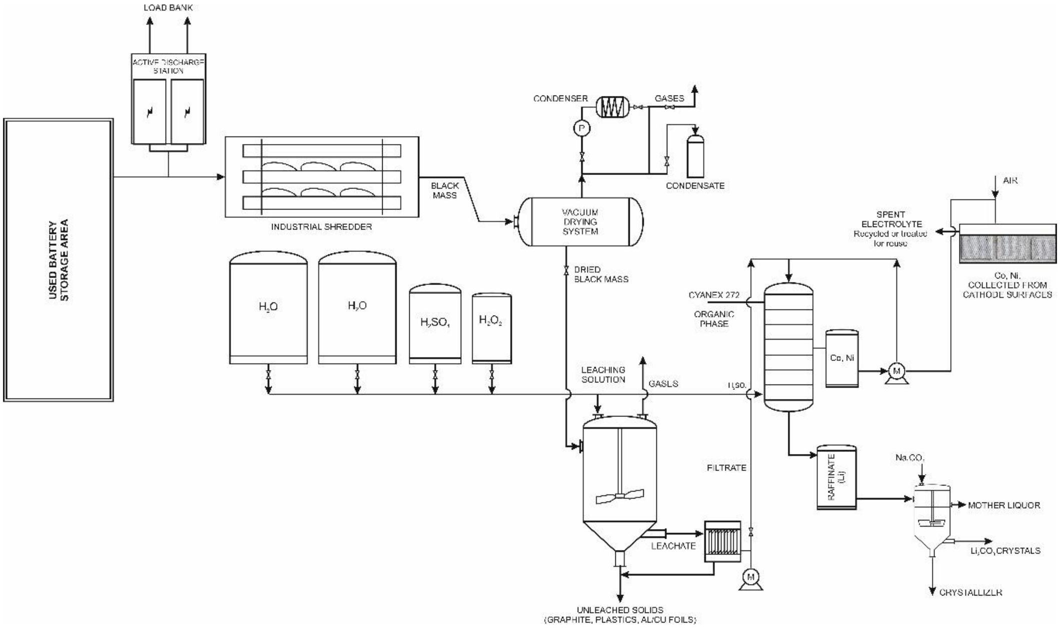

***Figure 1.*** *Schematic Diagram for 850 kg/day black mass lithium-ion battery recycling process*

**Conclusions**

This pilot project demonstrates the technical and economic viability of a scalable LIB recycling process tailored for Armenia's projected waste stream by 2028–2029. The use of hydrometallurgical methods ensures high CRM recovery rates while maintaining environmental compatibility. As EV adoption grows, establishing local recycling capacity will be crucial for Armenia's resource security and green transition. Moreover, embedding urban mining practices into national waste and industrial policy can catalyze new circular industries and align the country with international best practices in sustainable materials management.

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**References**

V.Marukhyan, S.Tatikyan, T.Tatikyan, The Use of Renewable Energy Resources for Ensuring the Energy Security of the Republic of Armenia, in Proceedings of the NPUA scientific conference, Electrical Engineering, Energetics, Yerevan, 2023, N1.

S.Nardini, M. De Rosa, Overview of the Research Methodologies and Approaches in Energy and Climate

Security, HORIZON-WIDERA-2023-ACCESS-02-02, STREACS, D 2., March 27 (2025)

V.Z. Marukhyan, G.P. Vardanyan, A.J. Khachatryan, Analysis of energy storage methods and accumulation systems, in Proceedings of the NPUA scientific conference, Electrical Engineering, Energetics, Yerevan, Armenia, /2024, N

# Metal Leaching from E-Waste Using Phosphonium-Based Hydrophobic Deep Eutectic Solvent

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***keywords:*** *hydrophobic deep eutectic solvents, metal Leaching, printed circuit boards, e-waste*

## Introduction

The fast-paced rise in digital economies has accelerated the generation of waste consumer electronics around the globe. Waste electronic devices contain a wide variety of toxic substances such as heavy metals (e.g., arsenic, mercury, cadmium, lead, cobalt, nickel), inorganic pigments, and halogenated organic additives (e.g., fire retardants). The continuously increasing volume of improperly discarded landfill e-waste warrants unprecedented management efforts due to environmental concerns from the release of hazardous materials and the loss of useful secondary resources [1]. There is considerable scope in the recovery of various elements from e-waste owing to their appreciable content in technology-critical metals (e.g., gold, silver, and palladium), base metals (copper, aluminum), and rare earth elements [2].

Numerous methods are reported for the extraction and recovery of metals from e-waste among which hydrometallurgy is highly quantitative and requires the least thermal energy investments. However, traditional chemical treatments employed in hydrometallurgy for leaching, extraction, and recovery, often generate corrosive liquid waste and require multi-stage sample processing. In this regard, alternative environmentally-conscious approaches are highly desirable [3].

Deep eutectic solvents (DESs) are a promising class of designer solvents for advancing various applications such as organic synthesis, ionothermal and solvothermal synthesis, resource extraction from biomass, and catalytic reactions. In solvometallurgy, such solvents are attracting increasing attention from the scientific community owing to their (i) low vapor pressure, (ii) tunable physical and chemical properties, (iii) straightforward preparation, and (iv) adequate physicochemical stability on storage. The present work examines the development of five phosphonium-based hydrophobic deep eutectic solvents (HDESs) for selective metal leaching from waste mobile phone printed circuit boards (PCBs).

## Materials and methods

98% methyl triphenylphosphonium bromide (methyl), 98% ethyl triphenylphosphonium bromide (ethyl), 98% n-butyl triphenylphosphonium bromide (butyl), 99% tetrabutyl phosphonium bromide ((butyl)$_4$), 98% n-heptyl triphenylphosphonium bromide (heptyl), ethylene glycol (EG) 99.5% and ICPMS grade aqueous $HNO_3$ (70%.wt), ferrocene (99%) were purchased from different sources and used as received. The DESs were prepared by mixing each phosphonium bromide precursor with EG at a 1:2 mol ratio, except for (butyl)$_4$ (1:8). Each mixture was heated at 60 °C in an oil bath for homogenous mixing. The structural analysis of the prepared HDESs is elucidated via complementary NMR, FTIR, and GC-MS analyses. A list of physicochemical properties including the room temperature viscosity, pH, contact angle, and ionic conductivity were determined. The solvents HDESs were used for metal leaching from pulverized mobile phone waste PCBs under static conditions and at variable processing temperatures (40-70 °C) using a sample mass loading of 100 mg in 1 mL of HDESs.

## Results and discussion

The conductivity of the HDESs at room temperature (Fig.1A) dropped with increasing alkyl chain length in the phosphonium component in the order of methyl (38.44 µS/cm), ethyl (31.37 µS/cm), butyl (24.31 µS/cm), and heptyl (17.87 µS/cm) . The (butyl)$_4$ system with a salt-to-EG mol ratio of 1:8, had a greater conductivity value (114.61 µS/cm) due to lower viscosity compared to the other HDESs. All HDES were found to be acidic, with a pH value (Fig.1B) decreasing in the order of methyl (5.32), ethyl (5.24), butyl (4.81), (butyl)$_4$ (3.79), and heptyl (2.51). The electrochemical properties of two HDESs, (butyl)$_4$ and heptyl, selected for their high and low conductivity values, respectively, were evaluated for the ferrocene redox chemistry. Their cyclic voltammograms (Fig.1C) predict their practical usage as electrolytes in emerging applications (e.g. non-aqueous redox flow batteries). Among the prepared series of HDESs, the heptyl system remained liquid for about 90 days of storage at room temperature, suggesting adequate physical stability compared to the other solvent systems. The shelf life and structural integrity of the heptyl HDES were also confirmed by FTIR after heating at temperatures as high as 70 °C, whereas the other HDESs were thermally stable up to 60 °C and disintegrated beyond 80 °C. Given their acidic character and thermal stability range, the prepared HDESs were explored for the static metal leaching from pulverized waste PCBs at mild temperatures (40-70 °C). An obvious color change in the HDESs was observed after the leaching Fig.1D,E. ICP-MS analysis of the leaching efficiencies indicated selective Cu and Sn leaching by the various HDESs, with the yield generally increasing with the treatment temperature (Fig.1F,G). The heptyl system showed excellent leaching efficiency for copper (62%) and tin (88%) at 70 °C. Detailed solvent characterizations, leaching studies, miscibility studies, and electrochemical properties are established. A mechanistic analysis of the selective leaching with the HDESs is established using ICP-MS, GC-MS and NMR studies.

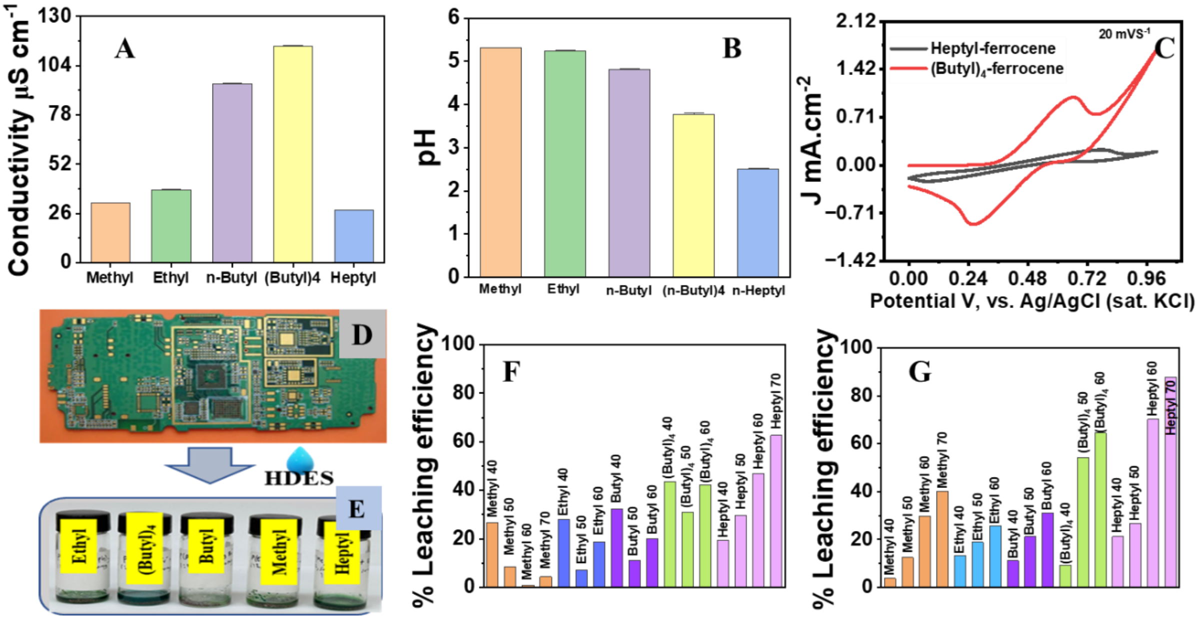

**Figure 1** (A) Conductivity, (B) pH of the HDESs, (C) Cyclic voltammograms of ferrocene as redox compound in heptyl and (butyl)$_4$ HDESs as novel organic electrolytes, measured at room temperature. (D) optical image of a waste mobile PCB, (E) visible color change of the HDESs after static leaching experiments using pulverized PCB samples. Leaching efficiency of the reported HDESs as a function of the processing temperature for (F) copper and (G) tin.

## Conclusion

Phosphonium-based HDESs derived from different phosphonium bromide and ethylene glycol are reported. The electrochemical properties, conductivity, pH and viscosity of the solvents were also evaluated. The acidic character of the HDESs was examined for metal leaching from used mobile PCBs under static conditions and mild processing temperatures (40-70 °C). At a fixed mass loading, the heptyl HDES showed excellent leaching efficiency for Cu (62%) and Sn (88%) Sn at 70 °C.

## References

1) K. Liu, Q. Tan, J. Yu, M. Wang., 2023. A global perspective on e-waste recycling. *Circular Economy.*, 2, 1, 100028.
2) Bookhagen, B., Koeberl, C., Juang, L., & DeRosa, D. A., 2017. Mineral resources in mobile phones: a case study of boston and vienna teachers and students. *Journal of Geoscience Education*, *65*, 2, 113–125.

3) Z. Wang, X. Zhao, Y. Chen, C. Wei, J. Jiang., 2024. A review of designable deep eutectic solvents for green fabrication of advanced functional materials., *RSC Sustain*., 738–756.

# From Urban Pruning to Sustainable Films: Unlocking the Value of Tree Residues

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***keywords:*** *biorefinery, urban pruning, lignin, films*

## Introduction

The presence of urban trees is essential for enhancing environmental quality in cities, although managing the waste generated by their regular pruning often presents both logistical and environmental challenges. Nevertheless, this waste, composed mainly of lignocellulosic biomass—rich in lignin, cellulose, and hemicellulose—offers a significant opportunity for sustainable valorisation through the production of high value-added products. In this case study conducted in San Sebastián (Spain), a comprehensive process was proposed to valorise pruning waste from the London plane tree, the most abundant species in the local urban landscape. Special emphasis was placed on extracting lignin, which was then combined with chitosan as a matrix to formulate films with potential applications in the food industry. The development of these films exhibited enhanced physicochemical properties, particularly with respect to thermal stability and ultraviolet radiation resistance, thereby supporting their potential as environmentally friendly alternatives to conventional plastics. This study underscores the value of urban pruning waste as a promising renewable raw material for the fabrication of sustainable materials. Furthermore, these findings provide a foundation for future research involving this and other species, contributing to the development of renewable resources while offering an effective strategy for managing this challenging category of urban waste.

## Materials and methods

Lignin utilised in the preparation of the films was obtained following the procedure outlined in Figure 1. Initially, after collection and conditioning of the raw material, an autohydrolysis step was performed to extract oligosaccharides, which were reserved for other applications, in accordance with the methodology described by Dávila et al. (2017). Subsequently, the autohydrolysed solid underwent a delignification process under the conditions specified by Morales et al. (2020). Finally, the films were fabricated according to the protocol reported by Izaguirre et al. (2021). For this study, different amounts of lignin were incorporated at concentrations of 0%, 0.1%, 0.5%, and 1% (w/w), relative to the weight of the chitosan employed.

## Results and discussion

Various techniques were employed to characterise the films. FTIR spectra revealed bands attributed to hydroxyl (O–H) and primary amine (N–H) groups, with increased intensity of signals related to methyl groups and conjugated carbonyls as lignin content rose, suggesting the formation of intermolecular bonds between lignin and chitosan. X-ray diffraction (XRD) analysis showed a reduction in the semicrystalline crystallinity of chitosan upon lignin addition, indicating structural alteration. Thermogravimetric analysis (TGA) demonstrated a significant increase in thermal degradation temperature and char residue, evidencing improved thermal stability with lignin incorporation (Table 1). UV-vis spectra revealed a decrease in transmittance in both the visible and UV regions, enhancing ultraviolet radiation blocking capacity (Table 1).

Mechanically, lignin promoted a considerable increase in tensile strength and Young's modulus, accompanied by a slight decrease in elongation at break, reflecting increased material rigidity. These findings indicate effective integration of lignin into the chitosan matrix, optimising its functional properties without compromising structural integrity.

***Table 1.*** *Experimental results of thermal degradation and optical properties of films*

| **Formulation** | **TGA** | | **UV-vis** |
|---|---|---|---|
| | **Degradation Temperature (T50°C)** | **Final residue (%)** | **UV protection** |
| **L 0% (no lignin)** | Baseline value | 27.77 | Low |
| **L 0.1%** | Slight increase | Slight increase | Slight improvement |
| **L 0.5%** | Greater increase | Greater increase | Improved protection |
| **L 1%** | Significant increase (≈45°C) | Highest (34.01) | Maximum UV protection |

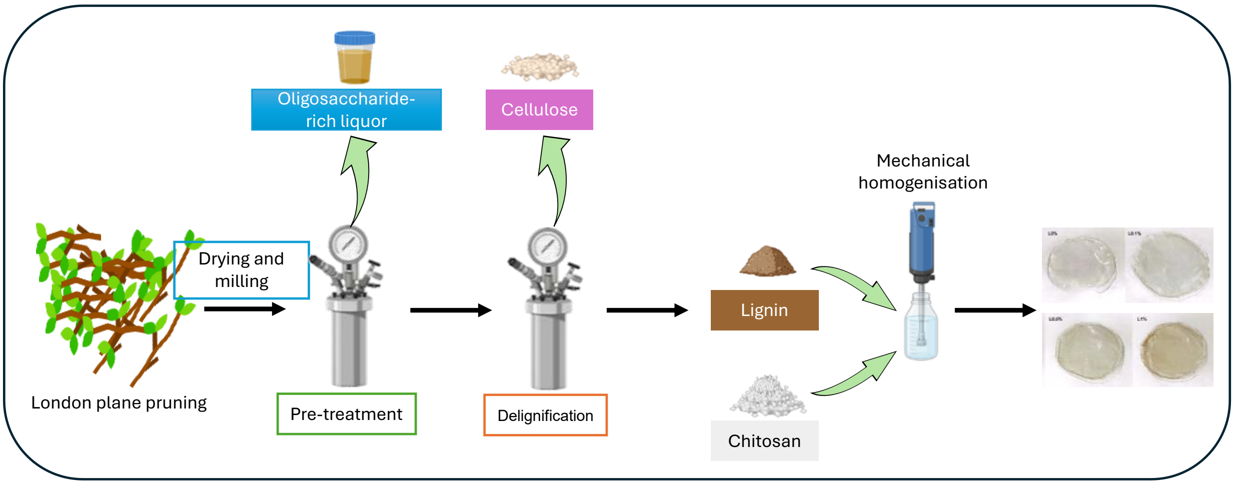

***Figure 4.*** *Process schematic for the preparation of films*

## Conclusions

The incorporation of lignin into chitosan films enhanced their structural, thermal, optical, and mechanical properties, confirming good compatibility between both biopolymers. These improvements were achieved even at low lignin concentrations. Importantly, the use of lignin derived from urban pruning waste adds significant value, promoting waste valorisation within a circular economy framework. This approach not only improves film performance but also contributes to more sustainable and eco-friendly material development.

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## References

Dávila, I., Gullón, P., Andrés, M.A., Labidi, J., 2017. Coproduction of lignin and glucose from vine shoots by eco-friendly strategies: Toward the development of an integrated biorefinery. Bioresour. Technol. 244, 328–337.

Izaguirre, N., Gordobil, O., Robles, E., Labidi, J., 2020. Enhancement of UV absorbance and mechanical properties of chitosan films by the incorporation of solvolytically fractionated lignins. Int. J. Biol. Macromol. 155, 447–455.

Morales, A., Hernández-Ramos, F., Sillero, L., Fernández-Marín, R., Dávila, I., Gullón, P., Erdocia, X., Labidi, J., 2020. Multiproduct biorefinery based on almond shells: Impact of the delignification stage on the manufacture of valuable products. Bioresour. Technol. 315.

# Session 7: Sustainable agriculture and waste management

# Traditional and Indigenous Knowledge and Conservation Practices of Forest Food Species in Guinean Forests of West Africa (GFWA) Biodiversity Hotspot

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***Keywords:*** *Traditional Ecological Knowledge; Forest Food Species; Guinean Forests of West Africa; Biodiversity Conservation; West Africa*

## Introduction

he Guinean Forests of West Africa (GFWA) are globally recognized as a biodiversity hotspot that supports numerous forest food species critical to the nutrition, health, and livelihoods of forest-dependent communities. Traditional and Indigenous Knowledge (TIK) has long played a pivotal role in the sustainable use and conservation of these species. However, such knowledge is increasingly under pressure from socio-environmental transformations and limited policy recognition.

## Materials and Methods

This review synthesizes current literature on ethnobotanical, ecological, and cultural aspects of forest food species conservation in the GFWA. Peer-reviewed sources and grey literature were examined to identify key species, traditional conservation practices, and the institutional and environmental factors influencing TIK systems.

## Results and Discussion

The study highlights a diverse array of tree-based food species commonly used in GFWA, including *Adansonia digitata*, *Annona senegalensis*, *Blighia sapida*, *Dacryodes edulis*, *Dialium guineense*, *Garcinia kola*, *Irvingia gabonensis*, *Parkia biglobosa*, *Spondias mombin*, *Treculia africana*, *Vitex doniana*, *Xylopia aethiopica*, and *Ziziphus mauritiana*. These species provide fruits, seeds, leaves, and other plant parts essential to local diets and economies.

Traditional conservation practices include taboos, sacred groves, seasonal bans, and customary institutions that help regulate use and promote regeneration. Despite their effectiveness, TIK systems are threatened by deforestation, climate variability, generational knowledge loss, urbanization, and marginalization in formal conservation frameworks. Notably, there is limited integration of traditional governance with scientific forest management and national conservation policies. Research gaps persist regarding cross-cultural variation in practices, species-specific strategies, and mechanisms for policy integration.

## Conclusions

Preserving TIK is essential for sustaining biodiversity and local food systems in the GFWA. There is an urgent need for transdisciplinary approaches that bridge indigenous and scientific knowledge systems, and for policy reforms that recognize and empower traditional forest stewardship as part of broader conservation and resilience strategies.

## References

1. Assogbadjo, A.E., Avakoudjo, G. (2024). Traditional and Indigenous Knowledge and Conservation Practices of Forest Food Species in GFWA. *Literature Review*.
2. IPBES (2019). Global assessment report on biodiversity and ecosystem services.
3. Cunningham, A.B. (2001). Applied Ethnobotany: People, Wild Plant Use and Conservation. Earthscan PublicationsFAO (2015).
4. FAO (2015). Indigenous peoples and forest management.

# Optimization of Microwave Assisted Delignification of Apple Tree Pruning Using Deep Eutectic Solvents

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***keywords:*** *apple tree pruning; delignification; deep eutectic solvents; biorefinery.*

## Introduction

Apples are widely produced both for their raw consumption or for their industrial processing in order to produce juice and other fermented beverages, such as cider. In fact, in 2023-2024, the global production of apples reached 84.3 million metric tons (USDA, 2024). Cider is an alcoholic beverage obtained only by the complete or partial fermentation of apples. In 2023, 25,282.92 hL were consumed in Europe, and Spain is the second leading country in the European cider market, with 1,042,650 hL in 2018-2023 period (AICV, 2024). Besides the fruit residues that this industry produces, apple tree pruning (ATP) waste is also annually generated in huge amounts. This residue belongs to the lignocellulosic biomass, which is mainly composed by cellulose, hemicelluloses and lignin, and could be further valorized in order to obtain both chemicals or products for many added-value applications by diverse biorefinery processes. Till date, many processes have been applied for the fractionation of lignocellulosic biomass, among which the chemical and physicochemical ones have been the most remarkable. Nevertheless, the elevated energetic demand, costly equipment and/or non-environmentally friendly steps/reagents, have leaded to emerging novel, innovative and sustainable techniques and solvents such as ionic liquids and Deep Eutectic Solvents (DESs) (Baraka et al., 2025). Moreover, in order to overcome the aforementioned drawbacks, the use of intensification techniques such as ultrasounds or microwaves is being explored. In this context, the aim of the present work was to explore the effect of microwaves on the delignification of ATP using a DES.

## Materials and methods

ATP residues were kindly supplied by a local farmer, and they were subsequently milled and sieved to a particle size < 5 mm and subjected to a pre-treatment. The pre-treatment of ATP was performed by microwave assisted extraction at previously optimized conditions: 80 °C, 12.5 min and LSR of 10:1 with choline chloride-lactic acid (ChCl:LA) (1:10). The pre-treated solid (P-ATP) was then delignified using a microwave reactor (MILESTONE flexiWAVE) and ChCl:LA (1:2) DES. The optimization of the delignification was performed employing a three-level two factor experimental design with 9 experiments and 2 replicates of the central point. The selected input variables were time ($x_1$, min) and temperature ($x_2$, °C), and the output variables were the delignification yield ($y_1$, %) and the solubility ($y_2$, %). The optimization was performed by a response surface methodology (RSM), where the delignification yield was maximized and the solubility minimized. The data were fitted using a secondary-order polynomial described by Eq.1.

$$y = \beta_0 + \sum_1^2 \beta_i x_i + \sum \sum_{i<j=2}^2 \beta_{ij} x_i x_j + \sum_{i=1}^2 \beta_{ii} x_i^2 + \varepsilon \qquad \textbf{\textit{(Eq. 1)}}$$

where $y$ is the predicted response, $\beta_0$ is the constant coefficient, $\beta_i$, $\beta_{ij}$, and $\beta_{ii}$ are the coefficient of interaction, linear and quadratic, respectively, and $x_i$ and $x_j$ are the independent variables.

The fitness of the generated model was expressed by the coefficient of determination ($R^2$), significance of the regression coefficients and the F-test value obtained from the analysis of variance (ANOVA).

## Results and discussion

The experimental conditions and results for the 11 experiments are shown in Table 1. A positive correlation was observed for both output variables as the time and the temperature were increased. The minimum delignification and solubility values were observed for the shortest times (5-15 min) and lowest temperature (90 °C). Conversely, the highest delignification yield (86%) and solubility (≈ 58%) was seen for the most severe experiment (25 min at 150 °C).

***Table 1.*** *Experimental conditions and results for each experiment of the design.*

| **Exp.** | **Time (min), $x_1$** | **Temp. (°C), $x_2$** | **Delig. (%), $y_1$** | **Solubility (%), $y_2$** | **Exp.** | **Time (min), $x_1$** | **Temp. (°C), $x_2$** | **Delig. (%), $y_1$** | **Solubility (%), $y_2$** |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 25 | 150 | 86.02 | 57.74 | **7** | 5 | 150 | 75.38 | 44.24 |
| **2** | 15 | 120 | 47.53 | 24.41 | **8** | 15 | 150 | 72.31 | 43.52 |
| **3** | 15 | 120 | 55.71 | 31.07 | **9** | 25 | 120 | 57.75 | 29.47 |
| **4** | 5 | 120 | 39.07 | 21.18 | **10** | 5 | 90 | 24.22 | 8.88 |
| **5** | 25 | 90 | 27.97 | 12.36 | **11** | 15 | 120 | 44.68 | 22.58 |
| **6** | 15 | 90 | 21.91 | 10.02 | | | | | |

The regression parameters in Table 2 showed a good fit of the model, so the optimization was carried out. The optimal conditions were 5 min and 134 °C, which were verified by carrying out a triplicate of this point.

***Table 2.*** *Regression parameters.*

| **Coefficient** | **Delig. (%), $y_1$** | **Solubility (%), $y_2$** | **Coefficient** | **Delig. (%), $y_1$** | **Solubility (%), $y_2$** |
|---|---|---|---|---|---|
| **Intercept ($b_0$)** | 46.76[a] | 25.02[a] | **Variable $x_1x_2$ ($b_{12}$)** | 1.72 | 2.51 |
| **Variable $x_1$ ($b_1$)** | 5.51[c] | 4.21[b] | **Variable $x_1^2$ ($b_{11}$)** | 3.50 | 1.80 |
| **Variable $x_2$ ($b_2$)** | 26.60[a] | 19.04[a] | **Variable $x_2^2$ ($b_{22}$)** | 2.21 | 3.24 |
| **$R^2$** | 0.960 | 0.971 | ***p*-value (F)** | 0.0015 | 0.0007 |

[a] Significant coefficients at a 99% confidence level.
[b] Significant coefficients at a 95% confidence level.
[c] Significant coefficients at a 90% confidence level.

## Conclusions

In this study the optimization of a microwave assisted delignification was performed for ATP using ChCl:LA as solvent. The results showed the high adequacy of the model, leading to an optimal point with reduced operational time and temperature, but a promising delignification yield.

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## References

AICV. European Cider; Fruit Wine Association. European Cider Trends 2024. Available online: https://aicv.org/en/publications.

Baraka, F., Langari, M.M., Beitia, I., Dávila, I., Labidi, J., Morales, A. and Sillero., L., 2025. Enhancing lignocellulosic biomass pretreatment with choline chloride-based deep eutectic solvents. *J. Environ. Chem. Eng.*, 13, 117087.

USDA, United States Department of Agriculture, Foreign Agricultural Service. Available at: https://www.fas.usda.gov/data/production/commodity/0574000.

# Application of Remote Sensing Technologies for Sustainable Forest Fire Monitoring and Management

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***keywords:*** *remote sensing of the Earth, Super View, Sentinel-2, deforestation, temperature anomalies, forest fires; organic waste.*

## Introduction

This study presents the results of research on the application of Earth remote sensing (ERS) data for operational monitoring of forest ecosystems, particularly in detecting and assessing the consequences of wildfires. A new concept – "area of active thermal anomalies" – is introduced, enabling preliminary identification of territories affected by fire, even under conditions of cloud cover or absence of data from specific satellites. The effectiveness of satellite data for detecting thermal anomalies, fire outbreaks, and changes in forest cover with varying time lags has been substantiated. The proposed methodology allows for comprehensive monitoring of forested areas, detection of illegal logging, identification of logging types and tree species affected, spatial analysis of boundaries, and assessment of fire-induced damage. The results can serve as a tool for informed decision-making in the fields of environmental safety and forest management.

## Materials and methods

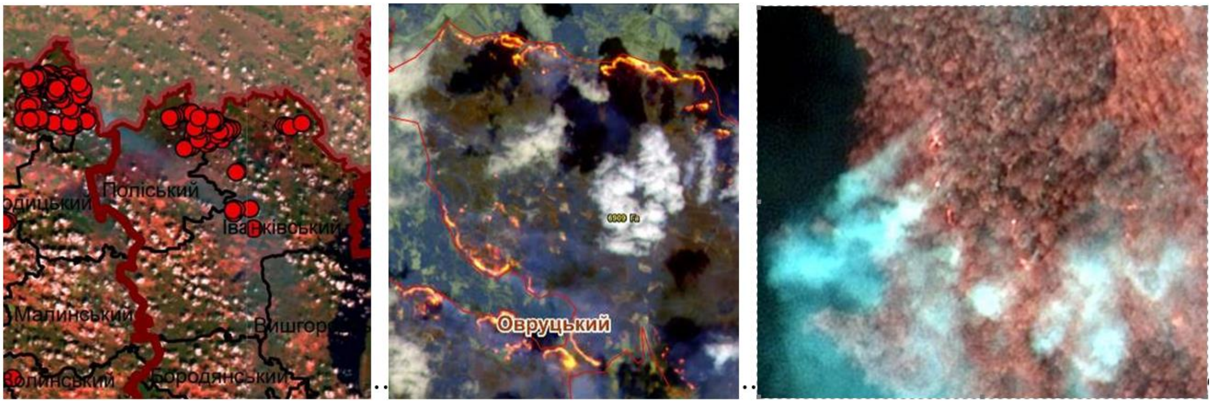
The method used in this study involves a sequential workflow. First, test areas were identified—specific forest regions that had undergone changes due to fires or logging, with available ground-based information from forest enterprises. Next, the accessibility of satellite imagery was analyzed, and suitable Earth Observation (EO) data were selected for further processing, taking into account cloud coverage, sun angle, and image acquisition parameters. The selected imagery was then processed in a GIS environment (ArcGIS, QGIS), using specific spectral bands to detect thermal anomalies. Image analysis was conducted using data from SuperView-1, Sentinel-2, and TERRA/AQUA (MODIS) satellites. This stage resulted in the identification of point or area-based thermal anomalies, which were interpreted as fire outbreaks. If necessary, thematic maps of forest cover changes were generated, followed by a comprehensive description of the results.

The proposed methodology enables effective satellite monitoring of forest areas and supports rapid response to wildfire events. It makes it possible to determine the administrative affiliation of a forest parcel to a specific forestry unit, block, and compartment. The approach also allows for the acquisition of low- and medium-resolution EO data with detected thermal anomalies and facilitates immediate processing and delivery of information to end users (such as foresters) in convenient formats [1-2]. Additionally, high-resolution satellite imagery can be used to identify changes in forest cover related to logging, burn scars, tree diseases, and other events. At the final stage, thematic maps are generated, and geospatial portals are populated with up-to-date data.

## Results and discussion

Thermal anomalies, hotspots, and wildfires were identified based on EO data from various satellites, according to the described methodology (Fig. 1).

The use of satellite imagery in the infrared (IR) range is a key step in the process of remote forest fire detection. IR images allow for the rapid identification of thermal anomalies, which may indicate potential fire outbreaks or areas of elevated surface temperature. These anomalies are then confirmed and refined using imagery from the optical (visible) spectrum, enabling the reliable detection of open fire sources on the ground. In the subsequent stage, the contours and areas of burn scars observed in the satellite imagery are compared with cadastral maps of the forest fund. This spatial comparison allows for accurate localization of affected areas, determination of their administrative affiliation, and assessment of the extent of forest damage.



a b c

***Figure 1.*** *Examples of images with identified thermal anomalies from MODIS data (a), hotspots from Sentinel-2 data (b), and wildfires from SuperView data (c).*

As a result of the research, the authors introduced the concept of the "area of active thermal anomalies," which enables the preliminary estimation of the territories affected by wildfires in cases where their exact boundaries cannot be determined (due to cloud cover or the absence of satellite imagery). This indicator reflects the minimum area of land damaged by fire, based on the identified thermal anomalies (TAs) (Fig. 2).

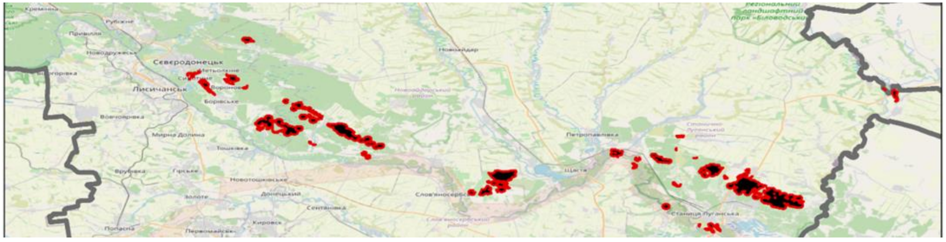


***Figure 2.*** *Example of a map of active thermal anomaly areas.*

## Conclusions

The concept of the "area of active thermal anomalies" was introduced, allowing for preliminary identification of fire-affected areas even in the absence of direct satellite imaging due to cloud cover or data gaps. This indicator reflects the minimum area impacted by fire based on interpreted thermal anomalies.

The study scientifically substantiates the feasibility of using ERS data for comprehensive monitoring of forest resources, enabling effective control and informed decision-making by relevant ministries and agencies.

The proposed remote sensing methodology using high-frequency satellite imagery of large forested areas enables:

- detection of forest cover changes;
- identification of the timeframe, type of logging (clear-cutting or selective), and affected tree species;
- delineation of site boundaries and identification of violations of logging regulations;
- detection of fire outbreaks and geolocation of fire epicenters;
- monitoring of wildfire dynamics and forecasting of potential spread;
- assessment of environmental and economic damage caused by fires.

## References

Szostak, M., Hawryło, P., & Piela, D. (2017). Using of Sentinel-2 images for automation of the forest succession detection. European Journal of Remote Sensing, 51(1), 142–149. https://doi.org/10.1080/22797254.2017.1412272

Opryshko, O.; Pasichnyk, N.; Kiktev, N.; Dudnyk, A.; Hutsol, T.; Mudryk, K.; Herbut, P.; Łyszczarz, P.; Kukharets, V. European Green Deal: Satellite Monitoring in the Implementation of the Concept of Agricultural Development in an Urbanized Environment. Sustainability 2024, 16, 2649. doi: 10.3390/su16072649

# Scalable Deployment of IoT Systems for Sustainable Precision Olive Farming in Laconia, Greece

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***keywords:*** *Precision agriculture; IoT; sustainable farming; olive grove; smart traps; agri-data analytics; pest management; digital education; $CO_2$ mitigation; traceability.*

## Introduction

This paper presents the first-year results from the large-scale application of precision agriculture systems in Laconia (Greece), under the Operational Program (2024–2027) of the Agricultural Olive Oil Cooperatives of Agioi Apostoloi and Palaiopanagia – Producer Organizations (ΟΕΦ), co-funded by the EU. The initiative aims to enhance the environmental, agronomic, and economic sustainability of olive trees cultivation in the region through data-driven decision-making.

In particular the Agricultural Cooperatives of Olive Producer Organizations of Ag. Apostolon and Palaiopanagias (Laconia, Greece) had launched pioneering 4-year Operational Programmes (2024–2027) focusing on the integration of sustainable practices in olive farming.

At their cores lie the application and the deployments of precision agriculture systems, developed by Gridnet SA in collaboration with Pangaea R&D and Intratech sa. This initiative aligns with multiple Sustainable Development Goals (SDGs) including affordable energy, climate action, and life on land.

## Technological Framework and Deployment

The applied systems combine smart sensors, cloud-based data analytics, and advanced field applications. The deployment involves the installation of AgroNIT Smart Traps and associated software across, more than 5000 of olive groves. The smart traps provide real-time data on pest populations (especially Bactrocera oleae) and environmental conditions, enabling early and accurate phytosanitary actions.

By leveraging a federated, low-power communication infrastructure (NB-IoT, LTE-M, LoRA-WAN), the system ensures broad coverage and reliability in rural landscapes. The collected data is processed using AI algorithms and made accessible to agronomists and producers via a secure digital platform (https://agronit.gr/).

## Training and Stakeholder Engagement

An innovative element of this program is the digital training and support platform (https://farmacademy.gr/), which facilitates asynchronous education for over 900 farmers, agronomists, and field workers. The platform includes multimedia modules, assessments, and feedback loops. It addresses a key barrier in rural settings—limited digital access and training participation due to seasonal workload.

Through this platform, users engage in thematic modules such as integrated pest management, sustainable fertilization, traceability systems (ISO 22005), and social conditionality. This has ensured high levels of compliance, awareness, and data-driven decision-making among all actors.

## Sustainability Impact and Evaluation

The project is already demonstrating early-stage impact. By reducing pesticide usage through precise application and enhancing monitoring, the Cooperative expects a measurable decrease in chemical inputs and CO2 emissions from waste biomass (via smart shredding systems). Data collected in 2024-todate from demo plots and user feedback confirm improvements in fruit quality, traceability, and agronomic resilience.

Furthermore, the inclusion of smart IoT components contributes to energy efficiency and operational sustainability. The use of cloud-based data services minimizes resource consumption while enabling large scale scalability. Ongoing evaluation protocols include expert assessments, farmer participation metrics, and machine-derived agronomic indexes.

## Conclusion

The Laconia case represents a successful pilot of how IoT-enabled precision agriculture systems such as AgroNIT and IoT.Cubes can be deployed at scale in traditional Mediterranean farming landscapes. The initiative showcases the convergence of sustainability, digital innovation, and cooperative governance.

Future work includes expanding the AI capabilities of the platform, enhancing predictive analytics, and integrating renewable energy microgrids.

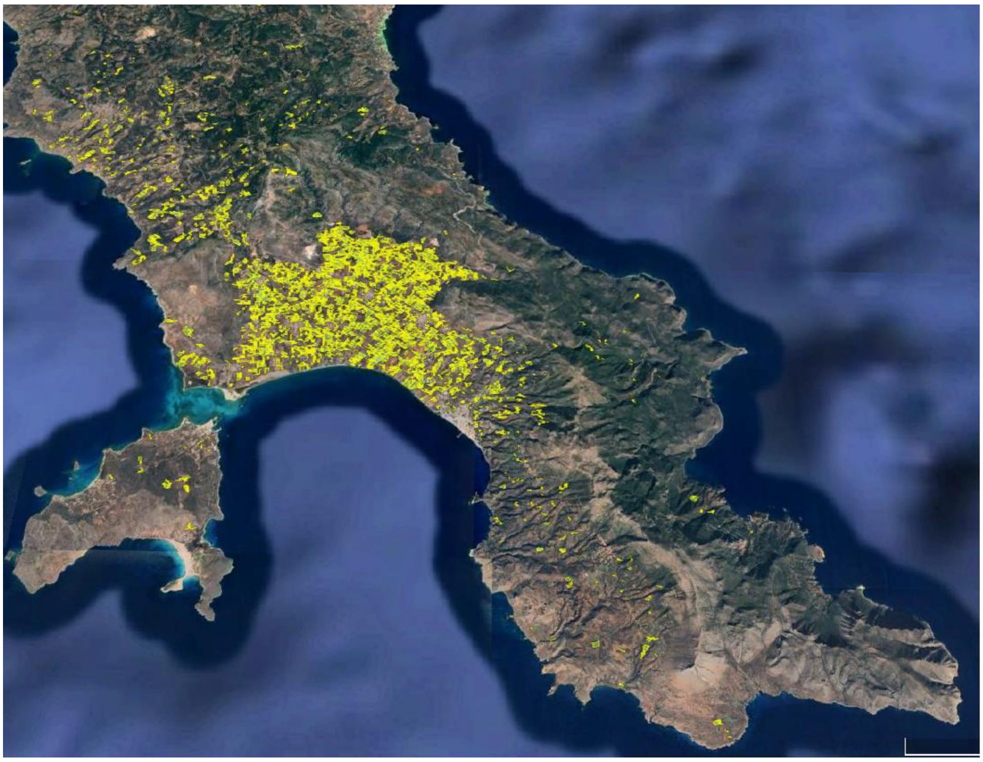

***Figure 1 - Geospatial Depiction of 5000+ Olive Groves at the Southernmost Mainland Tip of Europe***

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## References

- Thomaidis T., Panagopoulou G., Vorrias V. (2022). Pangaea.IoT.Cubes – Enabling Smart Agriculture. 3rd SustEng Conf., Rethymno 2024
- I. Moutsinas et.al., ISHS Acta Horticulturae 1409: X-International Symposium on Irrigation of Horticultural Crops, Nov. 2024, ISBN: 9789462614086, “Use of the AgroNIT smart-farming IoT ecosystem to support irrigation management and assess its impact on fruit trees’ economy and nutrition in Greece”
- I. Moutsinas et.al., Food & Environment, Athens, 2022, “Application of the AgroNIT smart-farming and decision-support platform to support the cultivation of major tree crops in Thessaly, Greece. Proc. 10th International Conference on ICT in Agriculture”

# Microplastics an Emerging Environmental Pollutant in Agriculture: Interaction Between Microplastics and Soil Humic Substances on an Agricultural Crop

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***Keywords:*** *micro-nano plastics, plastic-polyethylene-mulching film, soil-extracted humic acid, absorption, agricultural crop*

## ABSTRACT

The fate of micro-nano plastics, due to the plastic-polyethylene-mulching film (PMF) degradation in agricultural settings, can lead to negative consequences, potentially affecting soil and potentially posing risks to plant and animal health. In the present work, the micropollutant of soils from PMF is visually and spectroscopically evaluated with emphasis on the adsorption of nano-plastics onto soil-extracted humic acid in a strawberry crop. “Saturated NaCl solution”, stereoscopy, UV/vis spectroscopy, TG analysis and fluorescence spectroscopy were used to evaluate the degradation and adsorption of PMF. For the modeling of adsorption of nano-plastics onto Humic acid, PMF was dissolved in 18M $H_2SO_4$ solution for 4 months, while soil-extracted humic acid was isolated according to the IHHS protocol. Using UV/Vis and fluorescence spectroscopy the calibration curves showed linear behavior for both stock solutions, namely plastic and humic acid. Visual evaluation of soil samples which are collected by vertical fractionation using sieves of different diameters, for a sample with a particle size >3.15mm, based on flotation in saturated NaCl solution and for a sample with a particle size >0. 9mm under a stereoscopic examination by using a 1:30 focus lens, showed microplastics of different sizes in the soil matrix. Also, FT-IR analysis of soil samples, with a particle size <0.2 mm, showed that the spectrum was identified by 60% as plastic type polyethylene. This indicates that micro- and nano-plastics have infiltrated in the soil matrix. Absorption experiments between nano-plastic solution (45,469mg/L) and soil humic acid solution (25mg/L), by using UV/Vis spectroscopy, revealed an absorption of nano-plastic onto the humic acid by 50 %. In addition, the fenton reagent which was introduced into the plastic- humic acid solution showed that the humic acid degraded by 25%. This percentage, according to TG analysis, corresponds to a thermodynamically unstable fraction of humic acid that thermally degrades at temperature <450 °C. A comparative analysis of the UV/Vis absorption spectra before and after the Fenton reaction showed the existence of a spectra which looks like a humic acid spectrum with a horizontal plateau at 280 nm, indicating an absorption of nano-plastic on it. According to the TG analysis this humic acid fraction has a higher thermodynamic stability and thermally decomposes at a temperature >450 °C. This study demonstrates that the use of plastic membranes to cover soils leads to their degradation and the formation of micro- and nano-plastics over time. These plastics bind to soil components like humic acid resulting in significant degradation of cultivated soils

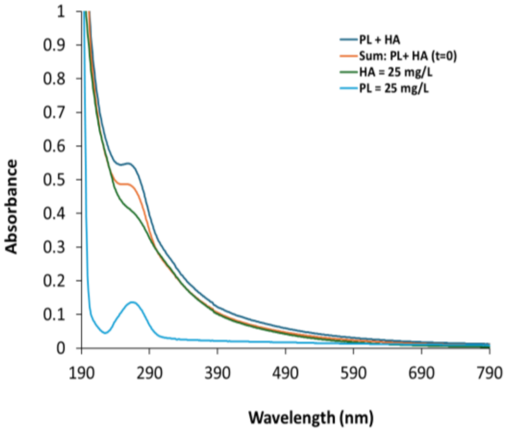

**Figure 1:** UV/Vis spectrum of humic 25 mg/L and plastic 45.469 mg/L and combination of the two.

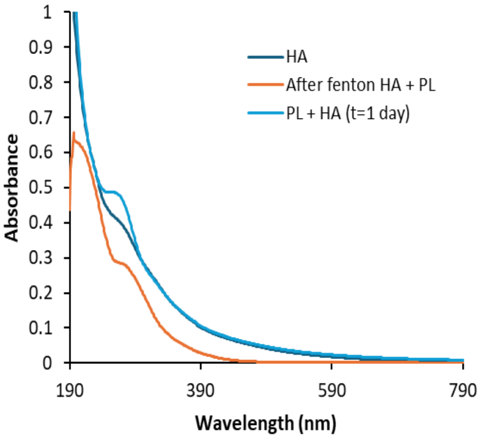

**Figure 2:** UV/Vis absorption spectrum after the Fenton reaction. Experimental conditions at pH= 3,$[\mathrm{Fe}^{+2}]$= 6.25 mg/L, $[\mathrm{H_2O_2}]$= 166.5 g/L

## References

Belhachemi, A., Maatoug, M., Canela Garayoa, R. & Canela-Garayoa, R. (2022) ‘Comparative analysis by UV-vis and FT-IR spectroscopy of the chemical degradation of polyethylene used as greenhouse cover film’, Journal of Elastomers and Plastics, 54(6), pp. 891–905. https://doi.org/10.1177/00952443221077439.SAGE Journals+4

Glaze, W.H. & Kang, J.W. (1989) ‘Advanced Oxidation Processes for Organic Contaminant Destruction’, Critical Reviews in Environmental Science and Technology, 23(3), pp. 177–192. https://doi.org/10.1080/10643380500326564.

International Hum ic Substances Society (IHSS) https://humic-substances.org/what-are-humic-substances-2/m

Isari, E.A., Papaioannou, D., Kalavrouziotis, I.K. & Karapanagioti, H.K. (2021) ‘Microplastics in Agricultural Soils: A Case Study in Cultivation of Watermelons and Canning Tomatoes’, Water, 13(16), 2168. https://doi.org/10.3390/w13162168.

Lehmann, J. & Kleber, M. (2015) ‘The contentious nature of soil organic matter’, Nature, 528(7580), pp. 60–68. https://doi.org/10.1038/nature16069.

Park, D.H., Oh, S.B. & Hong, S.C. (2022) ‘In Situ Fluorescent Illumination of Microplastics in Water Utilizing a Combination of Dye/Surfactant and Quenching Techniques’, Polymers, 14(15), 3084. https://doi.org/10.3390/polym14153084.

Pignatello, J. J., Oliveros, E., & MacKay, A. (2006). Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Critical Reviews in Environmental Science and Technology, 36(1), 1–84. https://doi.org/10.1080/10643380500326564

Rillig, M.C., Ziersch, L. & Hempel, S. (2017) ‘Microplastic transport in soil by earthworms’, Scientific Reports, 7, Article number: 1362. https://doi.org/10.1038/s41598-017-01594-7.

Sa’adu, I. & Farsang, A. (2023) ‘Plastic contamination in agricultural soils: a review’, Environmental Sciences Europe, 35, Article number: 13. https://doi.org/10.1186/s12302-023-00720-9.

# Session 8: Sustainable water management and reuse

# Modification of Membranes by using the Layer by Layer Technology for the Removal of Cr(VI) anions from groundwaters

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***keywords:*** *Cr(VI); ultrafiltration; layer-by-layer membranes; drinking water treatment; sustainable remediation.*

## Introduction

Hexavalent chromium (Cr(VI)) is a widespread and highly toxic contaminant found in natural and industrial water bodies. Due to its carcinogenic and mutagenic nature, its removal from drinking water is of critical importance. Conventional chemical treatment methods often produce large volumes of hazardous sludge and require high reagent consumption, posing sustainability challenges. This work proposes a membrane-based, environmentally friendly alternative to address these issues.

## Materials and methods

A novel membrane modification strategy based on Layer-by-Layer (LbL) assembly of polyelectrolytes is being developed. Commercial ultrafiltration membranes made of polysulfone (PSf) or polyacrylonitrile (PAN) are being modified through alternate deposition of poly(acrylic acid) (PAA) and either polyethyleneimine (PEI) or poly(diallyldimethylammonium chloride) (PDDA). Glutaraldehyde is applied as a crosslinking agent to enhance membrane stability. Membrane characterization includes surface morphology, contact angle, zeta potential, and scanning electron microscopy (SEM).

## Results and discussion

At this stage, membrane development and optimization are ongoing. The surface morphology, hydrophilicity, and charge properties of the LbL membranes were characterized and compared to those of unmodified membranes. The results showed that the LbL deposition process led to a smoother surface with enhanced hydrophilicity and altered surface charge. The effect of this deposition on the membranes' separation performance was also investigated. Upcoming experiments will evaluate the membranes' efficiency in removing Cr(VI) from synthetic aqueous solutions simulating drinking water matrices. The expected outcome is a significant improvement in Cr(VI) retention, with minimal chemical use and low energy requirements.

## Conclusions

This study aims to develop a sustainable membrane-based approach for the removal of Cr(VI) from drinking water. The method focuses on reducing environmental footprint while maintaining high separation performance. Results are expected to validate the method's potential as an alternative to conventional chemical treatments.

***Acknowledgements:*** This research is co-financed by the European Union and Greek national funds through the Operational Programme "Human Resources Development, Education and Lifelong Learning", under the call "Partnerships of Excellence in Research and Innovation – SUB1.1" (Action Code: 16289, acronym: Smart-Mem-Mat).

## References

Peng, H. and Guo, J., 2020. Removal of chromium from wastewater by membrane filtration, chemical precipitation, ion exchange, adsorption, electrocoagulation, electrochemical reduction, electrodialysis, electrodeionization, photocatalysis and nanotechnology: a review. Environmental Chemistry Letters, 18, pp.2055–2068.

Liu, Y., Chen, G.Q., Yang, X. and Deng, H., 2019. Preparation of Layer-by-Layer Nanofiltration Membranes by Dynamic Deposition and Crosslinking. Membranes, 9, p.20.

Xanthopoulou, M. and Katsoyiannis, I.A., 2019. Chromium ions removal from groundwaters by functionalized ultrafiltration membranes. New Materials, Compounds and Applications, 3, pp.38–46.

# Sensors selection for Real-Time Recovery of Textile Dyeing Wastewater

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**Keywords:** *Textile wastewater; real-time monitoring; sensor selection; recovery; reuse*

## Introduction

Textile dyeing is highly water-intensive, with up to 200 L of water used per kilogram of fabric, especially during wet treatments and rinsing stages, generating highly variable and contaminated effluents (Yaseen and Scholz, 2019). Washing and rinsing baths offer strong reuse potential, yet quality-based separation remains difficult. Key reuse parameters include temperature, pH, conductivity, color, and chemical oxygen demand (COD) (Yin et al., 2019). Real-time monitoring of these parameters is essential for effective wastewater recovery. Dynamic control using online sensors significantly improves recovery efficiency and supports circular water practices (Moretti et al., 2024). However, sensor selection is challenging due to the harsh characteristics of dyeing effluents, requiring both analytical precision and operational robustness. This study aims to develop an algorithm that can manage wastewater flows in real time based on the characteristics of the wastewater. The first step is to strategically place designated sensors within the wastewater baths according to the characterization of the wastewater samples.

## Materials and methods

The study was conducted in a textile dyehouse at the small medium enterprise (SME). The plant operates a batch dyeing process that uses a high-temperature (HT) machine. Samples were collected from all process baths involved in the fabric dyeing process, and the wastewater was characterized. The measurement of temperature, pH, and conductivity was conducted using a Hach HQ40d multimeter, while color measurements were taken with a Hach DR6000 spectrophotometer. COD measurements were performed using a test kit. Following the analysis of the results, the necessary criteria for sensors were determined.

## Results and discussion

### *Characterization results*

Figure 1 shows the baths used in the plant to dye 100% cotton fabric from a single recipe. The results of the wastewater characterization for each bath generated in the batch dyeing process are also shown in Figure 1. The results indicate that the wastewater characteristics of each bath vary. Furthermore, the characteristics of each bath within each recipe vary depending on the fabric type and dyeing requirements. Therefore, it is crucial to determine the quality of the wastewater using real-time sensors, especially for the recycling of rinsing baths, and to direct the wastewater to the appropriate recycling areas based on the results. Despite the wide range of sensors and analyzers available on the market for the purpose of measuring water quality conductivity, color and COD sensors or analyzers.

### *Sensor selection criteria*

In the stage of selection of sensors, it is necessary to take into account the values measured in wastewater resulting from the dyeing process. Specifically, sensors that operate over a wide pH range and at high temperatures should be selected. These sensors can be tailored to specific requirements through custom fabrication. The selection criteria for sensors are summarized in Table 1.

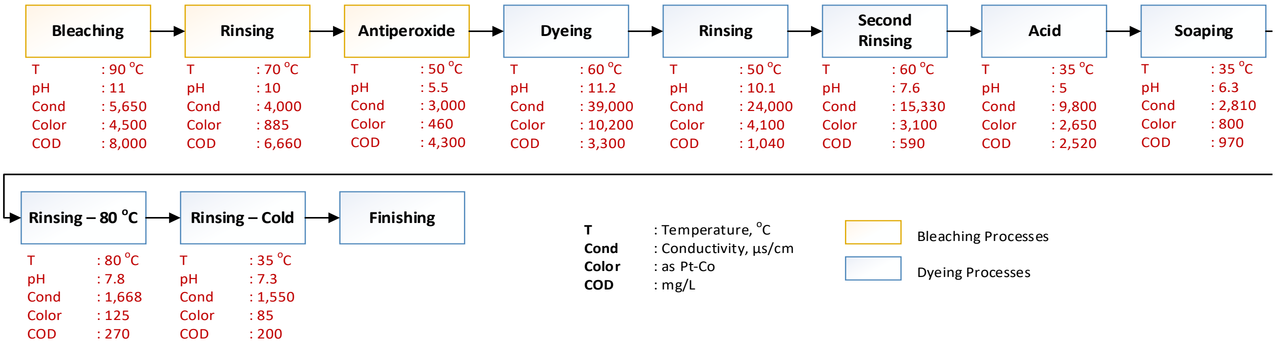

***Figure 1**. Wastewater characterization for each bath*

***Table 1**. Sensor selection criteria*

| Parameter | Determined Range in Textile Baths | Preferred Sensor Type | Selection Rationale |
|---|---|---|---|
| Temperature | 35–90°C (up to 130°C) | High-temperature resistant | Suitable range: 20–150°C |
| pH | 5.5 – 11.2 | Potentiometric transmitter | Wide pH range: 0–14 |
| Conductivity | 1,550 – 39,000 µs/cm (can reach 70,000 µs/cm) | Inductive conductivity transmitter | Effective in high salinity conditions |
| Color | 85 - 10,200 Pt-Co | Spectrophotometric transmitter | Multi-wavelength absorbance measurement |
| COD | 200 – 8,000 mg/L | UV-254 sensor or analyzer | Fast and real-time COD estimation |

Note: All selected sensors must be resistant to high temperature (up to 140°C) and chemical exposure. Stainless steel or chemically inert materials are preferred for sensor bodies.

## Conclusions

The recovery and reuse of textile dyeing wastewater, particularly from rinsing and washing baths, offers significant potential for improving water efficiency and sustainability in the textile industry. However, the variability and complex composition of these effluents necessitate the implementation of robust, real-time monitoring systems for their recovery. The integration of online sensors capable of accurately measuring key parameters such as pH, conductivity, temperature, color, and COD is critical to achieving reliable separation and reuse of wastewater streams. However, the successful implementation of such systems is dependent on the judicious selection of sensor technologies that are not only analytically reliable but also resilient to the harsh and fluctuating conditions. It is recommended that future research continue to concentrate on the field validation and integration of advanced sensor platforms within smart water management frameworks for the textile sector.

***Acknowledgements:*** The authors would like to acknowledge the support from the "SMART4ENV project, titled "Enhancing the Scientific Capacity of TÜBİTAK MAM in the Field of Smart Environmental Technologies for Climate Change Challenges". The project is funded by the European Union's Horizon Europe programme under Grant Agreement No 101079251. The data collection and sensor selection studies were supported by The Scientific and Technological Research Council of Türkiye (TÜBİTAK) under Project No. 3237017. The authors gratefully acknowledge TÜBİTAK for its financial support.

## References

Yaseen, D.A., Scholz, M., 2019. Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. Int. J. Environ. Sci. Technol. 16, 1193–1226. https://doi.org/10.1007/s13762-018-2130-z

Yin, H., Qiu, P., Qian, Y., Kong, Z., Zheng, X., Tang, Z., & Guo, H., 2019. Textile Wastewater Treatment for Water Reuse: A Case Study. Processes, 7(1), 34. https://doi.org/10.3390/pr7010034

Moretti, A., Ivan, H. L., & Skvaril, J., 2024. A review of the state-of-the-art wastewater quality characterization and measurement technologies. Is the shift to real-time monitoring nowadays feasible?. Journal of Water Process Engineering, 60, 105061.

# Session 9: Biosolids management and valorization

# Conversion of Sewage Sludge to Lipids for Biofuels

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**Keywords:** *black soldier fly, sewage sludge, biodiesel, compost, sustainable waste management*.

## Introduction

The black soldier fly larvae (*Hermetia illucens* L., BSFL) growth is a well-established method to be integrated into the waste management systems in dealing with organic wastes, even at a commercial scale where the matured BSFL are then harvested to be used as animal feed, supplement oil and even for biodiesel production (Guo et al., 2021; Salomone et al., 2017).

Sewage sludge (SS) is a byproduct of wastewater treatment and a significant nuisance waste. The annual production of SS has been increasing due to rapid human growth and city developments, and the need to treat more wastewater. Black Soldier Fly has intrinsic advantages for SS treatment, among them the low risk of pathogens transmitting by the flies due to their avoidance of human residence. The BSFL can also survive in a wide range of surrounding environments and inhibit the growth of microbial pathogens in its feeding substrates (Mohd-Noor et al., 2017).

This study explored the potential of BSFL bioconversion as a novel approach to sludge valorisation, focusing on optimising biomass production and lipid accumulation. By leveraging BSFL's ability to efficiently process organic waste, this method offers a cost-effective, scalable, and environmentally friendly alternative to conventional SS treatment.

## Materials and methods

A series of controlled experiments was conducted to assess the effects of different SS-based feed compositions and rearing conditions on BSFL performance. The study included six experimental setups, ranging from small-scale (4 kg) to large-scale (25 kg) trials, scaling tests (15 kg × 3), along with specialised experiments evaluating nursery conditions, sludge ratio effects, and incubator-based feed transition strategies. Various sludge compositions, including blends with apple waste and olive mill solid waste (OMSW), were tested to determine the most effective diet for maximising larval survival, lipid yield, and biomass production.

Samples were collected from each experiment to evaluate the BSFL performance, including biomass yield estimation, survival rate, lipid quantification, and statistical analysis associated with a multidimensional evaluation of larval growth efficiency and biochemical composition as described in Figure 1.

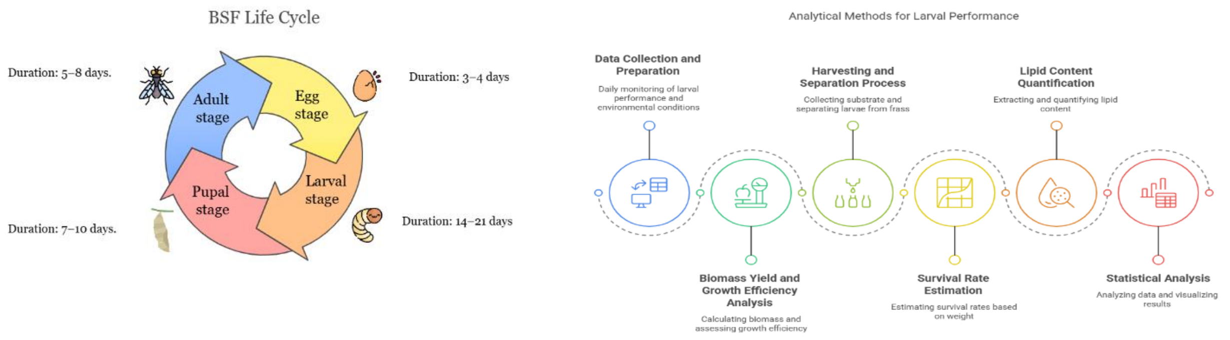

*Figure 1: Life cycle of the BSF (Hermetia illucens), showing the four developmental stages (left). And*

*Analytical approach for evaluating BSFL growth and composition (Right).*

## Results and discussion

BSFL exhibited high survival rates across multiple trials (82% to 97%), with the optimal feed mix (50% sludge, 25% apple waste, 25% OMSW) achieving the highest survival rate (97%). In contrast, diets with excessive sludge content (>75%) negatively impacted larval growth and survival. Lipid accumulation peaked between days 10-15, earlier than maximum biomass production. When the BSFL was grown at the nursery stage on check feed (CF) and then transferred to the Mix biomass the calculated conversion of the feed into BSFL biomass was 21% and the feed into lipids was 6.3%; however, when the BSFL was grown at the nursery stage on the mix and transferred into CF the calculated conversion of the feed into BSFL biomass was 43.5% and the feed into lipids was 11.35%. Transitioning larvae from sludge-based feed to nutrient-rich chicken feed in later stages significantly enhanced lipid reserves, indicating the potential for optimized feeding strategies in large-scale applications.

BSFL effectively reduced sludge volume by 50-70%, depending on substrate composition. The feed conversion rate (FCR) (75.6%) was recorded in large-scale experiments, demonstrating BSFL's potential for efficient organic waste processing at industrially relevant scales. Microbial analysis of Frass (larval excrement) showed a six-fold increase in microbial colony counts compared to the initial sludge, suggesting enhanced microbial activity beneficial for composting and soil applications. However, higher concentrations in Frass indicated the need for additional post-treatment measures (e.g., composting, pasteurisation) to ensure microbial safety for agricultural reuse. To mitigate microbial risks, integrating post-treatment methods such as composting, thermal pasteurisation, and controlled drying can ensure the safe use of BSFL-derived products in agriculture and bioenergy applications. Large-scale trials at partially controlled environmental conditions (a heating plate beneath the substrate, activated below 24°C) confirmed the feasibility of BSFL bioconversion for sewage sludge treatment, with consistent survival rates (83–87%) and stable lipid yields across multiple replicates. However, high-density rearing slightly reduced individual larval weight, suggesting the need for further optimisation in large-scale production systems. The results indicate that balanced feed formulations, optimal rearing conditions, and feed transition strategies can significantly enhance BSFL bioconversion efficiency.

## Conclusions

This research reinforces the viability of BSFL as a sustainable solution for SS management, transforming problematic waste into lipids and soil additives. The integration of BSFL into circular economy systems has clear promise for environmental, agricultural, and biofuel applications. Integrating BSFL-based waste treatment into existing wastewater management infrastructures, where this approach could significantly reduce landfill dependency, lower sludge treatment costs, and contribute to global sustainability efforts. Implementing these advancements will not only enhance industrial-scale feasibility but also drive regulatory acceptance, accelerating the global adoption of BSFL-based waste management as a sustainable alternative to conventional sludge treatment.

***Acknowledgements:*** This work was partially supported by MERC (Middle East Regional Cooperation - U.S. Agency for International Development) grant M38-021, and by Tel-Hai Academic College as a scholarship to Ms. M. Khoury.

## References

Guo H, Jiang C, Zhang Z, Lu W, Wang H. 2021. Material flow analysis and life cycle assessment of food waste bioconversion by black soldier fly larvae (*Hermetia illucens* L.). Sci Total Environ ;750:141656.

Mohd-Noor, S.-N., Wong, C.-Y., Lim, J.-W., Uemura, Y., Lam, M.-K., Ramli, A., Bashir, M. J., Tham, L., 2017. Optimization of self-fermented period of waste coconut endosperm destined to feed black soldier fly larvae in enhancing the lipid and protein yields. Renew. Energy 111, 646–654.

Salomone, R., Saija, G., Mondello, G., Giannetto, A., Fasulo, S., Savastano, D. 2017. Environmental impact of food waste bioconversion by insects: application of Life Cycle Assessment to the process using *Hermetia illucens*. J Clean Prod;140: 890-905.

# Quantifying European Biomass Flows and Certifying Residual Biomass Valorization: A Case from the Region of Central Macedonia, Greece

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***keywords:*** *biological resources, certification schemes, sustainability analysis, material flow analysis*

## Introduction

The 2018 EU Bioeconomy Strategy has provided incentives for the development of new value chains, which use biological residues and waste as raw materials to produce high value bio-based products. However, for the establishment of such value chains, their sustainability should be ensured from an environmental, social and economic perspective. BioReCer (Biological Resources Certifications Schemes) is an EU funded project which has developed a framework to facilitate the certification of secondary biomass in bio-based value chains and support their establishment in the European market. This framework includes sustainability and circularity criteria validated in four case studies (Greece, Italy, Spain, and Sweden) with different feedstocks derived from four important EU sectors, **i.e. the agricultural, the urban and industrial, the fishing, and the forestry.** Furthermore, a decision-making platform was developed, which can be used by interested stakeholders, to track and trace the biological feedstocks, to be informed about their circularity, and advised on the further requirements needed to be certified. The overall scope of the project is to promote the use and acceptance of added value bio-based products and to enhance circular systems.

In this study, the residual biomass from the four aforementioned sectors was quantified to evaluate their potential for valorization in bio-based value chains. Furthermore, detailed input/output tables (I/O Tables) of two value chains were developed, concerning the valorization of agricultural biomasses from the Region of Central Macedonia (RCM). Finally, the environmental sustainability of the valorization of straw, peach tree pruning and peach fruit pulp for the production of bio-based compost was assessed through Life Cycle Assessment (LCA).

## Materials and methods

The quantities of available biomass for the four sectors under study were identified through Material Flow Analysis (MFA) [1]. MFA is a useful tool for the assessment of a bio-based value chain, supporting the calculation of sustainability and circularity indicators as well as the implementation of an LCA. Recent data were retrieved from databases related mainly to the primary sector production and the generation of waste. When data were lacking or incomplete, reliable assumptions were also made, based on literature and the opinion of field experts. Additionally, a value chain applicable to the RCM was defined with the use of extended I/O Tables. The I/O Table provided quantitative data across the value chain, as well as energy and resources need and emissions generation. For the LCA analysis, statistical data for the RCM, primary industrial data, expert's opinion, conversion coefficients and literature data were used. The value chain under investigation focused on the production of biofertilizers from wheat straw, peach tree pruning and peach pulp (Figure 5).

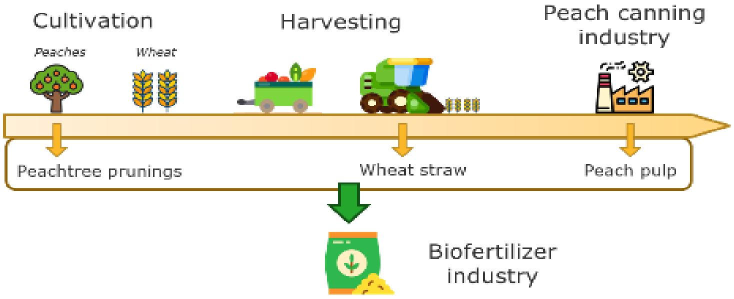

***Figure 5.*** *Value chain under study: production of biofertilizers*

Finally, a comparative LCA analysis was also conducted between the bio-based scenario, which referred to the production of the biofertilizer, and a reference scenario, which examined the production of conventional fertilizer, including also the conventional management processes of residual biomass (e.g. open burning of straw and pruning and landfilling of peach pulp). The study followed a "cradle-to-gate" approach, excluding infrastructure processes. The Functional Unit (FU) used for the system analysis was 1 kg of produced biofertilizer. For the environmental assessment SimaPro v10.2, Ecoinvent database (v3.10) and the Environmental Footprint 3.1 (adapted) V1.01 / EF 3.1 impact method were applied.

## Results and discussion

MFA was implemented for the countries of EU-28 to detect the secondary biomass generation and uses in an annual basis. Even though the quantity of the available residual was found to be significant, it is mainly used for lower-value applications, such as energy, or it is not valorized at all (e.g. landfilling or incineration). Specifically, fishery by-products are mainly disposed to landfills, anaerobically digested or composted. Approx. 20% of the total fisheries is used for the production of crude fish-meal and crude fish oil without any further treatment to produce value-based products. Composting and anaerobic digestion are also the main treatment methods for the organic fraction of municipal solid wastes, since only 2% is used in the bio-based industry. The sewage sludge (SS) is mainly directly applied in agriculture, arising environmental concerns for this practice. The valorization of SS in the bio-based industry is developing, but the quantity used in these applications remains low (0.3%). Similar observations have been made for the agricultural, agro-industrial and forestry residue, since only 3% of them are used for the production of added value products.

A dataset was created in the form of an extended I/O table for the production of 1kg o biofertilizer. For the production 1 kg of biofertilizer (wet mass, WM), 0.17 kg of straw (dry mass, DM), 0.103 kg of pruning (DM) and 0.525 kg of pulp (DM) are needed. Figure 6 illustrates the single-score LCA results for both the bio-based and reference scenarios. The results indicate that the bio-based scenario appears to offer greater environmental benefits, especially in terms of particulate matter and climate change. These improvements are mainly attributed to the valorization of agro-industrial residues, which lead to the avoidance of open burning as well as landfilling, both major contributors to air pollution and greenhouse gas (GHGs) emissions.

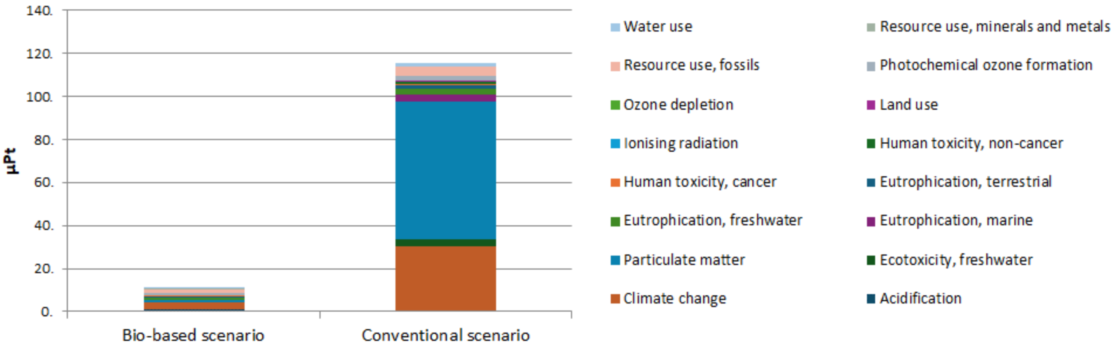

***Figure 6:*** *Comparison of the bio-based and conventional scenarios with the Environmental Footprint method*

## Conclusions

In the present study the quantities and uses of the biological feedstocks in four European sectors were mapped and a bio-based value chain from the RCM was identified and compared to the conventional one, in terms of environmental sustainability. The methodologies used can contribute to resource efficiency, environmental impact minimization, and facilitation of circular bioeconomy practices, through the establishment of biological resources certification schemes.

***Acknowledgements:*** This study was implemented in the context of BioReCer project (https://biorecer.eu) that receives funding from the Horizon Europe framework program under the Grant Agreement No. 101060684.

## References

[1] P.H. Brunner, H. Rechberger, Practical handbook of material flow analysis, The International Journal of Life Cycle Assessment, 9 (2004) 337-338, 10.1007/BF02979426.

# The role of demand-driven biogas plants in Europe's energy transition: potential for energy system stability and integration with other RES

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***keywords:*** demand-driven biogas plants, flexible energy production, stability energy system

## Introduction

Renewable energy sources (RES) are the foundation of Europe's transformation. Replacing fossil fuels with RES contributes to reducing greenhouse gas emissions, which is crucial for mitigating ongoing climate change and its increasingly noticeable impacts. Given the current geopolitical situation, including armed conflicts in Ukraine and the Middle East, heightened political tensions, and shifting energy policies of key producers such as the United States, the risk of supply chain disruptions and price fluctuations for coal, natural gas, and crude oil is increasing. The transition of the economy toward RES enhances energy self-sufficiency and shifts energy dependence from the global to the regional level. Reducing energy prices is also crucial for ensuring the competitiveness of industries, which are typically characterized by high energy intensity[i]. Thanks to EU policy and clearly defined climate goals, the production of green energy in the electricity sector is growing year by year and in 2024, it reached 46.9%. The most significant are currently wind power (39.1%), hydro power (29.9%), and solar power (22.4%), which together account for over 90% of total electricity production from RES[ii]. Compared to previous years, wind and solar energy have shown a consistent upward trend, primarily due to the wide availability of technology and falling production costs[iii]. Hydropower, while still a significant share of RES, is developing more slowly than other types, due to the limited number of suitable locations and its dependence on water availability[iv].This dependence occurs not only at the EU level but also globally[v,vi]

Despite benefits of increasing the share of energy from photovoltaic and wind turbines, their generation remains highly dependent on weather conditions. This inherent variability leads to daily fluctuations in production, resulting in voltage and frequency instability within the power system. The limited controllability of these sources increases the risk of extreme operational states, such as system overloads and blackouts. Overload situations are particularly prevalent on warm, windy days and arise from imbalances between electricity supply and demand: excessive electricity generation with significantly lower demand and a lack of sufficient energy storage. To prevent damage to the transmission infrastructure, system operators often resort to partial or complete curtailment of electricity production from RES[vii]. Due to high investment costs, the overwhelming majority of RES are not equipped with battery energy store system, which causes significant losses in available power. Installations that remain connected to the grid during such events are not necessarily in a more favorable position, as energy prices during these periods tend to be extremely low or even negative, rendering electricity sales economically unviable[viii]. The opposite trend is observed during morning and evening hours, when the absence of sunlight results in the limited PV generation, contributing to elevated electricity prices on the market. This phenomenon is commonly referred to as the "duck curve"[ix,x].

The growing demand for stable, zero-emission energy sources creates new opportunities for the expansion of biogas plants, which, alongside hydroelectric power stations, are the only forms of RES capable of fully controllable electricity generation. Currently, the majority of biogas installations in Europe operate continuously, producing electricity nearly 24 hours a day. In light of increasing challenges to ensure power system stability, biogas plants could play a key role as balancing assets. During periods of surplus generation from other variable RES biogas facilities, specifically a cogeneration engine, could be temporarily turn off.

The produced biogas could be then stored and used late, during peak demand periods, thereby enhancing grid flexibility and reliability.

**Materials and methodology**

Based on available literature, an analysis was conducted of the potential use of demand-driven biogas plants to stabilize power systems in individual EU countries and integrate them with other RES. The analysis was based on a review of available scientific literature, industry reports, strategic documents, and statistical data published by EU and national institutions. Three key aspects determining the implementation and efficiency of peak-load biogas plants were considered:

1. Substrate potential
2. Availability and technology development
3. Observed trends in energy markets in individual countries

**Results and conclusions:**

1. Despite varying levels of biogas production across EU countries, almost all Member States have operational biogas installations. Their total number is estimated at nearly 20,000, representing only 2.65% of the available production potential. Due to the high availability of waste from the agri-food and municipal sectors, the potential for sustainable biogas production in the EU is estimated at 101 bcm by 2040 and 151 bcm by 2050[xi,xii,xiii].
2. Virtually all leading biogas technology providers offer solutions enabling flexible plant operation. Biogas storage can be relatively easily integrated into existing infrastructure, both wet tanks mounted directly above the fermentation tank and dry tanks operating as separate installations. Ongoing advances in process automation and digital control technologies also facilitate remote and adaptive operation of biogas plants, allowing for more precise and flexible responses to fluctuations in electricity demand within the power system.
3. A marked increase in redispatching events points to a growing challenge of grid congestion and infrastructure overload. If this trend continues, it could further limit the profitability of RES, including biogas plants[xiv].
4. To date, the main obstacle to the broader implementation of demand-drive biogas plants has been the lack of appropriate financial incentives. Most existing installations operate under feed-in tariff or feed-in premium schemes that guarantee stable revenue, regardless of market price volatility. However, the expiration of these systems for older projects or regulatory changes, such as the lack of compensation in the event of negative energy prices, could provide a driver for the introduction of flexible production [xv,xvi].

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**References:**

[1] Stecuła, K. Renewable energy sources as an opportunity for global economic development. *SGEM* **2017**, *17*, 733–740. https://doi.org/10.5593/sgem2017H/43/S29.094

[1] Eurostat. Electricity from renewable sources reaches 47% in 2024. Available online: https://ec.europa.eu/eurostat/web/products-eurostat-news/-/ddn-20240123-1 (accessed on 31.07.25)

[1] Turduev, I.; Abdiraeva, N.; Mamatova, V.; Kyzy, A. Development of wind energy and solar energy. *E3S Web Conf.* **2025**, *614*, 01007. https://doi.org/10.1051/e3sconf/202561401007

[1] Tomczyk, P.; Wiatkowski, M. Challenges in the development of hydropower in selected European countries. *Water* **2020**, *12*, 3542. https://doi.org/10.3390/w12123542

[1] Taušová, M.; Mykhei, M.; Čulkova, K.; Tauš, P.; Petráš, D.; Kaňuch, P. Development of the implementation of renewable sources in EU countries in heating and cooling, transport, and electricity. *Sustainability* **2025**, *17*, 766. https://doi.org/10.3390/su17020766

[1] International Energy Agency (IEA). Renewables 2024. Available online: https://www.iea.org/reports/renewables-2024 (accessed on 31.07.25)

[1] Pijarski, P.; Saigustia, C.; Kacejko, P.; Belowski, A.; Miller, P. Optimal network reconfiguration and power curtailment of renewable energy sources to eliminate overloads of power lines. *Energies* **2024**, *17*, 22965. https://doi.org/10.3390/en17122965

[1] Wang, G.; Sbai, E.; Wen, L.; Sheng, M.S. The impact of renewable energy on extreme volatility in wholesale electricity prices: Evidence from Organisation for Economic Co-operation and Development countries. *J. Clean. Prod.* **2024**, *484*, 144343. https://doi.org/10.1016/j.jclepro.2024.144343

[1] Pitra, G.; Sastry, M. Impact analysis of Duck Curve phenomena with renewable energies and storage technologies. *J. Eng. Res. Sci.* **2022**, *1*, 52–60. https://doi.org/10.55708/js0105006

[1] Pitra, G.M.; Musti, K.S.S. Duck curve with renewable energies and storage technologies. In *Proceedings of the 2021 13th International Conference on Computational Intelligence and Communication Networks (CICN)*, Lima, Peru, 18–19 November 2021; pp. 66–71. https://doi.org/10.1109/CICN51697.2021.9574671

[1] Bumharter, C.; Bolonio, D.; Amez, I.; García Martínez, M.J.; Ortega, M.F. New opportunities for the European biogas industry: A review on current installation development, production potentials and yield improvements for manure and agricultural waste mixtures. *J. Clean. Prod.* **2023**, *388*, 135867. https://doi.org/10.1016/j.jclepro.2023.135867

[1] ECOHZ. Biomethane market in Europe. Available online: https://www.ecohz.com/blog/biomethane-market-in-europe (accessed on 31.07.25)

[1] European Biogas Association (EBA) Roadmap 2040: Biogases value chain calls for binding target to unlock circular and affordable energy for Europe. https://www.europeanbiogas.eu/publications/ (accessed on 31.07.25)

[1] Lauven, L.-P.; Geldermann, J.; Desideri, U. Estimating the revenue potential of flexible biogas plants in the power sector. *Energy Policy* **2019**, *128*, 402–410. https://doi.org/10.1016/j.enpol.2019.01.007

[1] Saracevic, E.; Koch, D.; Stuermer, B.; Mihalyi, B.; Miltner, A.; Friedl, A. Economic and Global Warming Potential Assessment of Flexible Power Generation with Biogas Plants. *Sustainability* **2019**, *11*, 2530. https://doi.org/10.3390/su11092530

[1] Saracevic, Ervin & Theuretzbacher, Franz & Wöss, David & Friedl, Anton & Miltner, Angela. (2020).

Economic and Technical Evaluation of Flexible Power Generation Scenarios for a Biogas Plant. Journal of

Sustainable Development of Energy, Water and Environment Systems. N/A. 10.13044/j.sdewes.d7.0289.

# The role of animal biomass in the biogas sector in Poland: current status and potential

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***keywords:*** *biogas; feedstock; manure; slurry; emissions.*

## Introduction

Poland is one of the largest animal producers in the European Union, with 6.191 million cattle, 9.078 million pigs and 3.5 million tons of poultry. Such production generates huge amounts of animal biomass: animal manures, slaughter and dairy waste and expired food of animal origin. Among all types of biomass produced in Poland – it is animal biomass that takes the first place in terms of the size of the production stream. It is also worth emphasizing that with almost 110 million tons of manure (excluding chicken droppings), Poland is its largest producer in the European Union. Manure due to its properties (dry matter content above 20% and tendency to self-heat during storage – which promotes strong emissions of greenhouse gases, such as $CH_4$ and $N_2O$). GHG emissions from manure are much higher than during storage of slurry. Therefore, from the point of view of climate protection, animal fertilizers should be managed in a different way than traditional storage in heaps.

In this case, the best solution is to use animal manures as a substrate for biogas plants. Although this technology produces extremely high levels of methane, it does so under controlled conditions inside fermentation tanks. In turn, the digestate, i.e., the by-product from the anaerobic digestion of animal manures, can be used in fields for fertilization purposes without generating further methane emissions.

The aim of the work was to analyze the current role of biomass of animal origin in the Polish biogas sector and to determine the potential for biogas and biomethane production using this type of substrate. It should be emphasized that in the analysis of the current use of animal biomass for energy production, the authors focused exclusively on the production of biogas and electricity, because Poland is one of the few EU countries where no biomethane plant operates.

## Materials and methods

Data from KOWR (an agency of the Ministry of Agriculture responsible for supervising the agricultural biogas sector) and data published by the Central Statistical Office (GUS) were used to analyze the actual use of animal-derived substrates in Poland. Data on the production efficiency of individual substrates from the research of the Ecotechnologies Laboratory, the largest Polish biogas laboratory, were used to calculate the amount of biogas produced in Poland. For calculation purposes, it was assumed that the energy value of methane is 0.009968 MWh/$m^3$, and the electrical efficiency of a typical cogeneration unit is 40%.

## Results and discussion

Based on the analyses carried out, it was found that the amount of animal manures used in the Polish biogas sector has been increasing over the last ten years. In the case of slaughterhouse waste, the situation has been variable over the years, with increased use and decreases noted (Table 1).

***Table 1.*** *List of selected raw substrates of animal origin used in agricultural biogas plants in Poland in 2015-2024 (tons)*

| Substrate | 2015 | 2016 | 2017 | 2018 | 2019 | 2020 | 2021 | 2022 | 2023 | 2024 |
|---|---|---|---|---|---|---|---|---|---|---|
| **Slurry** | 598 963 | 779 203 | 807 223 | 757 555 | 733 452 | 764 447 | 805 940 | 934 770 | 1 052 059 | 1 193 132 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Manure** | 45 342 | 81 934 | 82 703 | 85 422 | 84 923 | 91 681 | 91 076 | 95 467 | 119 088 | 132 528 |
| **Slaughterhouse waste** | 13 387 | 17 944 | 15 381 | 66 847 | 104 438 | 83 131 | 86 481 | 125 621 | 158 071 | 119 059 |
| **Chicken droppings** | 14 742 | 25 643 | 21 084 | 22 525 | 19 741 | 27 742 | 30 652 | 48 230 | 61 798 | 60 468 |
| **Stomach contents** | 8 133 | 23 146 | 24 477 | 18 387 | 10 607 | 11 348 | 8 538 | 14 003 | 13 379 | 41 780 |
| **Dairy industry waste** | 47 817 | 89 145 | 75 977 | 107 972 | 125 141 | 131 482 | 134 370 | 173 731 | 273 812 | 336 933 |

Based on the data presented in Table 1, the amount of electricity produced can be estimated, taking into account the average biogas yields (expressed in m$^3$ $CH_4$/ton of fresh matter) of individual substrates of animal origin – such a summary is included in Table 2.

| **Substrate** | **Biomass (t/a) (2024)** | **Efficiency ($CH_4$/t FM)** | **Methane production (m$^3$ $CH_4$/substrate)** | **Electric energy (MWh)** |
|---|---|---|---|---|
| **Slurry** | 1 193 132 | 12 | 14 317 584 | 142 718 |
| **Manure** | 132 528 | 42 | 5 566 176 | 55 484 |
| **Slaughterhouse waste** | 119 059 | 220 | 26 192 980 | 261 092 |
| **Chicken droppings** | 60 468 | 70 | 4 232 760 | 42 192 |
| **Stomach contents** | 41 780 | 65 | 2 715 700 | 27 070 |
| **Dairy industry waste** | 336 933 | 32 | 10 781 856 | 107 474 |

The total amount of electricity produced from animal waste in 2024 was therefore 636,029 MWh, with the largest share coming from slaughterhouse waste, followed by slurry and dairy waste. It is worth emphasizing that the amount of energy produced should theoretically be part of over 64% of all electricity (1 012 183 MWh) produced in the agricultural biogas sector in 2024. However, the efficiency of fermentation of some of the animal waste was perhaps not as high as assumed in the calculations based on the theoretical efficiency measured in the laboratory.

Meanwhile, the total potential of animal biomass in Poland is gigantic and very little is unused. Taking into account the amount of cow and pig manure alone, which in 2019 amounted to almost 107 million tons in Poland, which allows for electric energy production of 44.76 TWh (in continuous operation, 24 hours a day, excluding service downtime). This may constitute a significant contribution to the Polish power system, which is currently based on fossil sources in nearly 70%, primarily hard coal and lignite.

## Conclusions

The energy potential of biomass from the Polish animal production sector is enormous, and at the same time currently extremely underutilized, as it currently amounts to approx. 636 GWh. Meanwhile, manure alone can produce 44 TWh of electricity, and in combination with other types of substrates – the agricultural biogas sector based on animal biomass may in the future play a very important role in the Polish power system. It should also be emphasized that biogas plants, unlike other types of RES – can be fully controllable and monitorable during their operation and smoothly respond to changes in demand/supply of power in the national power system.

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# Influence of the type of straw on the intensity of sewage sludge composting

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***keywords:*** *Composting, sewage sludge, organic additives, ammonia emissions.*

## Introduction

Sewage sludge is being produced in increasing quantities in modern economies. Due to its high moisture content—typically between 75% and 85% (after thickening)—the options for its management are rather limited. Incineration is energetically unprofitable, while pyrolysis or gasification are technically unfeasible. Therefore, one of the most effective methods is to subject the sludge to biological valorization processes such as composting or anaerobic digestion.

However, investments in biogas plants require relatively high capital expenditure and are often beyond the financial reach of smaller wastewater treatment plants. In contrast, the composting process can be implemented even at treatment plants with low annual sludge production—on the order of several hundred to a few thousand tons.

Due to the very narrow C:N ratio, composting sewage sludge requires the use of an additional structural material with a high carbon content. Various types of straw can serve as such a material.

The aim of this study was to compare the effects of composting municipal sewage sludge with the addition of sawdust and various types of straw: maize, rapeseed, and wheat.

## Materials and methods

The study was conducted at the Poznań University of Life Sciences using four adiabatic composting bioreactors designed to model the composting processes of biological materials. Each bioreactor had a capacity of 165 liters and accurately simulated the composting conditions found in open windrows and large-scale composting chambers. In the experiment, a constant proportion of sewage sludge (50%) and sawdust (20%) was used in all mixtures. The remaining 30% consisted of various types of straw: wet maize, dry maize, wheat, and rapeseed. All composted mixtures were adjusted to the same carbon-to-nitrogen (C:N) ratio of 14.7.

## Results and discussion

During the study, an intensive thermophilic phase was achieved in all compost mixtures (with peak temperatures ranging from 72°C to 76°C). The highest temperature was recorded in the mixture with the addition of dry maize straw. This mixture also exhibited the longest thermophilic phase, lasting 23 days. Furthermore, the maximum concentration of ammonia emitted during the composting process was the lowest for this mixture—slightly below 800 ppm—while in the other mixtures, it ranged between 800 and 1000 ppm. The cumulative ammonia emission was also the lowest for the mixture with dry maize straw—just under 3 kg N-$NH_3$ per tonne of dry composted material. A slightly higher emission (3.2 kg N-$NH_3$/t d.m.) was measured for the mixture with wet maize straw, while significantly higher emissions (3.5–3.7 kg) were observed for mixtures with rapeseed and wheat straw.

## Conclusions

In conclusion, all composted mixtures (sewage sludge and organic additives) showed high compostability, which was evident through rapid heating of the compost mass, leading to temperatures that ensured sanitization of the feedstock (above 70°C). It should also be emphasized that maize straw—particularly dry—had a more beneficial effect on the composting process than rapeseed or wheat straw.

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**References**

Żukowska, G., Mazurkiewicz, J., Myszura, M., & Czekała, W. (2019). Heat Energy and Gas Emissions during Composting of Sewage Sludge. Energies, 12(24), 4782. https://doi.org/10.3390/en12244782

Dume, B., Hanč, A., Švehla, P., Chane, A., & Nigussie, A. (2021). Carbon Dioxide and Methane Emissions during the Composting and Vermicomposting of Sewage Sludge under the Effect of Different Proportions of Straw Pellets. Environmental Sciences Proceedings, 8(1), 7. https://doi.org/10.3390/ecas2021-10337

Bojarski, W., Czekała, W., Nowak, M., & Dach, J. (2023). Production of compost from logging residues. *Bioresource Technology*, *376*, 128878. https://doi.org/10.1016/j.biortech.2023.128878

Sołowiej, P., Pochwatka, P., Wawrzyniak, A., Łapiński, K., Lewicki, A., & Dach, J. (2021). The Effect of Heat Removal during Thermophilic Phase on Energetic Aspects of Biowaste Composting Process. Energies, 14(4), 1183. https://doi.org/10.3390/en14041183

# Advanced Wastewater Treatment: Integrating Microsieving with Gasification for Energy Recovery

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**Kew worlds**: wastewater, microsieve, gasification, energy saving, waste to energy

## Introduction

The treatment of urban and industrial wastewater leads to the production of sludge which contains organic matter, nutrients, and hazardous substances that makes difficult to dispose of. The treatment method used are anaerobic digestion, incineration, and pyrolysis, which are conventional and characterized by high energy costs, large facilities and greenhouse gas emissions. Treatment plants consume large amounts of energy with the aeration process being the most energy-intensive, accounting for 53% of total energy consumption. The increase in global wastewater production and rising energy costs make optimization necessary.

The European Union's goal is to convert WWTPs into energy-autonomous units by 2030, with a 55% reduction in emissions. In this context, energy recovery technologies such as gasification are being promoted. A pilot microsieving- gasification system was implemented at the Rethymnon plants as part of the LIFEB2E4SUSTAINABLE-WWTP project. The results of the implementation showed a significant reduction in energy consumption and the production of synthesis gas (syngas) capable of covering a large amount of the plant's needs. Finally, we note that the use of this technology can contribute to the conversion of plants to carbon neutrality, thereby enhancing sustainability.

## Materials and methods

Energy consumption in wastewater treatment plants is an important issue, and innovative solutions are being explored to achieve energy- neutral facilities. A pilot industrial- scale unit has been installed at the Rethymnon WWTP, which includes microsieving, drying, and gasification with an internal combustion engine. The aim is to remove biosolids before the aeration tank, reducing energy consumption, and to use as fuel for the production of syngas.

The dried biosolids with moisture content of 10-15% are formed into briquettes and fed into downdraft gasification reactor, which include drying, pyrolysis, combustion, reduction and ash removal zones. The syngas produced consists mainly of CO, $H_2$, and $CH_4$, but also contains pollutants (particles, tar, sulfur, chlorine), which are removed by a cyclone. Finally purified syngas is fed into the engine to produce heat and electricity.

The system is equipped with non-return valves and safety measures to prevent malfunctions. The integrated process is expected to reduce sludge production, improve plant performance, and offer a positive environmental footprint through energy recovery form biosolids.

## Results and discussion

The study evaluated the performance of a pilot microsieving-aeration system at the Rethymno WWTP. Microsieving achieved an average removal of 35% TSS, BOD 16% and COD 20%, significantly reducing the organic load and energy requirements for aeration. The average dry biosolids production was 3.5 kg/h with a solids content of up to 45%, suitable for gasification. The syngas produced ($H_2$ 15.5%, CO 16.4%, $CH_4$ 3.3%, $CO_2$ 7.5%) had a calorific value of 4.9 MJ/Nm³ and a yield of 1.92 Nm³/kg of fuel. The Cold Gas Efficiency calculation (54-60%) confirms high efficiency, in line with international literature. The results show that integrated technology can contribute significantly to the transition of WWTPs to energy neutral facilities

## Conclusions

The microsieving-gasification system at the Rethymno WWTP (2023-2024) with the aim of reducing energy consumption and recovering energy from biosolids. Microsieving achieved an average removal of 35% TSS,16% $BOD_5$, and 20% COD, leading to a 7.4% annual reduction in the plant's electricity consumption. The collected biosolids, after drying were used in the gasifier, with the clean PSS yielding high-quality syngas ($H_2$ 15.5%, CO 16.4%, $CH_4$ 3.3%, $CO_2$ 7.5%). Cogeneration reached a maximum electrical power of 9 kW and an average of 4.9 kW, significantly enhancing the unit's energy self-sufficiency. The results are in line with the EU's objectives (Directive 2022/0345) for energy-neutral facilities, proposing the system as a sustainable and scalable model for medium and large W WWTPs. The study demonstrates that integrated technology can transform WWTPs from energy consumers to producers, promoting circular and climate-neutral wastewater management.

## References

Alizadeh, S., Chowdhury, P., Ghodsi, V., Giaccherini, F., Sarathy, S., Santoro, D., Comeau, Y., 2023. Physico-chemical characteristics and biodegradability of primary effluent and particulate matter removed by microscreens. Water Environment Research 95. https://doi.org/10.1002/wer.10854

Cieślik, B.M., Namieśnik, J., Konieczka, P., 2015. Review of sewage sludge management: standards, regulations and analytical methods. J Clean Prod 90, 1–15. https://doi.org/10.1016/J.JCLEPRO.2014.11.031

Gao, N., Li, J., Qi, B., Li, A., Duan, Y., Wang, Z., 2014. Thermal analysis and products distribution of dried sewage sludge pyrolysis. J Anal Appl Pyrolysis 105, 43–48. https://doi.org/10.1016/J.JAAP.2013.10.002

Gikas, P., 2017. Towards energy positive wastewater treatment plants. *J. Environ. Manage.*, 203, 621–629.

Hao, X., Chen, Q., van Loosdrecht, M.C.M., Li, J., Jiang, H., 2020. Sustainable disposal of excess sludge: Incineration without anaerobic digestion. Water Res. https://doi.org/10.1016/j.watres.2019.115298

Marani, D., Braguglia, C.M., Mininni, G., Maccioni, F., 2003. Behaviour of Cd, Cr, Mn, Ni, Pb, and Zn in sewage sludge incineration by fluidised bed furnace. Waste Management 23, 117–124. https://doi.org/10.1016/S0956-053X(02)00044-2

Ruiz, J.A., Juárez, M.C., Morales, M.P., Muñoz, P., Mendívil, M.A., 2013. Biomass gasification for electricity generation: Review of current technology barriers. Renewable and Sustainable Energy Reviews 18, 174–183. https://doi.org/10.1016/J.RSER.2012.10.021

Wang, Ziyi, Gong, Z., Wang, Zhenbo, Li, X., Chu, Z., 2021. Application and development of pyrolysis technology in petroleum oily sludge treatment. Environmental Engineering Research 26, 1–15. https://doi.org/10.4491/eer.2019.460

# Spray Mode and Precursor Molarity as Key Parameters in Solution Spray Pyrolysis of Oxygen Electrodes for Low Temperature Reversible Solid Oxide Cells (SOCs)

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***keywords:*** *spray pyrolysis; solid oxide cells; low temperature; cathode.*

## Introduction

Reversible Solid Oxide Cells (rSOCs) enable efficient energy conversion and storage by operating in both fuel cell (SOFC) and electrolysis (SOEC) modes. In SOFC mode, they convert fuels like hydrogen into electricity; in SOEC mode, they use electricity to produce hydrogen or syngas. Their dual functionality makes them ideal for sustainable energy systems, but challenges remain, including high costs, material limitations, and reliability.

Lowering operating temperatures (from 750–950°C to 500–750°C) could relax these issues, but at the cost of increasing overpotentials—especially at the oxygen electrode—requiring nanostructured electrodes and ultra-thin electrolytes. Oxygen electrodes must function in both oxidizing and reducing conditions, demanding materials with high electrocatalytic activity, mixed (i.e. electronic and ionic) conductivity, porosity, stability, and TEC compatibility (1).

At >750°C, Lanthanum Strontium Manganite (LSM) with Yttria Stabilized Zirconia (YSZ) electrolyte is common, while Lanthanum Strontium Copper Ferrite (LSCF) with Cerium Gadolinium Oxide (CGO) electrolyte is better suited for <700°C (2,3). Nanostructured LSCF–CGO electrodes improve performance and durability. Combining LSCF with BSCF enhances oxygen reduction reaction (ORR) activity and stability (4, 5). However, high thermal expansion coefficient (TEC) and surface Sr segregation, along with the toxicity of cobalt, drive interest in Sr- and Co-free alternatives.

This study investigates Co-free LSF ($La_{0.5}Sr_{0.5}FeO_3$) thin films on dense CGO10 using Solution Spray Pyrolysis (SSP). Variables such as deposition temperature, time, precursor concentration (0.1 M and 0.025 M), and spray mode (continuous vs. interrupted) were examined for their effects on film morphology, structure, and adhesion, and compared to films made using organic solvents.

## Materials and methods

Aqueous solutions of La, Sr and Fe with a total ion concentrations of 0.1M and 0.025M where prepared by mixing the appropriate amount of their soluble nitrate salts in deionized water. The cation ratio in the resulting precursor solutions was La:Sr:Fe = 1:1:2. Dense ceramic pellets of CGO were prepared by uniaxially pressing certain amount of CGO powder in a hydraulic press at 187 MPa that was subsequently sintered at 1500°C for 8 hours.

The Solution Spray Pyrolysis (SSP) method (Figure 1) was then applied to spray the precursor solutions on the CGO substrate at temperatures in the range 103 to 114°C (± 4) °C. Solution and air were mixed at 2.5bar in a spray nozzle, which produced a spray with 10-100 μm diameter droplets. After continuous spraying at various time intervals (15min, 30min, 45min, 60min) the films were sintered in situ for 1h and then were placed in a high temperature tubular furnace at 700 °C for 4hr with heating – cooling rates of 3 °C /min, to be further sintered. The procedure was repeated under interrupting spraying (1min spray ON/1min spray OFF) for a total spraying time of 45min and 60min, under the same pressure and temperature conditions. All samples were characterized by X-Ray diffraction and SEM-EDS.

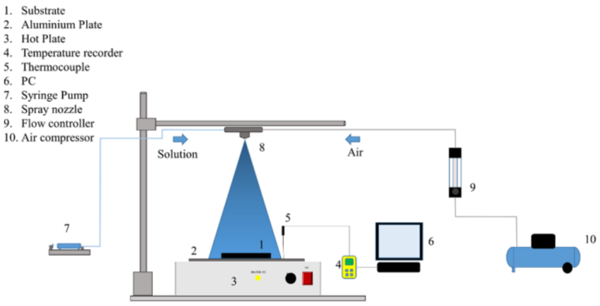

***Figure 1.*** *Spray Pyrolysis set up.*

**Results and discussion**

X-Ray results showed that the metal salts precursors fully decomposed to their corresponding ceramic oxides, namely $La_{0.5}Sr_{0.5}FeO_3$ (LSF). Due to the thin LSF layer, the CGO substrate was also detectable. SEM - EDS analysis revealed that the most coherent films were the ones formed under the on/off spraying mode (Table 1).

***Table 1.*** *Experimental conditions*

| Sample | Film (Total precursor ion concentrations, M) | Substrate | Spraying mode | Sintering scheme | $T_{dep}$ (°C) |
|---|---|---|---|---|---|
| **LSF1** | 0.1 | CGO10 | 15min | A | 103±4 |
| **LSF2** | 0.1 | CGO10 | 30min | A | 107±4 |
| **LSF3** | 0.1 | CGO10 | 45min | A | 114±2 |
| **LSF4** | 0.1 | CGO10 | 60min | A | 114±3 |
| **LSF3 - on/off** | 0.1 | CGO10 | 1 min spray on -1 min spray off (total spray on: 45min) | B | |
| **LSF4- on/off** | 0.1 | CGO10 | 1 min spray on -1 min spray off (total spray on: 60min) | B | |
| **LSF5** | 0.025 | CGO10 | 15min | A | 103±4 |
| **LSF6** | 0.025 | CGO10 | 30min | A | 107±4 |
| **LSF7** | 0.025 | CGO10 | 45min | A | 114±2 |
| **LSF8** | 0.025 | CGO10 | 60min | A | 114±3 |
| **LSF7 - on/off** | 0.025 | CGO10 | 1 min spray on -1 min spray off (total spray on: 45min) | B | |
| **LSF8- on/off** | 0.025 | CGO10 | 1 min spray on -1 min spray off (total spray on: 60min) | B | |

A: Intermediate sintering of first deposit layer in situ for 1h followed by additional sintering at 700°C for 4h.
B: In situ sintering step performed between two spray intervals (on/off) followed by the A sintering scheme.

**Conclusions**

Optimal conditions for deposition temperature and precursor solution concentration were determined that resulted in good adhesion and proper structure formation of the deposited films.

***Acknowledgements:*** The authors would like to thank Mrs. Katerina Breza, scientific personnel of CERTH for the SEM - EDS analysis and the PhD candidate Mr. Tsamos Dimitrios for the X-Ray analysis of the samples..

**References**

1. Kiratzis et al., Academia Green Energy, 2024, 1. https://doi.org/10.20935/AcadEnergy7390.
2. Krestou A.et al., ECS Transactions, 2021, 103 (1) pp123-138. 10.1149/10301.0123ecst.
3. Jiang S. P., Int. J. Hydrogen Energy, 2019, 44, (14) pp. 7448-7493. doi: 10.1016/j.ijhydene.2019.01.212.
4. Guan F. et al., Chin J Catal. 2018;39 pp1484–92. doi: 10.1016/S1872-2067(18)63118-3
5. Clematis D et al., Int J Hydrog Energy. 2019; 44 pp6212–22. doi: 10.1016/j.ijhydene.2019.01.128.

# Optimizing Drying Kinetics and Calorific Value Assessment of Wastewater Sludge for Enhanced Waste-to-Energy Gasification

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**keywords:** *Wastewater sludge; drying kinetics; calorific value; thin-layer drying models; gasification feedstock; waste-to-energy.*

The valorization of wastewater sludge (WWS) through waste-to-energy gasification offers a sustainable solution to sludge management challenges while contributing to renewable energy generation.. This study investigates the drying behavior and calorific value estimation of WWS to assess its feasibility as a domestic feedstock for gasification processes. Since drying is an energy-intensive pre-treatment step, optimizing drying conditions is essential to reduce energy consumption and improve the energy yield of the final product. Experimental drying of WWS was conducted at two controlled temperatures, 60°C and 80°C, to evaluate the effects of temperature-time combinations on drying kinetics. Data were fitted to four thin-layer drying models to determine the dominant drying mechanisms. Results showed that drying predominantly occurred during the falling rate period, governed by moisture diffusion. The logarithmic model best described drying behavior in layers 2 and 3 at both temperatures, whereas the Henderson and Pabis model was most accurate for layer 1 and Primary Settling Tank (PST) at 80°C.

Additionally, calorific value estimation of Fresh WWS from Drying Beds Layer 2 was found at the highest of 25.458MJ/Kg confirmed its potential as a viable energy source in gasification systems. The study provides critical insights into optimizing sludge drying protocols and improving calorific performance, contributing to effective integration of WWS in sustainable energy recovery strategies.

# Innovative wastewater technologies for the treatment of sewage sludge at overloaded activated sludge plants

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***keywords:*** *wastewater; gasification; biosolids; primary waste to energy*

Conventional wastewater treatment plants are highly energy-intensive and generate large volumes of biosolids, posing significant operational and environmental burdens (Tchobanoglous et al., 2003). Developing sustainable, energy-efficient technologies for sludge reduction and resource recovery is therefore an urgent priority. This study investigates an innovative integrated process that combines micro-sieving and gasification for the energy recovery of biosolids in municipal wastewater treatment plants (WWTPs). The system was installed at the Rethymno WWTP (Crete, Greece) as part of the LIFE B2E4SUSTAINABLE-WWTP project, aiming to enhance energy efficiency and support the transition toward energy-neutral treatment facilities.The pilot unit consisted of three main stages: micro-sieving for solids removal, thermal drying, and downdraft gasification. The produced syngas was cleaned and used in a cogeneration engine for electricity and heat generation. Experimental trials were conducted from November 2023 to December 2024, using various feedstocks—pure primary sieved solids (PSS), dried secondary sludge, and PSS–sludge mixtures. Results showed that pure PSS achieved the highest gasification performance, producing syngas with 15.5% $H_2$, 16.4% CO, 3.3% $CH_4$, and 7.5% $CO_2$, corresponding to a lower heating value (LHV) of 4.9 MJ/$Nm^3$, gas yield of 1.93 $Nm^3$/kg, and cold gas efficiency (CGE) of 54.1%. The cogeneration unit reached a peak electrical output of 9 kW and an average output of 4.9 kW, demonstrating the system's capability for on-site energy recovery. The integration of micro-sieving and gasification significantly reduced sludge volume and energy consumption in the aeration stage, aligning with EU Directive 2022/0345 (COD) targets for energy self-sufficient WWTPs. This approach offers a scalable pathway toward circular, low-carbon wastewater management.

***Acknowledgements:*** This study is supported by the Green Fund and the LIFE project (EC): "New concept for energy self-sustainable wastewater treatment process and biosolids management (LIFE B2E4sustainable-WWTP)", LIFE16 ENV/GR/000298.

## References

Tchobanoglous, G., Burton, F. and Stensel, D., 2003. *Metcalf and Eddy: Wastewater Engineering, Treatment and Reuse*, 4th ed.; McGraw Hill: New York, NY, USA.

# Session 10: Life cycle assessment

# Is Life Cycle Assessment essential for sustainability in heritage?

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***keywords:*** *cultural heritage; industrial heritage; mining heritage; LCA.*

## Introduction

Heritage encompasses properties and values passed down from previous generations, including historic buildings, artworks, cultural artefacts, and traditions [1]. Current conservation methods aim to preserve both structures and intangible cultural practices. Sustainable innovation in this field merges eco-friendly technologies with traditional methods, ensuring the asset's heritage integrity.

Climate change poses a major threat to heritage, especially coastal sites vulnerable to rising sea levels. Extreme weather—droughts, floods, storms and heatwaves - can damage or degrade historic structures, while air pollution accelerates decay in materials like marble and limestone.

Overtourism is another issue, straining sites and diminishing visitor experience [2]. To address these challenges, tools like life cycle assessment (LCA) and social life cycle assessment (s-LCA) can support a comprehensive, sustainable framework for conserving heritage while enhancing its authenticity and value for both locals and visitors.

## Materials and methods

Regarding the advancements of innovative conservation technologies, starting with the introduction of artificial intelligence, these applications are revolutionising heritage conservation. With the help of artificial intelligence and machine learning, it is now possible to analyse big data to predict deterioration patterns of structures and optimise maintenance. Climate adaptation technologies are also becoming increasingly vital for heritage preservation. Measures such as humidity control systems, flood barriers, and temperature-regulating materials are being implemented or developed specifically to address the challenges posed by changing environmental conditions [3]. Advancements in material science also offer novel protective materials, consolidants, and methods for preserving sites, aiming at minimising invasion and efficiency. Protective materials are designed to create a surface layer, less soluble than the underlying material, preventing its dissolution, while consolidants are designed to penetrate deeply into the substrates, binding the materials, increasing cohesion and improving mechanical properties[4].

While recent advances in conservation technologies provide powerful tools for heritage preservation and resilience to climate change, they also require careful evaluation of their long-term impacts. LCA plays a critical role in this process by offering a comprehensive and standardised methodology to quantify and compare the environmental effects of conservation materials and methods across all stages, from raw material extraction to application and disposal. By highlighting environmental hotspots and enabling the comparison of traditional versus novel materials, such as nano limes, calcium alkoxides, or solvent-free consolidants, LCA supports the identification of solutions that not only meet technical and conservation objectives but also minimise resource use, emissions, and ecological harm [5]. Complementing this, s-LCA addresses social aspects such as community benefit, stakeholder inclusion, and the preservation of local identity, ensuring that these conservation strategies are also socially responsible [6].

## How HI-EURECA-PRO project aims to address these Issues

The HI-EURECA-PRO project directly addresses heritage preservation's environmental and societal challenges by developing and testing innovative, sustainable methods and materials for cultural, mining and industrial heritage sites in Greece, Romania and Poland. Through a cross-collaboration with universities and ties with government and industry, it aims to create a regional innovation ecosystem (Fig. 1) that fosters knowledge and skill transfer for the green and digital transition. By integrating LCA and s-LCA, the project will ensure that new conservation approaches are both sustainable and beneficial to local communities. The ultimate goal is strengthening research excellence and creating a model for heritage-based innovation and sustainable development across Europe.

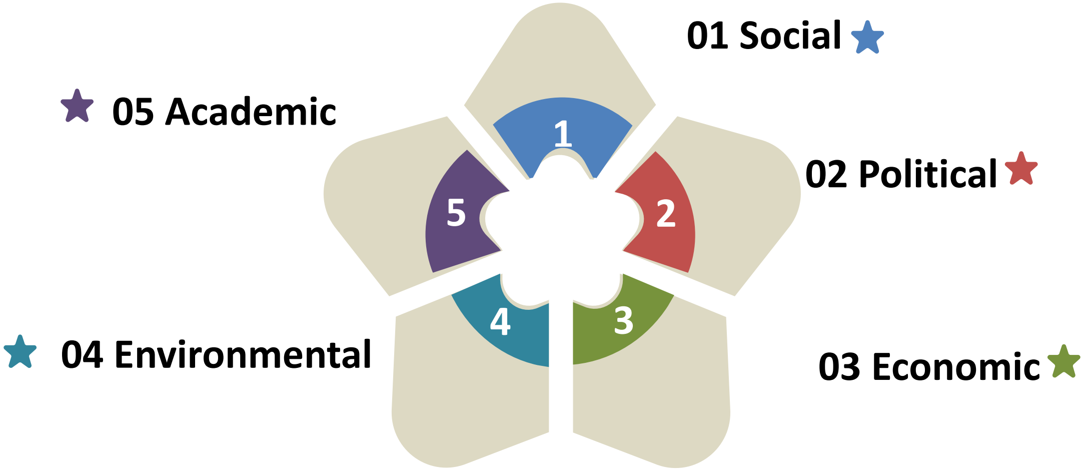

***Figure 1.*** *Example of the Demo ecosystem-Sustainable Cultural Heritage Network members in the Quintuple Helix of Innovation*

## Conclusions

Incorporating sustainable practices into heritage conservation has become essential, not optional. Due to the rapid progression of climate change, heritage sites require innovative protection strategies that honour their historical authenticity while ensuring their continued existence. Although emerging technologies present promising opportunities, they must be implemented thoughtfully. All technological interventions in conservation must adhere to the principles of minimal intervention and reversibility.

***Acknowledgements:*** *This study was supported by the HORIZON EUROPE programme, within the framework of the project HI-EURECA-PRO. Heritage Innovation in EURECA-PRO Alliance" funded by the European Commission (101136779). The author is solely responsible for the content of this paper. The European Commission is not responsible for any use that may be made of the information contained therein.*

## References

1. "heritage, n. meanings, etymology and more | Oxford English Dictionary." https://www.oed.com/dictionary/heritage_n?tab=factsheet#1764513
2. G. Skiniti, M. Lilli, N. Skarakis, S. Tournaki, N. Nikolaidis, and T. Tsoutsos, "A holistic approach for tourism carrying capacity estimation in sensitive ecological areas," *Environment Development and Sustainability*, Apr. 2024, doi: 10.1007/s10668-024-04805-0.
3. C. L. S. Blavier, H. E. Huerto-Cardenas, N. Aste, C. Del Pero, F. Leonforte, and S. Della Torre, "Adaptive measures for preserving heritage buildings in the face of climate change: A review," *Building and Environment*, vol. 245, p. 110832, Sep. 2023, doi: 10.1016/j.buildenv.2023.110832.
4. G. Graziani, E. Sassoni, G. W. Scherer, and E. Franzoni, "Resistance to simulated rain of hydroxyapatite- and calcium oxalate-based coatings for protection of marble against corrosion," *Corrosion Science*, vol. 127, pp. 168–174, Aug. 2017, doi: 10.1016/j.corsci.2017.08.020.
5. D. Pozzo, G. Masi, E. Sassoni, and A. Tugnoli, "Life cycle assessment of stone consolidants for conservation of cultural heritage," *Building and Environment*, vol. 249, p. 111153, Dec. 2023, doi: 10.1016/j.buildenv.2023.111153.
6. S. M. Khorassani, A. M. Ferrari, M. Pini, D. S. Blundo, F. E. G. Muiña, and J. F. García, "Environmental and social impact assessment of cultural heritage restoration and its application to the Uncastillo Fortress," *The International Journal of Life Cycle Assessment*, vol. 24, no. 7, pp. 1297–1318, Jun. 2018, doi: 10.1007/s11367-018-1493-1.

# Sustainable extraction of V and Ti from low-grade V-bearing titanomagnetite deposits

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***keywords:*** *critical raw materials; life cycle assessment; technoeconomic assessment; public acceptance; sustainability framework*

## Introduction

Vanadium (V) and titanium (Ti) are important strategic/critical raw materials (CRMs) that are widely used in many advanced products and industrial sectors due to their excellent physical and chemical properties (Zhu et al., 2023). Titanium is primarily extracted from minerals such as rutile ($TiO_2$) and ilmenite ($FeTiO_3$), while vanadium is commonly obtained from vanadium-bearing titanomagnetite (VTM) deposits, rich in V, Ti, Fe, as well as trace elements (Wang et al., 2025). Global titanium reserves are estimated at around 800 million tons, with high-quality rutile accounting for only 6% (USGS, 2025). As the grade of ores containing rutile currently declines, ilmenite (94%) has become the primary titanium source. On the other hand, global VTM reserves are estimated at 60 billion tons, far exceeding Ti-rich oxide deposits containing ilmenite and rutile.

## Materials and methods

In order to meet Europe's Critical Raw Materials Act (CRMA) benchmark of 10% domestic extraction and reduce its reliance on imported V and Ti, the AVANTIS HE project aims to develop a near-zero-waste, multi-metal extraction process for Europe’s low grade un-exploited resources such as VTM deposits and mining wastes i.e. historical & fresh V/Ti-bearing tailings (AVANTIS, 2025). With this low-carbon, cost-effective, and responsible mining approach the projects aims to sustainably produce V and Ti pre-concentrates, which can be further refined into high-purity Ti metal and $V_2O_5$, facilitating efficient resource use and minimizing environmental impact. In this sense, this integrated approach involves i) life cycle assessment (LCA) to evaluate the environmental impacts of V and Ti metal production on human health, ecosystems, and resources, ii) techno-economic assessment (TEA) to evaluate the economic viability of tailored combinations of the next-generation, low-carbon mining and beneficiation technologies over their operational lifetime, and iii) public acceptance (PA) / social license to operate (SLO) to assess the level of community acceptance with respect to land use, local conditions and other sensitive issues for the extraction of V and Ti from European resources (Figure 1) (Komnitsas and Eerola, 2024).

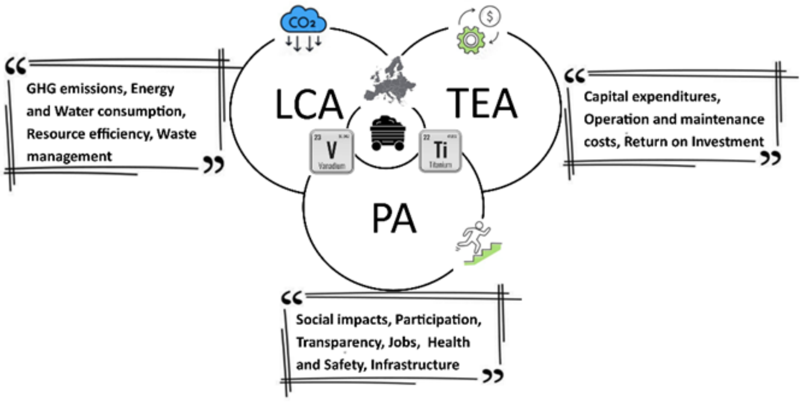

***Figure 1.*** *Integrated framework to evaluate sustainable extraction of V and Ti from low-grade VTM resources in Europe in the framework of the AVANTIS HE project*

## Results and discussion

This integrated framework will offer a comprehensive evaluation of the newly developed mining approach, which incorporates innovative selective blasting, fragmentation, and pre-concentration technologies such as bulk ore sorting, advanced flotation and magnetic separation to process complex, low-grade domestic V/Ti-bearing resource deposits that are currently not economically viable. Furthermore, it will maximize the V/Ti potential of Europe's low-grade, complex VTM deposits, reinforcing the EU's position in the V and Ti value chain enhancing resource sustainability, economic resilience, and technological innovation.

Special emphasis is also given, apart from reducing energy requirements, greenhouse gas (GHG) emissions and the overall footprint of V- and Ti- extraction, on health and safety (H&S) aspects. In this context, geochemical studies are performed to assess environmental and human health impacts of PHEs present in the processing chain. Leaching (pH-dependence and kinetic) tests are carried out to assess the potential release of elements and define possible management options (e.g., recycling, treatment, disposal). Human health-risk assessment is also implemented with the application of bioaccessibility tests (Komnitsas et al., 2025; Vathi and Komnitsas, 2025).

## Conclusions

In this study, the sustainable extraction of V and Ti from low-grade European VTM ores using a wide range of low-carbon, near-zero-waste technologies is assessed. Through the integration of environmental, economic, and social assessments, it aims to reduce EU import dependency, unlock domestic resources, and support the strategic goals of the recent CRMA.

***Acknowledgements:*** The authors would like to acknowledge the financial support of European Union in the frame of Horizon AVANTIS project “Sustainable, decarbonised co-extraction of vanadium and titanium minerals from Europe's low-grade vanadium-bearing titanomagnetite deposits”, https://avantis-horizon.eu/, Grant Agreement No. 101137552.

## References

AVANTIS, 2025. AVANTIS HE project - Sustainable, decarbonised co-extraction of vanadium and titanium minerals from Europe's low-grade vanadium-bearing titanomagnetite deposits, https://avantis-horizon.eu/

Komnitsas, K., Eerola, T. 2024. Public Acceptance and Responsible Mining towards Energy Transition, 11th International Conference on Sustainable Development in the Minerals Industry – SDIMI, Torino, Italy, July 9-11, 2024, https://www.sdimi2024.org/

Komnitsas, K, Vathi, D., Karmali, V. 2025. Geochemical environmental assessment of mining - metallurgical wastes and alkali activating materials“9th Slag Valorisation Symposium - From Residues to Resources and Resilience”, 8-11 April 2025, Leuven, https://slag-valorisation-symposium.eu/

Vathi, D., Komnitsas, K. 2025. Mobility of elements from tailings produced after flotation of low-grade, vanadium-bearing titano-magnetite ores, 12th International Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE 2025) and SECOTOX Conference, 25-29 May 2025, Mykonos, Greece, https://cemepe12.civil.auth.gr/

USGS, 2025. Mineral Commodity Summaries 2025 - Titanium mineral concentrates, https://pubs.usgs.gov/periodicals/mcs2025/mcs2025-titanium-minerals.pdf

Wang, J., Liu, B., Zhang, Y. and Jiang, T., 2025. Structural and Liberation Effect of Vanadium Titano-Magnetite by Microwave Pretreatment, *The Journal of The Minerals, Metals & Materials Society (TMS)*, https://doi.org/10.1007/s11837-025-07143-2

Zhu, F., Ma, Z., Qiu, K. and Peng, W., 2023. Separation of Ilmenite from Vanadium Titanomagnetite by Combining Magnetic Separation and Flotation Processes. *Separations*, 10(2), 95. https://doi.org/10.3390/separations10020095

# Posters

# Bioremendiation of secondary cheese whey effluent by *Pseudomonas* sp. phDV1

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***keywords:*** *Pseudomonas sp. phDV1; secondary cheese whey waste; Polyhydroxyalkanoates; Polyhydroxybuturic acid.*

## Introduction

The rapid proliferation of petroleum-based plastics has highlighted the need for sustainable alternatives, with polyhydroxyalkanoates (PHAs) surfacing as a favorable solution, due to their high biodegradability. PHAs are a certain type of bioplastic that can be produced by bacteria, when grown under stress conditions, in order to be used as an energy source [1]. The simplest and most studied PHA is poly(R)-3-hydroxybutyric acid (P(3HB)), commonly known as PHB. This biopolymer is structured intercellularly in the form of granules that are called carbonosomes, and despite its promising potential, the high production costs remain a bottleneck [1].

*Pseudomonas* sp. phDV1, a Gram-negative bacterium isolated from petroleum-contaminated soil in Denmark, has been reported to produce PHB when grown in various types of waste, such as phenol and wine industry waste [1,2]. In this context, a specific type of wastewater, secondary cheese whey (SCW), was used for PHB production. SCW is a by-product of cheese making, that contains significant nutrients such as lactose, nitrogen, phosphorus and mineral salts, ingredients that render it highly polluting for the environment but at the same time a suitable and cost-effective substrate for the production of bioplastic [3].

## Materials and methods

*Pseudomonas* sp. phDV1 was cultivated in two basic conditions containing SCW. Due to the lack of information on the ability of this specific bacterium to consume lactose, SCW was used as is and after hydrolysis, to utilize the simpler sugars that make up lactose, glucose and galactose. Hydrolysis was performed with commercially available lactase at a concentration of 36 mg/100 mL, under conditions of gentle horizontal stirring and a constant temperature of 55°C for 4 hours. Cultures of the bacterium were carried out only in the wastewater in its two forms, without the addition of any other media normally used for the growth of this species. In order to compare the growth and possible PHB production, SCW and hydrolysed SCW were used at lower concentrations while this time, M9 minimal medium was also used for this type of cultures. Liquid cultures were performed at 32°C and 200 rpm for 120 hours and 72 hours respectively. Growth was monitored by measuring optical density at 600 nm using a plate reader (Multiskan SkyHigh Microplate Spectrophotometer, ThermoFischer Scientific). All cultures were performed in triplicate, to ensure accurate and reliable results.

Potential PHB production was determined using Nile red staining. All samples were prepared using the protocol used by Geladas et al, 2025 [1]. Observation was performed with an oil-immersed lens under a Nikon ECLIPSE E800 microscope (Nikon Instruments Inc., Melville, NY, USA), with an excitation wavelength of 562/40 nm and an emission wavelength of 594 nm.

## Results and discussion

Growth curves were plotted for each condition under which *Pseudomonas* sp. phDV1 was cultured. The results showed that the bacterium was able to metabolize SCW in both forms, both with and without the presence of the M9 minimal medium. Growth was observed to be slower when cultivated in the wastewater alone, with the cultures lasting 120 hours, compared to the ones where M9 was present, that lasted 72 hours. The slower rate of development in the first conditions can be attributed to the fact that the sole presence of the wastewater increases the stress on the bacterium and so it needs more time to adapt to this environment.

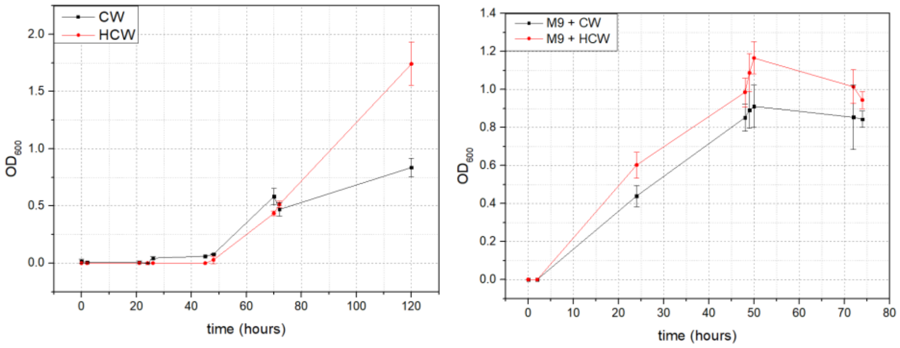

***Figure 1.*** ***(A)*** *Growth curves of Pseudomonas sp. phDV1 only in SCW (black squares) and hydrolysed SCW (red circles).* ***(B)*** *Growth curves of Pseudomonas sp. phDV1 M9 minimal medium with SCW (black squares) and hydrolysed SCW (red circles).*

As of the bacterium grew successfully in all the conditions tested, Nile Red staining was performed, so that possible PHB production would be detected. Both optical and fluorescence microscopy were carried out and the results confirmed that *Pseudomonas* sp. phDV1 was able to produce PHB when cultivated in pure SCW and hydrolysed SCW, whereas when cultivated in the presence of M9 minimal medium, the number of granules detected were much lower. These results can be attributed to the fact that, when grown in the wastewater alone, the stress on the bacterium is sufficient to allow it to accumulate PHB intercellularly. All fluorescence microscopy results are qualitative, and further research is needed to confirm the actual amounts of the biopolymer in each growth condition.

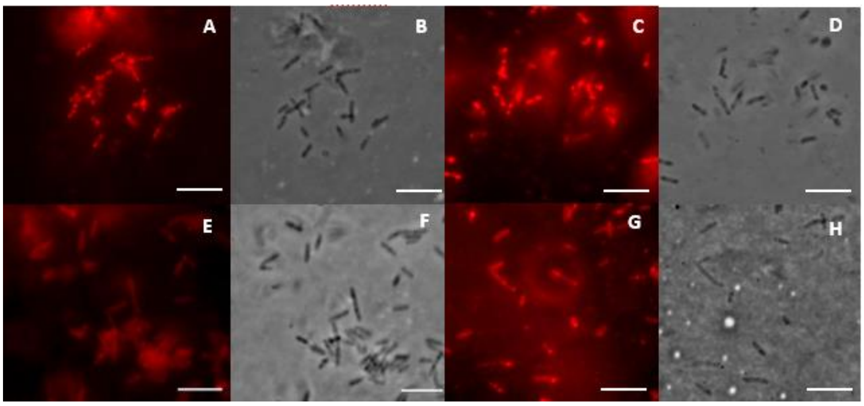

***Figure 2.*** *Optical and fluorescence microscopy of Pseudomonas sp. phDV1 cultivated in different conditions;* ***(A,B)*** *only in SCW* ***(C,D)*** *only in hydrolysed SCW* ***(E,F)*** *in M9 minimal medium and SCW* ***(G,H)*** *in M9 minimal medium and hydrolysed SCW. Scale bar represents 5 μm.*

## Conclusions

*Pseudomonas* sp. phDV1 has been shown to be able to accumulate PHB, when using SCW and hydrolysed SCW as the sole growth medium, while in cases where the waste was used with M9 minimal medium, very few granules were able to be observed. Further research is needed to determine the actual quantities of the bioplastic produced in the growth conditions mentioned above.

## References

1. Geladas, E. D., Lyratzakis, A., Drakonaki, A., Gkikas, G., & Tsiotis, G. (2025). Isolation and Characterization of Carbonosomes from *Pseudomonas* sp. phDV1 Grown Using Phenol as Carbon Source. *Microorganisms*, *13*(2), 369.
2. A. Drakonaki, E. Mathioudaki, E.D. Geladas, E. Konsolaki, N. Vitsaxakis, N. Chaniotakis, H. Xie, G. Tsiotis, Production of Polyhydroxybutyrate by Genetically Modified Pseudomonas sp. phDV1: A Comparative Study of Utilizing Wine Industry Waste as a Carbon Source., Microorganisms 11 (2023).

3. Fancello, F., Zara, G., Hatami, F., Scano, E. A., & Mannazzu, I. (2024). Unlocking the potential of second cheese whey: a comprehensive review on valorisation strategies. *Reviews in Environmental Science and Bio/Technology*, *23*(2), 411–441.

# Hydrogen-Rich Gas Production from the Steam Gasification of Olive By-products with Minimum Carbon Dioxide Emissions

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***keywords:*** *hydrogen; olive by-products; carbon dioxide.*

## Introduction

In the context of circular and low-carbon economy and sustainability, the study focused on exploring the production of hydrogen-rich gaseous fuels from olive by-products, with minimum carbon dioxide emissions to the environment. Fly ash from a lignite power plant and building demolition wastes were used to capture carbon dioxide during the process.

## Materials and methods

The experiments were conducted in a fixed-bed system, under a nitrogen/steam atmosphere and generated gases were analyzed by a thermogravimetric-mass spectrometry unit. The effects of temperature and sorbent/fuel ratio on fuel conversion, product gas composition, heating value and yield of hydrogen were examined and optimum conditions were determined.

## Results and discussion

The optimum Ca/C for fly ash was 1, while for building wastes was 2. Under these conditions, addition of fly ash captured 86.7 % of carbon dioxide emitted at 750°C, increased the concentration of hydrogen in the product gas by 56.9 %, reaching a value of 60.4 %mol, with a higher heating value of 13.3 MJ/$m^3$. Fuel conversion was 90 %dry and hydrogen yield was 1 $m^3$/kg. On the other hand, addition of building wastes captured 94.2 % of carbon dioxide emitted at 750°C, increased the concentration of hydrogen in the product gas by 90.4 %, reaching a value of 73.3 %mol, with a higher heating value of 13.4 MJ/$m^3$. Fuel conversion was 92.5 %dry and hydrogen yield was 1.34 $m^3$/kg.

## Conclusions

Both fly ash and building demolition wastes were proved to be successful as carbon dioxide sorbents from the steam gasification process, however building demolition wastes presented a better performance. The gaseous product from olive by-products was rich in hydrogen and suitable for many applications as a fuel.

# Optimal Wind Power Investments and Bidding Strategies in Electricity Market Considering Green Certificates Trading

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***keywords:*** *bi-level optimization; green certificates; electricity market; strategic offering; wind power investment.*

## Introduction

The increasing share of Renewable Energy (RE) in the global energy mix has significantly altered Electricity Market (EM) dynamics. The self-cannibalization effect, where higher RE penetration lowers wholesale electricity prices threatens market profit for RE producers. As a coping mechanism RE producers act strategically and curtail their production undermining the effectiveness of climate policies. Such policies include the Renewable Portfolio Standard (RPS) and the Green Certificates Market (GCM), designed to promote RE penetration in the energy mix. Approaches to derive the optimal bidding strategies for a producer in EM have been presented by Tsimopoulos and Georgiadis (2020). Dimitriadis et al. (2024) implemented hourly EM and GCM clearing and analyzed the impact of strategic bidding on profit maximization by comparing two RE aggregators possessing the same asset portfolios. Nguyen and Felder (2020) and Kwang et al. (2023) examined the generation investment problem considering GCM while treating GCs prices as variables. However, they adopted a centralized market framework. This work introduces a bilevel optimization model to capture the interrelation between RE investment decisions, a GC hourly trading mechanism, and strategic bidding. By jointly considering these mechanisms, the study provides a more comprehensive understanding of the challenges faced by RE investors in meeting RPS targets, securing profits, and adapting to evolving market conditions.

## Method

The proposed bilevel model incorporates EM and GCM clearing in a generation investment problem of a producer owning wind farms. The upper-level problem maximizes the profit of the strategic player, while deciding on the capacity of the new farms and the bidding strategies in both EM and GCM. The producer is considered a price-maker with a significant market share that can influence EM and GCM prices.

The lower-level problems mimic the clearing of EM and GCM respectively. Both markets are cleared on an hourly basis, aligning with new market trends (EnergyTag, 2021). In the GCM, Load Serving Entities (LSEs) are required to meet RPS targets by buying Green Certificates (GCs). One GC is issued for each MWh of electricity produced by RE. Regarding temporal representation, a static model is employed, focusing on a target year with hourly resolution to account for demand and renewable variability. Due to computational complexity, Chronological Time-Period Clustering (CTPC) is used to cluster similar operating conditions while preserving data sequence.

The model links electricity demand and the demand for GCs, as well as the share of RE in the energy mix and the availability of GCs. By applying Karush-Kuhn-Tucker (KKT) conditions, binary expansion techniques, and duality theory, the model is transformed into a Mixed Integer Linear Program (MILP), solvable by commercial optimization solvers. The proposed model is solved using GAMS/CPLEX and is applied on a modified 5-bus power system.

## Results and discussion

Table 1 summarizes the results for different RPS targets comparing scenarios where the producer bids strategically either only in GCM or in both EM and GCM.

In a system with a high RPS target (54%), there is a shortage of GCs, resulting in the GCM clearing at the maximum price (4.5$/certificate). This incentivizes new wind power investments, although it carries the risk of lowering EM prices due to the high penetration of RE in the energy mix. Indeed, EM prices decline. However, by adopting bidding strategies in both markets, the producer becomes the marginal producer, thereby setting the market price. In that case, the capacity of the new investments is chosen to secure a dominant market share while avoiding zero market prices. Exerting market power to increase EM prices is not profitable and a "volume-based" policy prevails.

Reducing the RPS target to 30% leads to a surplus of GCs, driving down the certificate price. As a result, a "volume-based" policy becomes unprofitable, and the producer opts for smaller investments. Nevertheless, under a low RPS target, adopting bidding strategies in both markets still increases profit, as zero prices are avoided through capacity withholding and EM prices rise during other operating conditions. Also, in this context, due to GCs surplus, the offering prices of the non-strategic wind farms affect the GCM clearing price and therefore the investment decisions. As the GCM biddings increase the strategic player decides on new investments, since the GCs price also increases. The capacity of the new investments is adjusted to benefit from the profit margin in GCM while not altering EM clearing prices since that would negatively affect the total profit by driving prices down due to excessive RE penetration.

***Table 5.*** *Results for different RPS targets and strategic decisions.*

| RPS target | Strategic bidding in EM | Revenue in EM (M$) | Revenue in GCM (M$) | Investment (MW) | GCs issued | GCs sold | Profit (M$) |
|---|---|---|---|---|---|---|---|
| **30%** | Yes | 23.5 | 1.2 | 40 | 3,982 | 3,912 | 19.9 |
| **30%** | No | 20.7 | 1.2 | 20 | 3,757 | 3,757 | 19.5 |
| **54%** | Yes | 40.0 | 3.5 | 180 | 6,586 | 6,586 | 22.0 |
| **54%** | No | 30.0 | 3.2 | 100 | 5,514 | 5,502 | 21.2 |

## Conclusions

This work presents a bilevel model to derive optimal investment and bidding strategies for a producer owning wind farms while participating in EM and GCM. The model incorporates the hourly coordination of EM and GCM clearing and captures the impact of different RPS targets and rivals' offering prices. The results demonstrate that increasing the RPS target or the rival offering prices encourages the investor to adopt a "volume-based" policy. Also, by acting strategically in both EM and GCM the producer avoids overinvestment that would entail frequent zero EM prices.

## References

Dimitriadis, C.N., Tsimopoulos, E.G., Georgiadis, M.C., 2024. Co-optimized trading strategy of a renewable energy aggregator in electricity and green certificates markets. Renew Energy 236, 121444. https://doi.org/10.1016/j.renene.2024.121444

EnergyTag, 2021. EnergyTag and granular energy certificates: Accelerating the transition to 24/7 clean power. https://www.energytag.org/wp-content/uploads/2021/05/EnergyTag-and-granular-energy-certificates.pdf

Kwag, K., Shin, H., Oh, H., Yun, S., Kim, T.H., Hwang, P.I., Kim, W., 2023. Bilevel programming approach for the quantitative analysis of renewable portfolio standards considering the electricity market. Energy 263. https://doi.org/10.1016/j.energy.2022.126013

Nguyen, H.T., Felder, F.A., 2020. Generation expansion planning with renewable energy credit markets: A bilevel programming approach. Appl Energy 276, 115472. https://doi.org/10.1016/J.APENERGY.2020.115472

Tsimopoulos, E.G., Georgiadis, M.C., 2020. Withholding strategies for a conventional and wind generation portfolio in a joint energy and reserve pool market: A gaming-based approach. Comput Chem Eng 134, 106692. https://doi.org/https://doi.org/10.1016/j.compchemeng.2019.106692

# Copper recovery from printed circuit boards: Alkaline glycine leaching system

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***keywords:*** *printed circuit boards; leaching; glycine; copper; recovery.*

## Introduction

The fast development of technology, the high-performance requirements, and the great demands in electrical and electronic equipment (EEE) make the replacement of printed circuit boards (PCBs) more frequent, resulting in large quantities of waste printed circuit boards (WPCBs) that need to be disposed of. WPCBs contains a variety of hazardous substances and heavy metals, namely halogenated flame retardants, cadmium, lead, and other metals that, in order of a sound environmental point of view, should be adequately managed, preferably recycled. On the other hand, PCBs are composed of base metals and precious metals, mainly copper, aluminum, tin, lead, zinc, silver, and gold being copper the major metal with 10 − 30 %, representing a high economic value (Oishi et al., 2007; Koyama et al, 2006).

Hydrometallurgical processes are commonly used to recover metals and are recognized as having the advantage of being easily controlled, having high leaching efficiencies, being predictable, having low capital cost, and may be viable under small-scale operations (Oishi et al., 2007). Various researchers studied copper leaching from WPCBs using different leaching agents, such as mineral acids, including sulphuric acid (Kumari et al., 2016; Oh et al., 2003), nitric acid (Choubey et al., 2015; Maguyon et al, 2012) and a mixture of acids (Arshadi et al., 2020; Tunali et al., 2020). However, these acids are not very selective concerning the leachable metals. Furthermore, nitric acid and aqua regia, due to their corrosive and highly toxic nature, may bring environmental risks. Thus, some authors have studied environmentally benign alternative reagents to recover metals such as glycine. These studies reported that amino acid has a high affinity for copper (Oraby et al., 2020; Tanda et. al, 2017).

This work evaluates copper recovery using glycine solutions to leach WPCBs samples followed by reductive precipitation. Factors that influence recovery, such as glycine concentration, pH and temperature, were assessed.

## Materials and methods

All the WPCBs samples used in this research were from obsolete computers. First, the large components as the universal serial bus (USB) and the high-definition multimedia interface (HDMI) were removed from the WPCBs. The samples were previously ground with a particle size of 1 mm to < 1.4 mm. For metals quantification, WPCBs samples were subjected to chemical attack with aqua regia, according to the ISO 11466:1995 standard.

The leaching tests were carried out in Erlenmeyer flasks using 0.5 or 2 mol dm$^{-3}$ glycine solution, 1 mol dm$^{-3}$ hydrogen peroxide solution under pH 8, 9 or 10 at room temperature and 60 ºC during 48 h, and a mechanical stirring of 500 rpm. Copper was recovered directly from the leaching solutions by reductive precipitation using zinc with the 2 times the stoichiometric amount that copper.

## Results and discussion

The results showed that the glycine concentration influenced leaching, being the most significant dissolution of copper, 44 %, using 2M at 48 h of leaching. At the highest alkaline pH of 10, the dissolution achieved was 31 %. The temperature increase to 60 ºC was not shown to be a significant parameter, with practically the same percentage of dissolution being obtained at room temperature. The dissolution obtained was not very high, probably due to the sample's particle size. This could be improved by using a smaller particle size to ensure sufficient liberation of the metals and increase the contact area between the metals and the solution. The copper recovery in the reductive precipitation leaching solutions using zinc was 99.6 % after 10 min.

## Conclusions

Glycine-peroxide solutions leach copper at room temperature, but the dissolution depends on the glycine concentration and pH. Reductive precipitation is a good alternative to electrowinning for copper extraction from alkaline glycine. This leaching agent can be a great alternative to the classic leaching agents mainly due to its high stability and environmentally friendly nature.

## References

Arshadi, M., Yaghmaei, S., Esmaeili, A., 2020. Evaluating the optimal digestion method and value distribution of precious metals from different waste printed circuit boards. J. Mater. Cycles Waste Manag., 22, 1690–1698.

Choubey, P.K., Panda, R., Jha, M. K., Lee, J.C., Pathak, D., 2015. Recovery of copper and recycling of acid from the leach liquor of discarded Printed Circuit Boards (PCBs). Sep. Purif. Technol. 156, 269–275.

Koyama, K., Tanaka, M., Lee, J., 2006. Copper Leaching Behavior from Waste Printed Circuit Board in Ammoniacal Alkaline Solution. Mater. Trans. 47 (7), 1788–1792.

Kumari, A., Jha, M.K., Lee, J., Singh, R.P., 2016. Clean process for recovery of metals and recycling of acid from the leach liquor pf PCBs. J. Clean. Prod. 112, 4826–4834.

Maguyon, M.C., Catalino, G., Alfafara, G., Migo, V.P., Movillon, J.L., Rebancos, C.M., 2012. Recovery of copper from spent solid printed circuit board (PCB) wastes of a PCB manufacturing facility by two-step sequential acid extraction and electrochemical deposition. J. Environ. Sci. Manag. 15 (1).

Oh, C.J., Lee, S.O., Yang, H.S., Ha, T.J., Kim, M.J., 2003. Selective leaching of valuable metals from waste printed circuit boards. J. Air Waste Manag. Assoc. 53 (7), 897–902.

Oishi, T., Koyama, K., Alam, S., Tanaka, M., Lee, J.C., 2007. Recovery of high purity copper cathode from printed circuit boards using ammoniacal sulfate or chloride solutions. Hydrometallurgy, 89 (1–2), 82–88.

Oraby, E.A., Huan, L., Eksteen, J.J., 2020. An alkaline glycine-based leach process of base and precious metals from powered waste printed circuit boards. Waste and Biomass Valorization, 11, 3897–3909.

Tanda, B.C., Eksteen, J.J., Oraby, E.A., 2017. An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions. Hydrometallurgy, 167, 153–162.

Tunali, M., Tunali, M.M., Yenigun, O., 2020. Characterization of different types of electronic waste: heavy metal, precious metal and rare earth element content by comparing different digestıon methods. J. Mater. Cycles Waste Manag, 23, 149–157.

# Influence of Operating Parameters on Lead Hydrometallurgical Leaching of Lead-Acid Batteries with NaCl

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***keywords:*** *lead recovery; leaching; sodium chloride; battery recycling; process optimization.*

## Introduction

The recycling of lead-acid batteries (LABs) is essential to mitigate the release of lead into the environment, a toxic metal widely used in these batteries. One of the main components of LABs is the lead paste, which contains various compounds such as lead sulfate ($PbSO_4$), lead oxide (PbO), and lead dioxide ($PbO_2$), found in the negative and positive plates.

To enhance lead recovery efficiency, the paste was pre-desulfated, converting $PbSO_4$ into PbO. This step reduced the formation of undesirable by-products and increased the reactivity of the metallic matrix. X-ray fluorescence (XRF) analysis confirmed the predominance of PbO (88.9%), low residual levels of $SO_3$ (6.9%), and the absence of $PbO_2$, indicating a less complex system and greater selectivity in the process.

Although pyrometallurgical processes are widely used for LAB recycling, they involve high energy consumption and significant emission of atmospheric pollutants, prompting the search for more sustainable alternatives.

Among these, hydrometallurgical leaching stands out, promoting the selective dissolution of lead compounds in aqueous media. In this study, sodium chloride (NaCl) was selected as the leaching agent due to its low cost, low toxicity, and environmental compatibility, in addition to providing chloride ions that facilitate the formation of soluble Pb–Cl complexes.

Thus, this work investigated the influence of NaCl concentration, temperature, and solid-to-liquid (S/L) ratio on the leaching efficiency of PbO, aiming to optimize the hydrometallurgical process for cleaner and more efficient lead recovery.

## Materials and methods

Leaching assays were performed to evaluate the influence of three operational parameters: NaCl concentration, temperature, and solid-liquid ratio (S/L). Lead concentrations in the solutions were determined by atomic absorption spectrometry (AAS).

For the study of NaCl concentration, solutions of 1 M, 4 M, 5 M, and 6 M were tested. In each assay, 5 g of battery paste was added to 200 mL of solution, under continuous stirring at room temperature (~25 °C).

To investigate the effect of the solid-liquid ratio, three proportions were evaluated: 40 g/L, 20 g/L, and 10 g/L, corresponding to the addition of 5 g, 10 g, and 20 g of sample in 200 mL of 4 M NaCl solution. All assays were conducted under constant agitation at room temperature, with sample collection over 24 hours.

Finally, the influence of temperature was assessed using the optimized concentration determined in the previous step. Leaching assays were performed with 5 g of sample in 200 mL of NaCl solution, at room temperature (~25 °C) and at 60 °C, under continuous stirring, with sampling conducted over 24 hours.

## Results and discussion

The increase in NaCl concentration significantly enhanced lead recovery. The 2 M solution resulted in 13.23% recovery after 24 h, whereas 5 M achieved 32.28% in just 6 h. No substantial gains were observed above 5 M, indicating a saturation limit.

Reducing the solid-liquid ratio (S/L) also improved leaching efficiency. The lowest tested ratio (2/200) led to 23.97% recovery in 2 h, while the highest (20/200) limited recovery to 3.49% in 8 h, likely due to greater chloride ion availability and improved mass transfer at lower S/L ratios.

The temperature increase further boosted recovery, with 31.48% obtained at 60 °C in 8 h. However, at 75 °C, an irregular behavior was observed, with an initial recovery of 23.97% in 2 h, followed by a decline, possibly associated with secondary phase formation or surface passivation.

These results highlight the influence of operational parameters, establishing 5 M NaCl, 60 °C, and a 2/200 S/L ratio as optimal conditions for efficient lead leaching.

***Table 1.*** *Summary of assay conditions and respective Pb recoveries*

| Assay | NaCl concentration (M) | S/L ratio (g/200 mL) | Temperature (°C) | Time (h) | Pb Recovery (%) |
|---|---|---|---|---|---|
| **Effect of concentration** | 5 | 5/200 | Ambient (~25 °C) | 6 | 32,28 |
| **Effect of S/L ratio** | 4 | 2/200 | Ambient (~25 °C) | 2 | 23,97 |
| **Effect of temperature** | 4 | 5/200 | 60 °C | 8 | 31,48 |

## Conclusions

The results demonstrate that the increase in the concentration of NaCl, the temperature and the reduction of the solid-liquid ratio favor the leaching of lead, with significant gains in the efficiency of the process. The concentration of 5 M, temperature of 60 °C and S/L ratio of 2/200 configure the optimal conditions, promoting recoveries of more than 30% in reduced times. However, a threshold beyond which gains become marginal or negative was identified, as observed with concentrations above 5 M and high temperatures. These results are relevant for the development of more efficient and environmentally appropriate hydrometallurgical routes in the recycling of LABs, highlighting the need for future studies for optimization on an industrial scale.

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## References

Ellis TW, Mirza AH (2010) The refining of secondary lead for use in advanced lead-acid batteries. J Power Sources 195:4525–4529.

Rao S, Liu ZQ, Wang DX, Cao HY, Zhu W, Zhang KF, Tao JZ (2021). Hydrometallurgical process for recovery of Zn, Pb, Ga and Ge from Zn refinery residues. Transactions of Nonferrous Metals Society of China, 31(2), 555–564.

Xie H, Zhang L, Li H, Koppala S, Yin S, Li S, Zhu F (2019). Efficient recycling of Pb from zinc leaching residues by using the hydrometallurgical method. Materials Research Express, 6(7), 075505.

# Adsorption of Reactive Red 120 dye by oxidized biochar from palm tree fibers

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***keywords:*** *adsorption; Reactive Red 120; isotherms models; wastewater treatment; palm tree fibers.*

## Introduction

Reactive Red 120 (RR120) is an anionic, triazine-based azo dye with low biodegradability, which significantly contributes to water pollution and poses risks to human health. Therefore, its effective removal from water and wastewater is considered essential. Among available methods, adsorption is recognized as a cost-effective and technically simple approach capable of removing a wide range of pollutants (Anastopoulos et al., 2024). Within the modern and novel trends towards water purification is the utilization of biomass-waste derived compounds to eliminate the environmental footprint. This emerging approach focuses on the transformation of agricultural residues, food waste, and other organic byproducts into value-added adsorbent materials. These sustainable materials not only offer a low-cost and abundant alternative to conventional adsorbents but also promote circular economy principles by converting wastes into functional remediation media.

This study investigates the removal of RR120 from aqueous solutions through adsorption onto oxidized biochar derived from palm tree fibers (OPF).

## Materials and methods

Palm tree fibers were collected from the University Campus of the University of Cyprus, washed with deionized water, carbonized at 600 °C for 1 h, and oxidized with 8 M $HNO_3$ under reflux conditions at 80 °C for 3 h, as described by Liatsou et al. (2016).

The amount of the adsorbed dye at the equilibrium state was estimated using the equation:

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (1)$$

The effect of pH on the adsorption of RR120 onto OPF was studied under the following conditions: the pH was varied from 2.0 to 10.0, while all other parameters such as: initial dye concentration (50 mg/L), adsorbent dose (0.1 g), contact time (1440 minutes), and temperature (293 K), were kept constant.

Adsorption isotherms were investigated at two different temperatures, 293 K and 323 K. The experiments were conducted under controlled conditions: the solution pH was adjusted to 2.0, the initial dye concentration ranged from 10 to 300 mg/L, and the adsorbent-to-solution ratio was maintained at 0.1 g per 0.05 L. All adsorption tests were performed at an agitation speed of 125 rpm.

## Results and discussion

Figure 1 shows the effect of pH on the adsorption of the dye RR120 onto OPF. At pH values above 4.0, adsorption is nearly zero, as the adsorbent surface is negatively charged due to deprotonated carboxylic groups, while RR120 exists in a fully anionic form because of its sulfonic groups. This leads to strong electrostatic repulsion between the dye and the adsorbent surface. In contrast, at pH values below 4.0, surface protonation (–COOH) reduces this repulsion, enabling π-π interactions between the aromatic rings of the dye and the graphitic domains of the adsorbent, as well as hydrogen bonding between the adsorbent's carboxylic groups and the sulfonic groups of RR120. Similar results were found by Tsiantouka et al. (2024), who investigated the adsorption of the dye RR120 using *Pyracantha coccinea* berries powdered biomass.

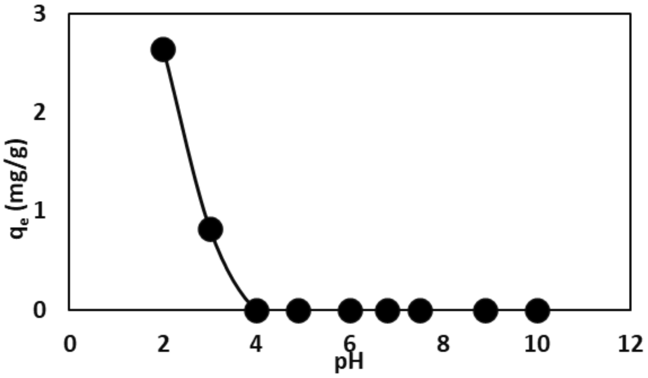

***Figure 1.*** *The effect of pH on the adsorption of RR120 dye by OPF.*

Figure 2 presents the adsorption isotherms of RR120 onto OPF at 293 K and 323 K. Increasing the initial dye concentration from 10 to 300 mg/L led to a significant rise in adsorption capacity from 1.3 mg/g to 5.8 mg/g at 293 K, and from 0.9 mg/g to 5.0 mg/g at 323 K. This increase is due to the higher concentration gradient, which acts as a driving force to overcome mass transfer resistance of dye molecules between the aqueous phase and the solid phase (Tsiantouka al., 2021).

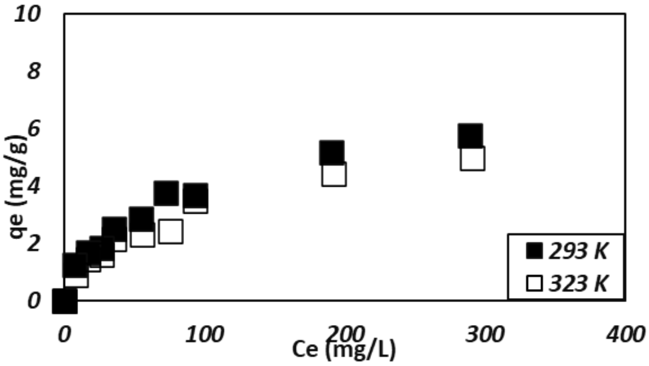

***Figure 2.*** *Adsorption isotherms of RR120 dye onto OPF at 293 K and 323 K.*

A slight decrease in adsorption with increasing temperature ($q_{max}$ decreasing from 6.8 mg/g at 293 K to 6.1 mg/g at 323 K), suggests the exothermic nature of the adsorption process. Similar results were reported by Kim et al. (2019), who investigated the adsorption of RR120 onto aminopropyl functionalized magnesium phyllosilicate.

## Conclusions

OPF is an efficient material for RR120 removal. The adsorption is favored in acidic pH, and the increase in temperature results in a slight reduction in adsorption capacity, indicating the exothermic nature of the process.

## References

Anastopoulos, I., Ahmed, M. J., Ojukwu, V. E., Danish, M., Stylianou, M., Ighalo, J. O. 2024. A comprehensive review on adsorption of Reactive Red 120 dye using various adsorbents. *J. Mol. Liq.*, 394, 123719.

Kim, Y. W., Kim, J. H., Moon, D. H., Shin, H. J. 2019. Adsorption and precipitation of anionic dye Reactive Red 120 from aqueous solution by aminopropyl functionalized magnesium phyllosilicate. *Korean J. Chem. Eng.*, 36, 101–108.

Liatsou, I., Michail, G., Demetriou, M., Pashalidis, I. 2017. Uranium binding by biochar fibres derived *from Luffa cylindrica* after controlled surface oxidation. *J. Radioanal. Nucl. Chem.*, 311, 871-875.

Tsiantouka, L., Haskis, P., Lykos, C., Mpeza, P., Patakioutas, G., Konstantinou, I., Barczak, M., Pashalidis, I., Anastopoulos, I. 2024. Biosorption of Reactive Red 120 dye by *Pyracantha coccinea* berries powdered biomass. *Sustain. Chem. Environ.*, 7, 100135.

# Valorization of industrial waste into silica based adsorbents for water OPPs removal

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***keywords:*** *adsorbent; OPPs; silica; sustainability.*

## Introduction

The growing contamination of water resources poses a threat to both human health and aquatic ecosystems.

This study explores the development of sustainable and eco-friendly adsorbents produced from agricultural waste and by products of the energy sector, aimed at removing harmful pollutants such as organophosphorus pesticides (OPPs). By integrating waste valorization with pollutant remediation, this research offers a cost-effective water treatment approach that supports circular economy principles and environmental sustainability (Satyam and Patra, 2024).

## Materials and methods

To support the development of the adsorbents, a comprehensive experimental procedure was conducted based on the work developed by Kim and Sung (2018). Briefly, the extraction comprises three main steps: production of ash by thermal treatment, alkaline digestion followed by acid neutralization. An overview of silica extraction process is illustrated in the schematic shown in Figure 1.

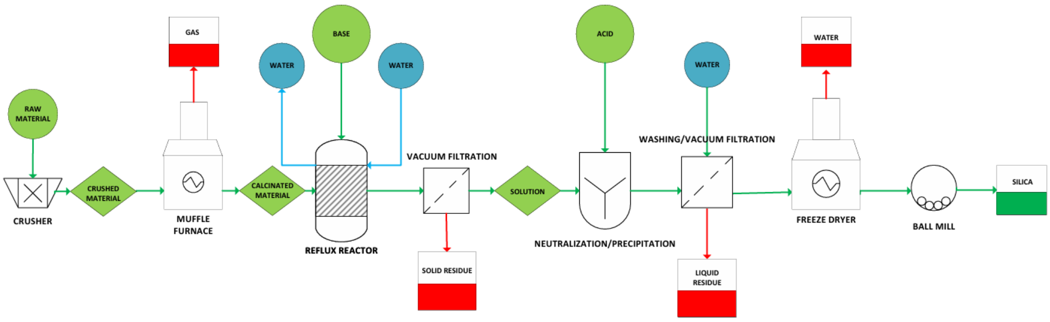


***Figure 1.*** *Diagram of silica extraction.*

A range of characterization techniques was employed to analyze the materials at various stages of the process. X-Ray Fluorescence (XRF) and Laser-Induced Breakdown Spectroscopy (LIBS) were used to determine the elemental composition of all samples. Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (FTIR-ATR) identified the functional groups present in the raw and processed materials. Thermogravimetric Analysis (TGA) assessed thermal stability and weight loss under oxidative and inert atmospheres. Dynamic Light Scattering (DLS) and Zeta Potential analyses provided insight into the adsorbents' behavior in aqueous media, revealing the size distribution of particle populations and their surface charge characteristics. Brunauer–Emmett–Teller (BET) analysis was used to determine surface area and average pore width, while Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) offered morphological insights and confirmed elemental composition, complementing previous analyses. The removal of pesticides following the adsorption experiments was achieved using an optimized liquid-liquid extraction procedure, with n-hexane as the extracting organic phase. The workflow is depicted in Figure 2.

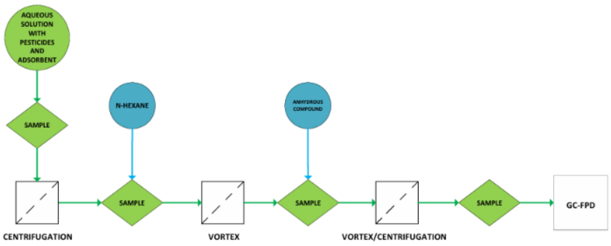


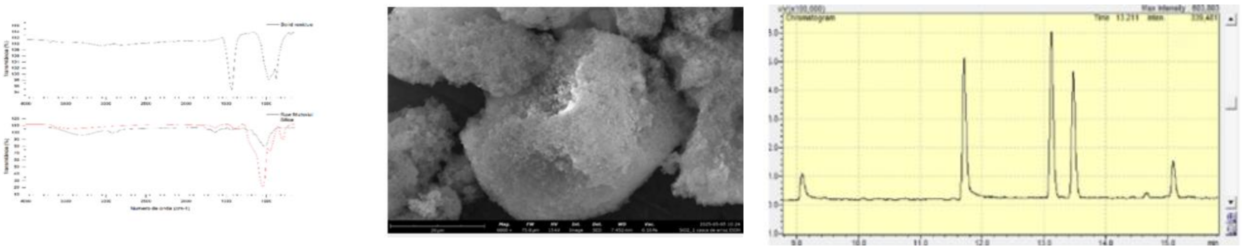
***Figure 2.*** *Diagram of pesticide extraction.*

Quantitative and qualitative analysis of the extracted pesticides was carried out using Gas Chromatography with a Flame Photometric Detector (GC-FPD).

## Results and discussion

Silica extraction yields ranged widely, from as low as 2% to as high as 97%, reflecting the diversity in composition and efficiency of the extraction process. The final silica products exhibited silicon purities between 8% and 33%, indicating varying levels of refinement depending on the source material. BET surface area analysis revealed values ranging from 42 to 305.96 m²/g, suggesting a strong potential for adsorption applications, particularly in materials with higher surface areas. An analytical methodology for the extraction of organophosphorus pesticides (OPPs) was successfully developed and optimized. Recovery rates for the pesticide extraction ranged from 4% to 89%, demonstrating the effectiveness of the method across different concentration levels and sample matrices.

Figure 3 presents representative results from one of the experimental processes, including FTIR spectra of all involved materials, SEM-EDS analysis of the final product, and a GC chromatogram of a standard solution containing the target OPPs in n-hexane.



*(g)* *(h)* *(i)*

***Figure 3.*** *A representative (a) FTIR spectra of the products involved in one of the processes, (b) SEM-EDS analysis of the respective final product and (c) the GC chromatogram of the OPP pesticides.*

## Conclusions

The study demonstrated that agricultural and industrial by-products can be effectively converted into adsorbents suitable for pesticide removal. While silica yield and purity varied, several materials showed strong adsorption potential. Additionally, an optimized extraction method allowed for the efficient recovery of 3 out of 6 targeted pesticides, supporting a sustainable, circular approach to water treatment.

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## References

Satyam, S. and Patra, S., 2024. Innovations and challenges in adsorption-based wastewater remediation: A comprehensive review*, Heliyon*, Volume 10(9), e29573.

Kim, D. and Sung, Y., 2018. Preparation of Lignin-Silica Hybrid Composite by Using the Alkaline Digestion Liquor of Rice Husk*, J. of Korea TAPPI*, 50(3), 86-93.

# Assessment of Marine Fuels Stability: A Storage Perspective

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***keywords:*** *Plastic Waste; Marine Fuels Stability; Storage Study.*

## Introduction

Plastic waste is one of the most widely used materials, with production continuously increasing. The global plastic production has reached approximately 414 million tons per year, with Europe contributing ~ 54 million tons in 2023. A significant portion of this plastic waste ultimately accumulates in the soil, posing serious environmental risks.

In this context, the Plastic2Fuels project aims to process plastic waste via combined thermocatalytic processes to produce marine diesel fuels. Marine fuels stability assessment constitutes a critical factor in ensuring the fuel performance, reducing operational problems due to fuel instability. Towards this, a dedicated storage study of the final product is in process in CPERI/CERTH. In particular, marine fuel diesel is stored for 12 months at ambient conditions (average temperature 10 $^{o}$C, humidity 70 % so far) in plastic containers outdoors under a shed, without direct exposure to sunlight. The final product is analyzed every month to evaluate potential degradation in its properties during storage. To date, the marine fuels are stable as verified by their qualitative monitoring in terms of Total Acid Number (TAN), density C, viscosity, and water content. Furthermore, the aging rate of the marine under accelerated conditions (combined temperature and air effect) was explored towards a comparison basis with the conventional storage study.

## Materials and methods

During conventional storage, the samples were placed in plastic containers shielded from sunlight and maintained under ambient environmental conditions, including temperature and humidity fluctuations. The monitoring period is 12 months, during which monthly analyses were carried out. These analyses included measurements of viscosity at 40$^{o}$C using the ASTM D445 method, water content using ASTM D1744, and TAN according to the ASTM D974 method. Furthermore, density at 15$^{o}$C and copper strip corrosion were measured with the ASTM D4052 method and the ASTM D130 method, respectively.

In parallel, accelerated oxidation tests were conducted in a controlled laboratory setup to simulate long-term degradation. The fuel was exposed to a temperature of 120°C with a continuous airflow of 600 ml/min for durations of 2, 4, and 10 hours. These conditions were selected to evaluate the stability and determine the copper strip corrosion classification, allowing comparison with real-time storage results.

## Results and discussion

The storage environment had an average temperature of 17°C and humidity of 67%, and no notable variations were observed in the acidity or other critical properties during this period. Similarly, the upgraded final marine diesel fuel, stored at an average temperature of 13°C and a humidity of 66%, maintained its stability over a five-month testing period (Figure 1). Particularly, the oxidative stability of the marine fuel remained constant at 27 hours, as measured by ELOT EN 15751, indicating no signs of degradation.

Under accelerated oxidation conditions, despite the exposure to elevated temperature and airflow, the marine fuel exhibited minimal degradation. The measured parameters remained within acceptable limits, and the copper strip corrosion classification remained at 3A, which is considered safe for fuel applications. However, a slight shift in the copper corrosion classification was observed, suggesting that, although the fuel remained stable, certain properties may be more susceptible to oxidative stress.

A comparative assessment of the examined storage conditions reveals that the conventional storage resulted in limited variation in the physical and chemical properties of the fuels. In contrast, the accelerated oxidation led to a faster decline in quality indicators, although not to levels that would render the fuel unstable. The observed changes in copper corrosion classification under both conditions highlighted the importance of this parameter as a sensitive indicator of dynamic aging.

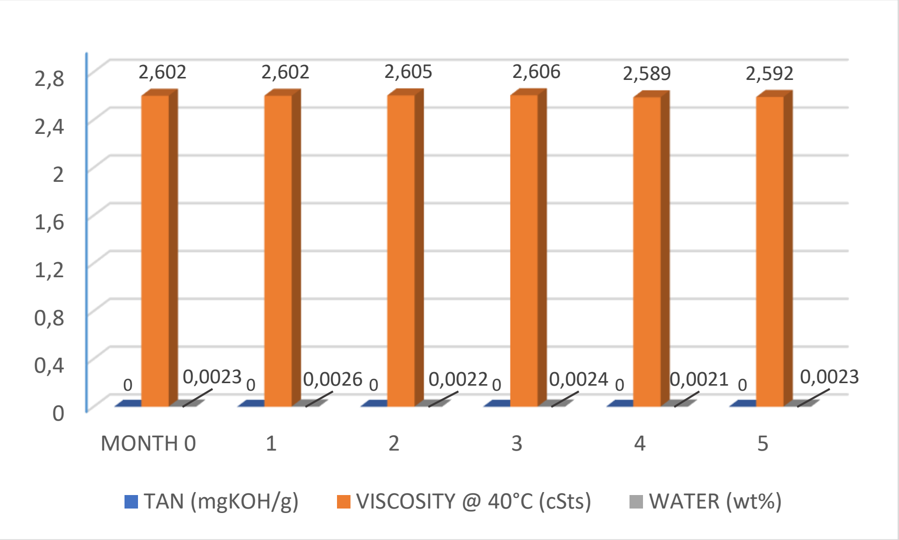

***Figure 1.*** *Marine diesel analyses*

## Conclusions

The marine fuels derived from plastic waste demonstrated excellent stability in both conventional and accelerated storage conditions. Their consistent performance over time, particularly in terms of oxidative resistance and minimal acid formation, confirms their suitability for long-term storage and use in maritime sector.

Conventional storage was found to be sufficient for preserving fuel quality for at least five months, while the fuels also proved resilient to accelerated aging processes with only minor changes observed. These findings support the practicality and reliability of plastic-derived marine fuels, reinforcing their potential role as a sustainable alternative energy source in line with circular economy principles.

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## References

Plastics Europe homepage, https://plasticseurope.org/knowledge-hub/plastics-the-facts-2024, last accessed 2024/11/18.

Ohra-aho, T. et al, 2024, Quality and Storage Properties of Upgraded Fast Pyrolysis Bio-Oil for Marine Transport. Energy Fuels, 38, 20, 19566–19583 (2024).

# IMMERSE Virtual Training on Critical Raw Materials: Preparing Responsible Professionals for a Sustainable Future

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***Keywords:*** *Critical Raw Materials; Mining Education; Immersive Learning; Sustainable Engineering; Clean Energy Transition*

## Introduction

## Materials and methods

The accelerating demand for critical raw materials (CRMs) driven by the twin forces of climate change and digital innovation poses significant challenges for the mining sector. European industry is exposed to significant risk in terms of the supply of CRMs due to its high import dependence on other countries and the high level of concentration of these materials in specific countries. Therefore, the challenge of ensuring that key sectors have access to a sufficient supply of CRMs to facilitate the acceleration of the energy transition is considerable. Addressing these challenges requires a new generation of professionals equipped not only with advanced technical skills but also with a deep understanding of sustainability principles. The IMMERSE project, an Erasmus+ initiative, responds to this urgent need by embedding immersive Virtual Excursions (VEs) on the Life of Mine (LOM) cycle of CRMs into the university curricula of its project partners specializing in mining engineering and geosciences (Leilabadi et al. 2024).

IMMERSE simulates real-world mining environments by means of VEs utilizing high-resolution, field-captured 360° panoramas. These immersive virtual settings enable students to navigate realistic mine sites containing CRMs in a safe, controlled learning space (Machairas et al 2025). The VEs modules are integrated into academic courses focused on mining, geology, sustainable ore processing, geotechnical engineering, low-impact extraction technologies, cutting-edge exploitation methods and environmental management, ensuring alignment with both accreditation standards and essential industry skills.

## Results and discussion

MMERSE addresses critical challenges in mining education by bridging the gap between theoretical learning and practical skills development. Pilot implementations at partner institutions have shown that students who engage with VEs report higher motivation and a deeper understanding of complex mining processes compared to traditional classroom methods. The immersive environments effectively simulate operational mine sites and sustainable practices, enabling learners to safely explore real-world scenarios without geographical limitations. Furthermore, IMMERSE's modular design enables continuous feedback and adaptation to student needs, fostering an interactive learning experience. By providing a scalable, cost-effective alternative to conventional field trips, IMMERSE helps to offset declining enrolment trends and equips future professionals with the technical expertise and strong ethical framework necessary for sustainable resource management. This brings mining education into closer alignment with the evolving demands of the clean energy transition.

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**References**

Leilabadi, Sh.., Lottermoser, B. G., Roach, M., Varouchakis, E. A., Machairas, E., Barrionuevo, F. G., Macia, M. T., Nieto, J. M. 2024. The IMMERSE Project: Virtual Excursions on Critical Raw Materials for the Clean Energy Transition. Mining Report 160(6), 601-607. https://mining-report.de/online-kiosk/mining-report-glueckauf-ausgabe-6-dezember-2024/

Machairas, E., Varouchakis, E., Lottermoser, B. G., Leilabadi, Sh., Roach, M., Barrionuevo, F. G., Macias, M. T., Nieto, J. M. 2025. Innovative Training in Critical Raw Materials: The IMMERSE Project's Role in Advancing Education for the Clean Energy Transition (No. EGU25-15577). Copernicus Meetings.

# Analysis of Phospholipid Fatty Acids (PLFAs) as a Soil Bioindicator: The Effect of Vineyard Abiotic Stress on the Soil Microfauna as a case study

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## ABSTRACT

**Introduction**:
The assessment of soil health in crop development is currently an important problem in agricultural engineering. **Aim:** In this work, the microflora profile of the grapevine rhizosphere is investigated as an bioindicator of soil quality by PLFAs technique. **Methodology:** Soil samples taken from the rhizosphere of vine and potted vine stumps were grown in petri dishes and evaluated by PLFAs technique using GC-MS chromatography. **Results-Discussion:** Culture in petri dishes showed that the presence of copper reduced the colony population while the presence of humus as a soil amendment increased the colony number even in copper contaminated soil. GC-MS chromatography for the case of field samples showed molecules identified as PLFAs, with C24 to C30 and concentration >1ppm only in the case of humus incorporation in the soil, while in potted management only one C24 molecule appears in the presence of copper. In the case of GLFAs we have most of the molecules with concentration >1ppm carrying carbon atom number C10, C13, C15, C17, C18, C24 in all treatments. Finally for the case of NLFAs, the molecule 1-Heptadecene [$C_{17}H_{34}$] appears in all the treatments at a concentration >1ppm except for the case of incorporation of humus in soil for the potting case, while the addition of copper in the potting case shows the most molecules compared to the other treatments. According to Hanif *et al.* (2012) microflora is arranged by a series of phospholipid traits peaks derived from microflora groups. Different colony populations and chemical molecules between treatments are a characteristic feature of changes in soil microflora. **Conclusion:** The presence of humus in the soil inactivates the effect of pollution on the rhizosphere microflora improving the yield of a vineyard.

***Keywords:*** *PLFAs technique, soil microfauna, humus, heavy metals, soil amendment*

## References

Akimbekov, N., Qiao, X., Digel, I., Abdieva, G., Ualieva, P., & Zhubanova, A. (2020). The effect of leonardite-derived amendments on soil microbiome structure and potato yield. Agriculture, 10(5), 147. https://doi.org/10.3390/agriculture10050147

Eduah, J. O., Arthur, A., Dogbatse, J. A., Amoako-Attah, I., & Afful, E. A. (2024). Ecological effects of soil physicochemical properties and copper speciation on the microbial properties associated with land use management in cacao production. Environmental Technology & Innovation, 34, 103500. https://doi.org/10.1016/j.eti.2023.103500

Fagnano, M., Agrelli, D., Pascale, A., Adamo, P., Fiorentino, N., Rocco, C., Pepe, O., & Ventorino, V. (2020). Copper accumulation in agricultural soils: Risks for the food chain and soil microbial populations. Science of the Total Environment, 734, 139434. https://doi.org/10.1016/j.scitotenv.2020.139434

Hanif, M., Atsuta, Y., Fujie, K., & Daimon, H. (2012). Supercritical fluid extraction of bacterial and archaeal lipid biomarkers from anaerobically digested sludge. Journal of Environmental Science and Technology, 13, 3022-3037;. doi:10.3390/ijms13033022

Olego, M. Á., Cuesta Lasso, M., Quiroga, M. J., Visconti, F., López, R., & Garzón-Jimeno, E. (2022). Effects of leonardite amendments on calcareous vineyard soil fertility, vine nutrition, and grape quality. Plants, 11(3), 356. https://doi.org/10.3390/plants11030356

Mackie, K. A., Müller, T., Zikeli, S., & Kandeler, E. (2013). Long-term copper application in an organic vineyard modifies spatial distribution of soil micro-organisms. Soil Biology and Biochemistry, 65, 245–

253. https://doi.org/10.1016/j.soilbio.2013.06.006
Nakatsu C.H., (2005). Microbial Processes|Community Analysis. Encyclopedia of Soilsin the Environment. Elsevier. Available from: https://doi.org/10.1016/B0-12-348530-4/00156-9
Quideau, S. A., McIntosh, A. C. S., Norris, C. E., Lloret, E., Swallow, M. J. B., & Hannam, K. (2016). Extraction and analysis of microbial phospholipid fatty acids in soils. Journal of Visualized Experiments, 114, e54360. https://doi.org/10.3791/54360

# The use of coffee grounds as fuel

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***keywords:*** *biomass, coffee grounds, biofuel.*

## Introduction

Coffee is one of the most popular beverages in the world and generates huge amounts of coffee grounds (CG). If not recycled, coffee grounds pose a significant environmental burden. Scientific research indicates that thanks to their physical and chemical properties and high content of organic compounds, including fats (15-21% oil), they have high potential as a renewable energy source, in particular as a fuel.

Coffee grounds have a high calorific value, comparable to or even higher than some fossil fuels or wood biomass. The average calorific value of dry coffee grounds is around 20-21 MJ/kg, and after processes such as torrefaction (thermal treatment of biomass at high temperatures but in an oxygen-free atmosphere), it can increase to as much as 32 MJ/kg. This is comparable to the calorific value of hard coal (23-28 MJ/kg).

Another very important aspect of coffee grounds processing is the reduction of their disposal in landfills, where their decomposition in anaerobic conditions leads to the emission of methane, a greenhouse gas that has a much more harmful effect on the environment than $CO_2$.

## Challenges and pre-treatment

The direct use of fresh coffee grounds is difficult due to their high moisture content (up to 50-60% after brewing), which significantly reduces their calorific value, and the presence of certain compounds that affect the combustion process and emissions. Reducing the moisture content is crucial for efficient combustion. The ideal moisture content should be below 35%. To produce pellets or briquettes, the moisture content of coffee grounds should be limited to 15% or less. In addition, the mechanical strength of pellets or briquettes made from coffee grounds does not meet transport standards. Another major challenge is that the combustion of pure coffee grounds leads to high $NO_x$ and CO emissions.

## Ways of using coffee pellets as fuel

**Pelletizing and briquetting** coffee grounds in combination with other types of biomass (wood sawdust, straw) are effective methods of fuel preparation. They have a significant impact on improving the physical properties of fuel, such as bulk density, ease of transport, storage, and dosing into boilers. By blending coffee grounds with other types of biomass, it is possible to influence the emissions and physical properties of the fuel produced.

**Pyrolyzing** used coffee grounds is an effective waste management solution for the coffee industry. The bio-oil produced in this process contains oxygenated and hydrophobic compounds, such as fatty acids, fatty acid esters, paraffins, olefins, and caffeine. The bio-oil yield from coffee grounds can reach 62%. Due to the abundance of coffee grounds and their behavior during pyrolysis, it can be concluded that coffee waste has great potential as a valuable bioenergy feedstock.

**Gasification** is the thermal conversion of biomass at high temperatures using a small amount of a gasifying agent, such as air, oxygen, water vapor, or $CO_2$. This process allows for the material's partial combustion but not its complete oxidation. This produces a combustible gas called syngas. Using the synergistic effect of water vapor and $CO_2$ in coffee grounds gasification can achieve approximately 95% carbon conversion and nearly 72% cold gas yield.

**Carbonization** is a process of thermal treatment of biomass in an oxygen-free environment. This process leads to an increase in the amount of energy per unit of fuel mass, which is important for storage and transport. Research indicates that subjecting coffee grounds to this process at 200°C produces excellent biochar, which can be used as a substitute for existing fossil fuels.

## Conclusions

Coffee grounds are a valuable source of biomass with high energy potential. Their combustion, particularly combined with other biofuels, can help reduce waste and decrease dependence on fossil fuels. However, fuels produced from mixtures of different types of biomass and coffee grounds should be tested for gas emissions, particularly $NO_x$ and CO. Coffee grounds can also be converted into high-energy fuels through pyrolysis, gasification, or carbonization processes. Unfortunately, these methods require high energy input, which limits their use for energy purposes.

***Acknowledgements:*** *None*

## References

Jeníček, L., Tunklová, B., Malaťák, J., Neškudla, M., Velebil, J. 2022. Use of Spent Coffee Ground as an Alternative Fuel and Possible Soil Amendment. Materials (Basel). 15(19):6722. doi: 10.3390/ma15196722.

Atabani, A.E., Al-Muhtaseb, Ala'a H., Kumar, Gopalakrishnan., Saratale, Ganesh Dattatraya,. Aslam, Muhammad,. Khan, Hassnain Abbas,. Said, Zafar., Mahmoud, Eyas. 2019. Valorization of spent coffee grounds into biofuels and value-added products: Pathway towards integrated bio-refinery. Fuel. V.254. 115640. https://doi.org/10.1016/j.fuel.2019.115640.

Sołowiej, P.; Neugebauer, M.; Esmer, O. 2024. Coffee Grounds as an Additive to Wood Pellets. Energies, 17, 4595. https://doi.org/10.3390/en17184595.

Nosek, R.; Tun, M.M.; Juchelkova, D. 2020. Energy Utilization of Spent Coffee Grounds in the Form of Pellets. Energies,13, 1235. https://doi.org/10.3390/en13051235.

Kusuma, Jefry., Indartono, Yuli S., Mujahidin, Didin. 2023. Biodiesel and activated carbon from arabica spent coffee grounds., MethodsX, V.10. https://doi.org/10.1016/j.mex.2023.102185.

Kafková, V.; Kubinec, R.; Mikulec, J.; Variny, M.; Ondrejíčková, P.; Ház, A.; Brisudová, A. 2023. Integrated Approach to Spent Coffee Grounds Valorization in Biodiesel Biorefinery. Sustainability, 15, 5612. https://doi.org/10.3390/su15075612.

Bejenari, V., Rusu, D., Anghel, I., Şofran, I.-E. and Lisa, G. 2025. Fire-starting briquettes with high spent coffee-ground content and various wax types. Biofuels, Bioprod. Bioref.. https://doi.org/10.1002/bbb.2810.

Rijo, B., Soares Dias, A. P., Ramos, M., de Jesus, N., Puna, J. 2021. Catalyzed pyrolysis of coffee and tea wastes. Energy, V. 235, 121252. https://doi.org/10.1016/j.energy.2021.121252.

Kibret, Henok Atile., Kuo, Yu-Lin., Ke, Ting-Yu,. Tseng, Yao-Hsuan. 2021. Gasification of spent coffee grounds in a semi-fluidized bed reactor using steam and CO2 gasification medium. Journal of the Taiwan Institute of Chemical Engineers, V. 119, p. 115-127. https://doi.org/10.1016/j.jtice.2021.01.029

# Agricultural biogas as a sustainable energy source for non-agricultural regions: the case of Lubuskie Province, Poland

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***keywords:*** *biogas, renewable energy, availability of substrates*

## Introduction

The European Green Deal constitutes a significant milestone in the EU's efforts to reduce its environmental impact, with a pronounced emphasis on the utilisation of renewable energy as a pivotal element in fostering sustainable economic growth and mitigating the effects of climate change. Despite the robust agro-food sector and the advantage of more agricultural land than Germany, Poland's biogas market is underdeveloped. The number of biogas plants in Poland is approximately 300, including 135 agricultural ones, with a combined capacity of just over 152 MW. In comparison, Germany has 9,500 plants and a capacity of 9,300 MW. The agricultural and processing industries in Poland generate significant quantities of by-products that are well-suited for biogas production. However, the sector's full potential remains untapped. In 2024, the leading feedstocks for biogas include post-slaughter residues, fruit and vegetable waste, slurry, and food processing waste.

The Lubuskie Voivodeship, located in western Poland, is one of the smallest and least industrialised regions in the country. The region exhibits a population density that is notably lower than the national average, and is distinguished by a substantial presence of forest cover, which accounts for almost 50% of the total area. The region's low energy demand, coupled with its favourable conditions for renewable energy – particularly wind, biomass, and biogas – create opportunities for further development. At present, nine agricultural biogas plants are in operation within the voivodeship, with capacities ranging from 0.25 MW to 1.14 MW, predominantly situated in the southern region of the region.

## Materials and methods

In order to estimate the amount of biogas energy that can be produced, the quantity of wet manure generated by different types of farm animals was calculated (1) based on statistical data. The feasibility of collecting manure is contingent upon the duration of the animals' stay in shelters, and the efficacy with which manure can be gathered and stored during this period. Consequently, the amount of manure that is actually collectable and available for biogas generation is expressed as a percentage (%), reflecting its true collectability and availability (2).

$$FM = AN \cdot ADM \cdot 365;\ \left[\frac{kg}{year}\right], \qquad (1)$$

$$ME = FM \cdot SM \cdot VDM \cdot RM \cdot AV;\ \left[\frac{m^3}{year}\right], \qquad (2)$$

Where:
FM – amount of fresh manure (kg·year$^{-1}$)
AN – number of animals,
ADM – average daily manure production per animal (kg·day$^{-1}$·animal $^{-1}$)
ME – biogas production potential (m$^3$/year)
FM – amount of fresh manure (kg·year$^{-1}$)
SM – solid matter content (%)
VDM – volatile dry matter content (%)

RM – raw material-specific methane production rate ($m^3 \cdot CH_4 \cdot kg^{-1} \cdot VDM^{-1}$)
AV – availability of animal manure

The biogas production potential from plant substrates and waste was calculated based on yield/generated waste, dry matter content, biogas yield. We assumed 5% production for all plant products and 100% of waste, which is summaries in equation 3.

$$PS = PY \cdot DM \cdot RM \cdot AV; \left[\frac{m^3}{year}\right], \quad (3)$$

Where:
PS – biogas production potential ($m^3$/year)
PY – harvested biomass/generated waste ($Mg \cdot year^{-1}$)
DM – dry matter content (%)
RM – biogas production potential ($m^3 \cdot kg^{-1}$)
AV – availability of resources, 5% was assumed for all plant raw materials and 100% for waste

## Results and discussion

The availability and characteristics of substrates for biogas production in the Lubuskie Voivodeship are influenced by spatial and temporal variability, reflecting national trends. Cattle manure is considered the most valuable animal-based feedstock due to its stable supply, high volume, and favourable composition for fermentation. Notwithstanding the decline in swine population numbers, the manure of these animals remains significant due to its high methane yield. The poultry sector is expanding rapidly, offering significant potential for growth; however, the emergence of avian influenza poses considerable challenges. The quantity and quality of manure from sheep, goats, and horses is less consistent. Among plant-based substrates, oilseeds and green maize are of increasing importance due to their fat content and ease of processing, while cereals are effective, particularly when co-digested with manure. Conversely, soft berries and tree fruit possess a comparatively restricted potential. The presence of industrial waste from the dairy, wood, and food sectors serves to further enhance the region's biogas capacity. The efficient utilisation of this diverse feedstock base is predicated on the implementation of co-digestion practices and the advancement of collection technologies. Nevertheless, regulatory, logistical and ethical barriers – including land use competition – continue to represent significant impediments to sustainable development.

## Conclusions

The utilisation of waste feedstocks in biogas production constitutes a pivotal component of the circular economy, conferring environmental benefits through the mitigation of methane emissions and the generation of renewable energy and organic fertilisers. The effective management of fermentation by-products has the potential to markedly reduce reliance on synthetic fertilisers, thereby supporting sustainable agricultural practices.

Notwithstanding the fragmented nature of its agriculture and the paucity of its industrial development, the Lubuskie Voivodeship demonstrates considerable potential for the development of biogas. The significant organic waste streams, particularly those originating from industrial poultry farming, could be utilised more efficiently. While emerging sectors such as viticulture present novel opportunities, the region's full biogas potential remains underutilised. The realisation of this potential is contingent upon the stabilisation of the regulatory framework and the addressing of social concerns, which at present limit the broader deployment of biogas technologies in the region.

# BSF larvae: a sustainable complementary solution for broiler carcass management

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***keywords:*** *black soldier fly larvae; complementary poultry carcass treatment; on-farm waste management; insect-based bioconversion; odor reduction.*

## Introduction

Mortality in intensive poultry farming generates substantial quantities of carcasses (3–5% of the broiler production cycle), posing significant sanitary and environmental challenges (Gwyther et al., 2011). In Israel, management typically involves on-site cookers, which are effective for odor and pathogen control but are energy-intensive and often cannot handle all carcasses, or on-site accumulation in pits followed by transport to distant licensed composting facilities at the end of the 6–8 week cycle.

The black soldier fly (*Hermetia illucens*, BSF) is a local, non-pest bioconverter of organic waste into valuable larval biomass suitable for animal feed (Józefiak et al., 2016), biofuels (Li et al., 2015), fertilizers (Cai et al., 2019), and biomaterials (Testa et al., 2025). However, BSF larvae thrive best at temperatures of 28–35 °C and show markedly reduced activity below approximately 24 °C. The aim of this study was to evaluate the potential of BSF larvae to serve as a complimentary approach alongside existing carcass management practices under field conditions, and at temperatures considerably lower than their optimal range.

## Materials and methods

A field experiment was conducted in Dovrat, Israel (March–April 2023; 4–33 °C), using three treatments: (1) neonate larvae (n=6), (2) 20 mg larvae (n=6), and (3) an untreated control (n=4). Each container held 6 L sawdust (to absorb moisture) and received 12.5 kg carcasses. On day 14, residual mass was measured, new larvae were added to all containers, with an extra 10 kg and 15 kg of carcasses to the neonate and the 20 mg treatments, respectively. The control was removed on day 8 due to odor. Final measurements were on day 28. Residual mass is expressed as a percentage of the total carcass mass added, normalizing for differences in input. Odor was scored (scale 0–5) on day 28 by two blinded assessors at 0 and 5 meters. Statistical analyses were performed in JMP using t-tests.

## Results and discussion

This study evaluated the performance of BSF larvae under field conditions, focusing on carcass mass reduction and odor mitigation. On day 14, the 20 mg group showed significantly lower residual mass than the neonates (46.2 ± 4.9% vs. 57.2 ± 6.8%), indicating more efficient decomposition by the larger larvae (t(9)=3.13, p=0.006). By day 28, residual masses were similar between groups (34.1 ± 0.6% vs. 36.6 ± 1.6%, t(6)=2.59, p=0.02), even though the 20 mg group processed a higher total mass of carcasses. The neonate treatment showed contamination by other fly species and considerable variability in BSF larval size, whereas the 20 mg group had no such contamination, with roughly half large uniform larvae and half pupae.

Odor at 0 m did not differ significantly between treatments (2.5 ± 0.5 vs. 2.3 ± 0.5, t(22)=1.25, p=0.22), while at 5 m the 20 mg group had slightly lower odor levels (0.6 ± 0.5 vs. 0.2 ± 0.4, t(20.5)=2.23, p=0.037). Both BSF treatments markedly reduced odor compared to the control, which was terminated early due to severe nuisance. In both BSF treatment, but not in the control, most carcass-derived liquids were absorbed by the sawdust, preventing free-standing effluents. These results, together with our previous studies, highlight that unmanaged effluents can lead to anaerobic zones not handled by the BSF larvae, causing strong foul odors.

Overall, these findings demonstrate that under aerated conditions, BSF larvae can effectively reduce poultry carcass mass and associated odors even under suboptimal field temperatures, and suggest that initiating treatment with 20 mg larvae is preferable to using neonates.

## Conclusions

This study demonstrates that BSF larvae can serve as an effective complementary approach for on-farm poultry carcass management under field conditions and suboptimal temperatures, providing a sustainable means to reduce mass and odor loads. However, future work should incorporate engineering solutions to better handle carcass-derived liquids, which represent a key limitation for large scale operation.

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## References

Gwyther, C. L., Williams, A. P., Golyshin, P. N., Edwards-Jones, G., & Jones, D. L. (2011). The environmental and biosecurity characteristics of livestock carcass disposal methods: A review. Waste Management, 31(4), 767-778.

Józefiak, D., Jozefiak, A., Kieronczyk, B., Rawski, M., Swiatkiewicz, S., Dlugosz, J., & Engberg, R. M. (2016). Insects—a natural nutrient source for poultry—a review. Annals of Animal Science, 16(2), 297-313.

Li, W., Li M., Zheng, L., Liu Y., Zhang Y., Yu, Z., Ma, Z., Li, Q. (2015). Simultaneous utilization of glucose and xylose for lipid accumulation in black soldier fly. Biotechnol Biofuels 8, 117

Cai, M., Ma, S., Hu, R., Tomberlin, J. K., Yu, C., Huang, Y., & Zhan, S. (2019). Rapid production of maggots as feed supplement and organic fertilizer by the two-stage composting of pig manure. Bioresource Technology, 284, 388-397.

Testa, E., Barbera, V., Fasoli, E., Giese, U., Belviso, M. R., Rossini, P., Bruno,D., Tettamanti, G., Orlando, M., Molla,G., Casartelli, M., & Galimberti, M. (2025). Electroconductive bionanocomposites from black soldier fly proteins for green flexible electronics. ACS Sustainable Chemistry & Engineering.

# Methane emission during degradation of microplastics in the aquatic environment

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***keywords:*** *pollution; greenhouse gases; surface water; microplastic degradation; emission.*

## Introduction

Environmental pollution by microplastics (MPs) significantly impacts climate change through greenhouse gas (GHG) emissions generated during plastic production, improper waste management, and the ability of microplastics to release greenhouse gases during their degradation. Approximately 99% of plastics are derived from non-renewable resources such as crude oil, natural gas, and coal. Projections indicate that by 2050, the plastics industry will account for 20% of global oil consumption [Oliveri Conti et al., 2024]. It is also estimated that between 1950 and 2015, around 6,300 million tons of plastic waste were generated, with approximately 79% ending up in landfills or directly in the natural environment [Geyer et al., 2017]. GHG emissions resulting from plastic degradation have not yet been considered in climate change projection models. So far, research has focused primarily on GHG emissions during the production and processing of plastics, neglecting the processes associated with plastic breakdown and the migration of carbon contained within plastics through biological activity or natural oxidation in the environment.

One of the few available data sets on GHG emissions from MPs degradation comes from the study by Royer et al. (2018). Their research demonstrated that polyethylene (PE) and polypropylene (PP) emit methane and ethylene under solar radiation exposure. Particularly intense emissions were observed for low-density polyethylene (LDPE). After 212 days of degradation, the methane emission rate was 5.8 nmol/g·d, and ethylene emission was 14.5 nmol/g·d. Zhang et al. (2020) investigated $CO_2$ and $N_2O$ emissions from polyethylene terephthalate (PET) over a short-term period of 7 to 30 days. However, there remains a lack of comprehensive and unequivocal data describing the mechanisms and magnitude of greenhouse gas emissions resulting from microplastic degradation. Moreover, to effectively mitigate the negative impacts of microplastics in the environment, further research in this area is essential.

Therefore, the aim of the present study was to supplement the existing knowledge and provide new insights into how the conditions of microplastic degradation influence greenhouse gas emissions.

## Materials and methods

Methane standards were obtained from Air Products (Allentown, PA, USA) at a concentration of 100 ppm. Gastight syringes were sourced from Hamilton (Reno, NV, USA). Methane emissions during the decomposition of microplastics in the aquatic environment were analyzed using rubber derived from used car tires. The tires were divided into fractions with particle sizes of 600 µm and 1000–3000 µm.

The incubation was carried out in 100 ml glass containers with screw caps. One gram of the analyzed microplastics and 20 ml of deoxygenated distilled water were added to the bottles. Control samples (blanks) were prepared in parallel without the addition of plastics. The prepared samples were tightly sealed in a helium atmosphere and incubated at 6±2°C and 18±2°C in the dark. Incubation periods were 30, 60, 180, and 360 days. Three replicates were prepared for each test variant. Samples were prepared in a helium atmosphere using a gas-tight glove box (Glove Box) from Plas Labs, Inc. (Lansing, MI, USA). Subsequently, 1 ml samples were withdrawn using gastight syringes for chromatographic analysis. The amount of methane was analyzed using a GC-2010 Plus gas chromatograph (Shimadzu, MD, USA) equipped with a Barrier Discharge Ionization Detector (BID).

## Results and discussion

The results of methane emission rates from MPs for two particle size fractions: 1000–3000 µm and 600 µm, incubated at 6°C and 18°C for 30, 90, 180 and 360 days are presented in Figure 1.

The methane emission rate for the 1000–3000 µm fraction at 6°C after 30 d was 1.83 nmol/g·d and then gradually decreased with time to 0.05 nmol/g·d after 360 days (Figure 1a). At 18 °C, emission values were initially lower after 30 days (0.32 nmol/g·d), but increased significantly after 90 days to about 2.96 nmol/g·d and then decreased to about 0.13 nmol/g·d and 0.12 nmol/g·d after 180 and 360 days.

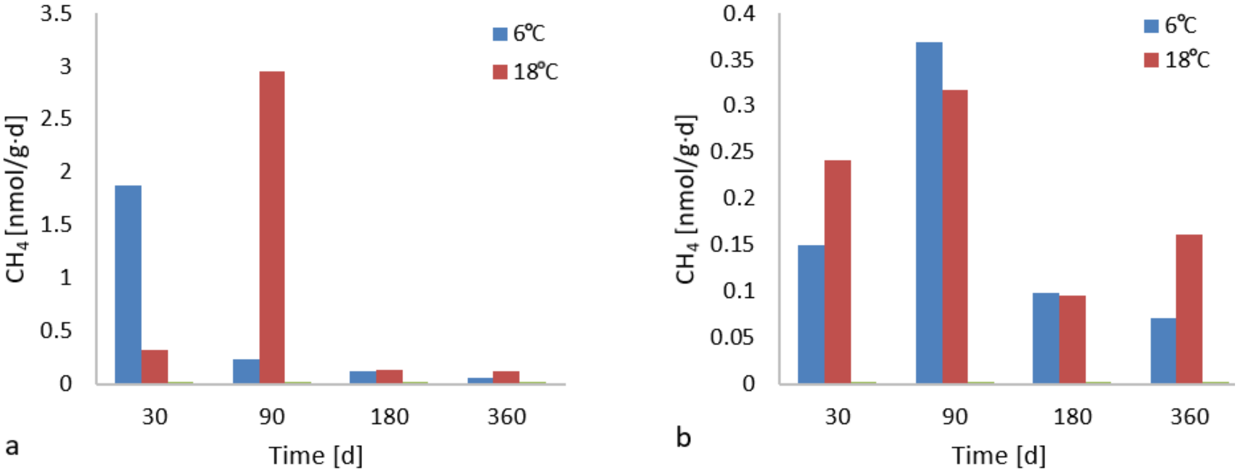

***Figure 1.*** *Methane emission rate during the decomposition of tire particles with a size of a) 1000–3000 µm; b) 600 µm.*

For the smaller fraction (600 µm), the methane emission rate at 6°C was 0.15 nmol/g·d after 30 days, increased slightly after 90 days to 0.37 nmol/g·d, and then decreased during the remaining incubation period to 0.07 nmol/g·d after 360 days (Figure 1b). At 18°C, methane emission rates were initially higher after 30 days (0.24 nmol/g·d), remained elevated after 90 days (0.32 nmol/g·d), and then decreased to 0.10 nmol/g·d after 180 days and increased slightly to 0.16 nmol/g·d after 360 days.

MPs particle size and ambient temperature jointly influence the decomposition kinetics and GHG emissions of MPs from used car tires in the aquatic environment. The obtained methane emission rates are similar to those reported by Royer et al. (2018). These findings confirm that GHG emissions occur during the decomposition of MPs, including those derived from butadiene-styrene rubber.

## Conclusions

During the degradation of car tires made of butadiene-styrene rubber in an aquatic environment, methane emissions occur, confirming their contribution to GHG generation. The significant influence of environmental conditions and the physical properties of MPs on GHG emissions during their degradation. Larger particles (1000–3000 µm) showed more pronounced changes in methane emissions over time, while smaller fractions (600 µm) exhibited more stable but lower emission rates. The methane emission rate tended to decrease over time, suggesting a slowdown of the degradation processes in the later stages of incubation.

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## References

Oliveri Conti, G., Rapisarda, P., Ferrante, M., 2024. Relationship between climate change and environmental microplastics: a one health vision for the platysphere health. *One Health Advances*, *2*(1), 17.

Royer, S. J., Ferrón, S., Wilson, S. T., & Karl, D. M., 2018. Production of methane and ethylene from plastic in the environment. *PloS one*, *13*(8), e0200574.

Geyer, R., Jambeck, J. R., & Law, K. L., 2017. Production, use, and fate of all plastics ever made. *Science advances*, *3*(7), e1700782.

Zhang, D., Cui, Y., Zhou, H., Jin, C., Yu, X., Xu, Y., ... & Zhang, C., 2020. Microplastic pollution in water, sediment, and fish from artificial reefs around the Ma’an Archipelago, Shengsi, China. *Science of the Total Environment*, *703*, 134768.

# Bridging the gap between academic water quality modeling and decision-making: towards usable and trustworthy tools for stakeholders

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***keywords:*** *water quality modeling; decision-making; stakeholders.*

## Introduction

Over the past two decades, water quality modeling has evolved rapidly. The integration of process-based methods with data-driven techniques like machine learning has enhanced predictive power and adaptability, especially in complex contexts such as urban systems and watershed-scale modeling, where data gaps and dynamic pollution patterns demand flexible tools (Gorgoglione et al., 2025; Vilaseca et al., 2023).

However, a persistent gap remains between academic model development and practical use by government agencies and stakeholders (Mer et al., 2020). Models often prioritize innovation and accuracy but are not aligned with operational needs, institutional constraints, or regulatory requirements. High data demands, opaque algorithms, and limited consideration of real-world workflows can undermine their credibility and usability. This misalignment hampers evidence-based decision-making. In urban water management, where regulatory compliance and public health are critical, models must be not only technically robust but also transparent, usable, and context-aware.

This paper examines key barriers to model adoption and proposes a framework to enhance the usability and relevance of academic water quality models for decision-makers.

## Key barriers to model adoption

Although academic water quality modeling has advanced significantly, several barriers continue to hinder its adoption by practitioners. A major issue is the complexity and low interpretability of many modern models, particularly those using machine learning. These often act as “black boxes,” obscuring how inputs relate to outputs, which limits stakeholder trust and regulatory credibility.

There is also a disconnect between model outputs and practical needs. Academic models often prioritize methodological innovation over usability, producing results that may not align with the spatial, temporal, or format requirements of planning and policy.

Data limitations further constrain model adoption. High-resolution datasets needed for calibration and validation are often unavailable, and many models lack mechanisms to handle missing or uncertain data, making them impractical in data-scarce environments.

Institutional constraints also play a role. Agencies may lack the flexibility, incentives, or capacity to adopt new tools, and staff are often unfamiliar with novel modeling approaches. Existing regulatory frameworks may reinforce reliance on traditional methods.

Finally, insufficient stakeholder involvement throughout the modeling process reduces relevance and trust. When users are excluded, models may overlook local knowledge, context-specific constraints, or operational priorities—leading to skepticism, regardless of technical performance.

These challenges point to the need for a more user-centered, transparent, and institutionally grounded modeling approach that complements scientific rigor with real-world applicability.

## Proposed Framework for Enhanced Model Usability

To address the barriers that hinder the adoption of academic water quality models in practice, we propose a framework grounded in usability, co-production, and institutional alignment. Rather than focusing exclusively on advancing model performance or methodological novelty, this framework emphasizes the integration of end-user needs and constraints throughout the modeling lifecycle, from problem formulation to implementation.

The first principle of the framework is early and sustained engagement with stakeholders. By involving water managers, regulatory agencies, and local experts from the outset, modelers can better align the objectives, indicators, and spatial-temporal scales of the model with operational needs. This co-production approach fosters trust, improves model relevance, and enhances the likelihood of long-term use.

Second, the framework advocates for model transparency and interpretability as a core design requirement. Even when employing advanced machine learning methods, efforts should be made to incorporate physically meaningful features, explainable algorithms, or visualization tools that help non-experts understand model behavior and outputs. Hybrid approaches that combine mechanistic and data-driven elements can offer a balance between accuracy and interpretability.

Third, the framework highlights the importance of flexible data handling and uncertainty communication. In many contexts, data limitations are the rule rather than the exception. Models should therefore include built-in strategies for dealing with missing data, uncertainty quantification, and sensitivity analysis. Providing users with clear information about model confidence and limitations enhances decision-making and accountability.

Fourth, institutional embedding is necessary to ensure that modeling tools can be used sustainably within existing governance structures. This includes adapting models to local policy frameworks, providing training and documentation, and building institutional capacity for model maintenance and update. Partnerships with public agencies and utilities can support this process and enable iterative feedback.

Finally, the framework stresses the need to document and evaluate model impact beyond academic metrics. This includes assessing how models inform planning, shape regulation, or improve environmental outcomes. By making these impacts visible, the value of academic modeling can be better recognized, further encouraging investment in collaborative and applied research.

Taken together, this framework proposes a shift in modeling practice toward a more inclusive, transparent, and operationally grounded approach, one that not only produces knowledge, but also supports informed and sustainable water management.

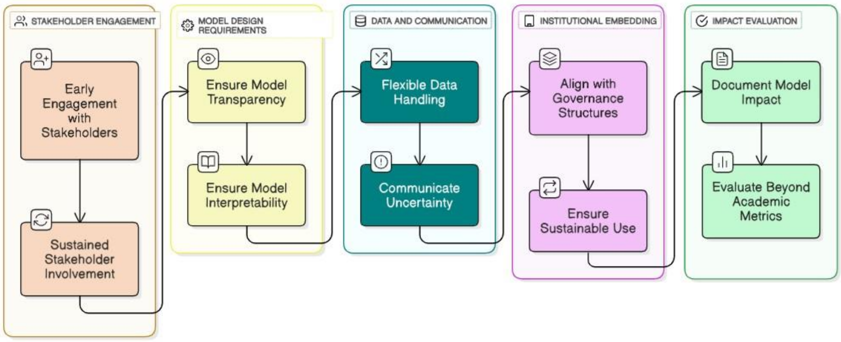

***Figure 1.*** *Proposed framework for improving water quality modeling usability.*

## Conclusions and perspectives

Bridging the gap between academic modeling and practical decision-making requires more than technical innovation, it demands a shift toward user-centered, transparent, and context-aware modeling practices. By engaging stakeholders, prioritizing interpretability, addressing data limitations, and embedding models institutionally, we can enhance their relevance and adoption. Future efforts should focus on documenting real-world impact and fostering sustained collaboration between researchers and practitioners.

***Acknowledgements:*** This study is partially supported by the Erasmus + Programme 2022.

## References

Gorgoglione, A., et al., 2025. Comparing neural network architectures for simulating pollutant loads and first flush events in urban watersheds: Balancing specialization and generalization. *Chemosphere*, 379, 144395.

Vilaseca, F. et al., 2023. Assessing influential rainfall–runoff variables to simulate daily streamflow using random forest. *Hydrological Sciences Journal*, 68(12), 1738–1753.

Mer, F., et al., 2020. Building trust in SWAT model scenarios through a multi-institutional approach in Uruguay. *Socio-Environmental Systems Modelling*, 2, 17892.

# Utilization of Agricultural By-Products and Waste Biomass for Energy Purposes

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***keywords:*** *lignocellulosic biomass; anaerobic digestion; pelleting; energy valorization; biogas feedstock storage.*

## Introduction

Large amounts of lignocellulosic agricultural residues and processing by-products remain unutilized despite their significant energy potential. In the context of climate change mitigation and rising energy demand, their sustainable transformation into bioenergy carriers is highly relevant. This study investigates the energy valorization potential of various agricultural waste materials including wheat straw pellets, oat husk pellets, cow manure pellets, sunflower husk pellets, lupine cleaning waste, and sunflower cake. The research focuses on two technological approaches: direct anaerobic digestion and pelletization followed by combustion. Additionally, the study aims to identify solid, energy-dense materials that can be easily stored and serve as a strategic energy buffer for biogas plants during interruptions in the supply of primary feedstocks.

## Materials and methods

The biomass samples were pelletized using a granulator (G-200, 7.5 kW, 150 kg/h) to produce uniform, compacted material suitable for both storage and energy conversion. The process parameters, including die temperature and motor load, were recorded. Physical and chemical characterization of each sample included dry matter content (EN ISO 18134-3:2015), volatile solids (BS EN 12879:2000), cellulose (Seifert method), and lignin (TAPPI T 222 om-06). Anaerobic digestion trials were conducted in batch bioreactors according to DIN 38414-8 and VDI 4630 standards to assess methane potential.

The quality of produced pellets was evaluated based on mechanical durability (PN-EN ISO 17831-1:2016-02), bulk density (PN-EN ISO 17828:2016-02), and size (PN-EN ISO 17829:2016-02). Higher heating value (HHV) was determined using a Leco AC600 calorimeter in accordance with PN-EN ISO 18125:2017-07. Energy inputs were monitored using a class S energy quality analyzer (MI 2883), enabling the estimation of net energy balance for both combustion and anaerobic digestion pathways.

## Results and discussion

Table 1 presents the cumulative methane and biogas yields of the tested pelletized substrates calculated on a fresh matter basis. Anaerobic digestion trials revealed considerable differences in methane yields among the materials, each of which was tested in triplicate under standardized conditions. The results demonstrate that agricultural by-products vary significantly in their biodegradability and bioenergy potential, which is essential for assessing their role as emergency or supplementary feedstocks in biogas plants..

***Table 1.****Cumulative methane and biogas yields of selected pelletized substrates based on fresh matter (FM)*

| Substrate | Methane content [%] | Cumulative methane [$m^3$/Mg FM] | Cumulative biogas [$m^3$/Mg FM] |
|---|---|---|---|
| **Wheat straw pellets** | 49.99 | 198.02 | 396.15 |
| **Oat husk pellets** | 49.36 | 235.60 | 477.35 |
| **Cow manure pellets** | 53.72 | 83.51 | 155.46 |
| **Sunflower husk pellets** | 52.33 | 105.11 | 200.86 |
| **Lupine cleaning waste** | 50.06 | 251.48 | 502.40 |

| | | | |
|---|---|---|---|
| **Sunflower cake** | 57.06 | 318.99 | 559.04 |

Among the samples, sunflower cake produced the highest cumulative methane volume (318.99 $m^3$/Mg FM), followed by lupine cleaning waste (251.48 $m^3$/Mg FM) and oat husk pellets (235.60 $m^3$/Mg FM). In contrast, cow manure pellets exhibited the lowest performance (83.51 $m^3$/Mg FM), indicating limited biogas potential despite relatively high organic content. These findings highlight the relevance of feedstock selection in ensuring process efficiency and energy output, especially in scenarios of disrupted primary substrate supply.

To ensure flexibility and continuity in biogas production, a strategy based on the pelletization of agricultural and waste biomass was proposed. Pelletized substrates can be stored for extended periods without significant quality loss and utilized when the supply of primary feedstocks is disrupted. This concept is illustrated in Figure 1.

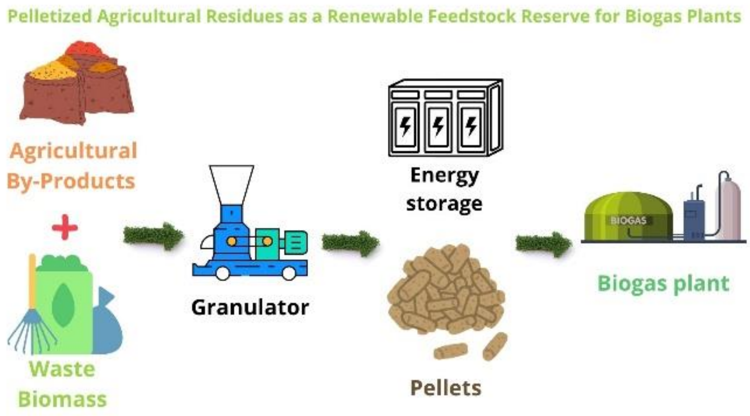

***Figure 1.*** *Conceptual scheme of biomass pelletization as a method of energy storage for biogas plants.*

## Conclusions

The study confirms that pelletized agricultural residues can serve as viable substrates for anaerobic digestion and bioenergy production. Among the tested materials, sunflower cake and lupine cleaning waste demonstrated the highest methane yields, indicating their strong potential as supplementary energy sources in biogas plants. The results also highlight the importance of substrate selection in optimizing biogas output, particularly during interruptions in the supply of primary feedstocks. Additionally, the pelletized form offers advantages in terms of storage, handling, and transport, making these materials strategically valuable for ensuring continuity and flexibility in biogas production systems.

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## References

1. Hendriks, A.T.W.M.; Zeeman, G. Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresour. Technol. 2009, 100, 10–18. https://doi.org/10.1016/j.biortech.2008.05.027
2. Witaszek, K.; Pilarski, K.; Niedbała, G.; Pilarska, A.A.; Herkowiak, M. Energy Efficiency of Comminution and Extrusion of Maize Substrates Subjected to Methane Fermentation. Energies 2020, 13, 1887. https://doi.org/10.3390/en13081887
3. VDI 4630. Fermentation of Organic Materials – Characterisation of the Substrate, Sampling, Collection of Material Data, Fermentation Tests. Verein Deutscher Ingenieure, Düsseldorf, Germany, 2006.
4. Kaparaju, P.; Serrano, M.; Thomsen, A.B.; Kongjan, P.; Angelidaki, I. Bioethanol, biohydrogen and biogas production from wheat straw in a biorefinery concept. Bioresour. Technol. 2009, 100, 2562–2568. https://doi.org/10.1016/j.biortech.2008.11.011

# The influence of substrate extrusion process on the energy and economic efficiency of biogas plant exploitation.

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***keywords:*** *biomass; extrusion; anaerobic digestion; energy efficiency*

## Introduction

The agricultural sector currently underutilises organic waste in the form of so-called lignocellulosic biomass, which can include maize straw, rapeseed straw, leaves and hay (Panigrahi and Dubey, 2019). In recent years, technologies to manage these wastes have been increasingly developed. As an example, they can be used in agricultural biogas plants, where heat or electricity can be produced. By carrying out a methane fermentation process, it is possible to dispose of biodegradable substances that are a burden on the ecosystem. The full utilisation of these raw materials as a substrate for biogas production is only possible after pretreatment, which allows the lignocellulosic structures to be broken down. This has the effect of increasing the efficiency of biogas production, including methane (Tong et al. 1990; Kozlowski et al. 2018; Dach et al. 2014). One of the pre-treatment methods is extrusion. Extrusion is a HTST (High Temperature Short Time) type of process due to the fact that the material in the extruder stays in it from several seconds to several minutes and is exposed to high temperature.

Agricultural biomass with an increased content of ligni-cellulose compounds is not normally used in biogas plants due to decomposition problems (straw has a structure that is difficult to access for fermentation bacteria). However, their use can bring a significant effect by increasing the energy efficiency and profitability of biogas plants. The production of methane in the anaerobic digestion process is a proven technology, but it is characterized by low profitability. Biogas installations without financial initiative in the form of green and yellow certificates or fixed feed-in tariffs for the sale of electricity and heat would not be cost-effective and could not compete with conventional fuels such as coal or natural gas. There are a lot of factors causing this state of affairs, e.g., the high costs of substrates for biogas production, a limited supply of local raw materials, and limited availability of innovations that would make biogas energy production cost-effective (Witaszek et al. 2020).

The aim of the work was to investigate the impact of extrusion of two types of straw (cereal and rapeseed) on increasing the efficiency of methane production and the energy and economic efficiency of the operation of a biogas plant with a capacity of 0.5 MW.

## Materials and methods

In the study, 2 types of extruded substrates were used to feed the biogas plant: cereal straw and rapeseed straw. Both types of straw were shredded using a CF420B flail shredder (Pavolt, Zrębice, Poland) to particle sizes below 10mm and then extruded using a TS-45 single-screw extruder (Z.M.Ch Metalchem, Gliwice, Poland), and then all substrates were tested for methane yield according to standard methodologies (DIN 38414/S8 and VDI 4630) (Dach et al. 2014). Biogas yield testing was conducted under standard methane fermentation conditions in sets of 3 tank biofermenters (Czekała 2017). The organic dry matter content of the inoculum varied from 1.5 to 2%. Dry matter and organic dry matter were checked before testing and the substrates were placed in an airtight digestion reactor. The reactors were placed in temperature-controlled water (approximately 39°C), which simulated the actual operating conditions of commercial biogas plants. The volume and qualitative composition of the gases produced were measured every 24 hours. The fermentation process was stopped when the daily biogas production was less than 1% of the total biogas production. Samples were tested in triplicate. Biogas yield (m3 $Mg^{-1}$) was expressed in terms of fresh matter, dry matter and dry organic matter, as described by Dach et al. (2014).

In the calculation of the efficiency of the biogas plant operation, two variants of biogas plant power supply were tested:

1. Variant 1: cereal straw + pig slurry and extruded cereal straw + pig slurry;

2. Variant 2: rapeseed straw + pig slurry and extruded rapeseed straw + pig slurry.

Energetic and economic calculations were carried out according to a standard methodology, based on market prices in Poland in May 2024 and taking into account the additional amount of electricity used during the extrusion of both types of straw.

## Results and discussion

In both variants, an increase in methane production from straw was observed, but this increase was relatively small (8.4% in the case of wheat straw and 11.6% in rapeseed straw). The increase in the efficiency of methane production from the same amount of straw resulted in a decrease in the mass necessary to power a biogas plant with a capacity of 0.5 MW, from 5150 to 4759 Mg/year in the case of wheat straw and from 4950 to 4400 Mg in the case of rapeseed straw, respectively. In this case, there are savings due to the smaller amount of straw needed, at the level of 23.4 kEUR in variant I and 29.9 kEUR in variant II.

However, during further calculations, it must be taken into account that the extrusion process requires additional electricity, which increases the cost of this technology. Therefore, taking into account the cost of electricity necessary for the extrusion process, it should be concluded that in both variant I and variant II, the revenue from the sale of electricity from a biogas plant powered by straw is higher in the variant without extrusion, respectively 278.7 kEUR in the case of wheat straw and 202 kEUR in the case of case of rapeseed straw.

## Conclusions

On the basis of the research carried out, it was observed that the application of the extrusion technique to lignocellulosic raw materials had a differential effect on the properties of potential substrates for biogas plants. The extrusion process increases the efficiency of $CH_4$ production during anaerobic digestion of lignocellulosic substrates such as various types of straw. In the studies discussed, the increase in $CH_4$ production was so low (8.4% in the case of cereal straw and 11.6% in rapeseed straw) that it did not cover the increase in electricity consumption resulting from the operation of the extruder. As a consequence, the use of the extrusion process in the analyzed variants of biogas plants gave a negative economic result. Therefore, it should be concluded that further research is necessary on the optimization of the extrusion process in order to increase the efficiency of $CH_4$ production from straw with reduced energy demand. It would be desirable to extend the scope to include further publicly available raw materials. The next step could be the use of advanced technologies such as heat recovery systems (recuperators) or efficient cooling systems. They enable the key parameters of the process to be monitored in real time, identify potential problems and respond quickly to any irregularities. As a result, they will contribute to the efficiency, quality and profitability of the process.

## References

1. Panigrahi, S.; Dubey, B.K. A critical review on operating parameters and strategies to improve the biogas yield from anaerobic digestion of organic fraction of municipal solid waste. *Renew. Energy* 2019, *143*, 779–797.
2. Tong M., Smith LH., McCarty PL. 1990. Methane fermentation of selected lignocellulosic materials. Biomass, 21: 239-255.
3. Kozłowski K., Dach J., Lewicki A., Cieślik M., Czekała W., Janczak D., Brzoski M. 2018. Laboratory simulation of an agricultural biogas plant start-up. Chem. Eng. Technol., 41(4): 711-716. https://doi.org/10.1002/ceat.201700390
4. Dach J., Czekała W., Boniecki P., Lewicki A., Piechota T. 2014. Specialised internet tool for biogas plant modelling and marked analysing. Adv. Mater. Res., 909, 305–310. https://doi.org/10.4028/www.scientific.net/AMR.909.305.
5. Witaszek K., Pilarski K., Niedbała G., Pilarska A. A., Herkowiak M. Energy Efficiency of Comminution and Extrusion of Maize Substrates Subjected to Methane Fermentation. *Energies*. 2020; 13(8):1887. https://doi.org/10.3390/en13081887
6. Czekała W. 2017. Concept of in oil project based on bioconversion of by products from food processing industry. J. Ecol. Eng., 18, 180–185. https://doi.org/10.12911/22998993/76211.

# Biogas yield – theory and practical experience

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***keywords:*** *biogas plant; substrates; biogas efficiency; agricultural wastes.*

## Introduction

For optimal biogas production, the proper selection of feedstock is crucial. It is important not only to provide the appropriate amount of organic matter but also to consider the chemical composition, interactions between substrates, and fermenter load. Any change in the mixture composition affects the anaerobic digestion process, which can have significant implications for biogas production efficiency and the plant's profitability.

The aim of this study is to calculate the theoretical biogas potential of selected substrates used in an operating agricultural biogas plant in relation to its actual performance. The study will allow for the assessment of synergies or antagonisms in the development of co-substrate formulations, against the background of domestic substrate consumption in agricultural biogas plants in Poland.

## Materials and methods

Three data sets were used in this study. The first is information from the reporting of the National Support Centre for Agriculture (KOWR), the institution overseeing the operation of agricultural biogas plants, as defined by Polish law. This data set includes annual summaries of substrates used to produce agricultural biogas in Poland [KOWR 2025].

The second dataset was obtained from an agricultural biogas plant with an installed electrical capacity of 1 MW, located in southeastern Poland. The data, provided by the agricultural biogas producer, comes from 2019-2021 and includes information such as: substrate name and quantity, code (in the case of waste), quantity of agricultural biogas used to generate electricity, quantity of electricity generated (including that used for own needs), and quantity of by-product resulting from agricultural biogas production. The data was aggregated quarterly, allowing for the tracking of the system's response to seasonal changes in substrate formulation.

The third data set was used to calculate the theoretical biogas yield from the substrates used in the tested biogas plant. A tabular method was used for calculations, based on averaged results from literature sources [Podkówka et al. 2012].

## Results and discussion

Analysis of KOWR data for 2011-2023 demonstrates the growing importance of the biogas sector in Poland, which aligns perfectly with the assumptions of a circular economy. Total biomass utilization is increasing each year, along with the construction of new biogas plants. By-products and waste are a key element of this growth (Fig. 1), which may indicate more effective organic waste management and favorable financial conditions for biogas production from waste substrates. The use of animal-derived biomass in biogas plants is growing, but at a much slower pace.

Analysis of data from an operating 1 MWe biogas plant showed that the use of various types of substrates (sourced from i.e., sugar refineries, dairies, and fruit and vegetable processing plants,) directly translates into seasonal changes in biogas and electricity production. The highest biogas and electricity production was recorded annually in the fourth quarter, which may indicate greater availability of high-energy substrates (beet pulp, fruit and vegetable pomace). Average annual biogas production exceeded 3 million m³, while electricity production reached 6,000-7,000 MWh, of which up to 95% was sold. Low internal consumption demonstrates the plant's high efficiency and operational effectiveness.

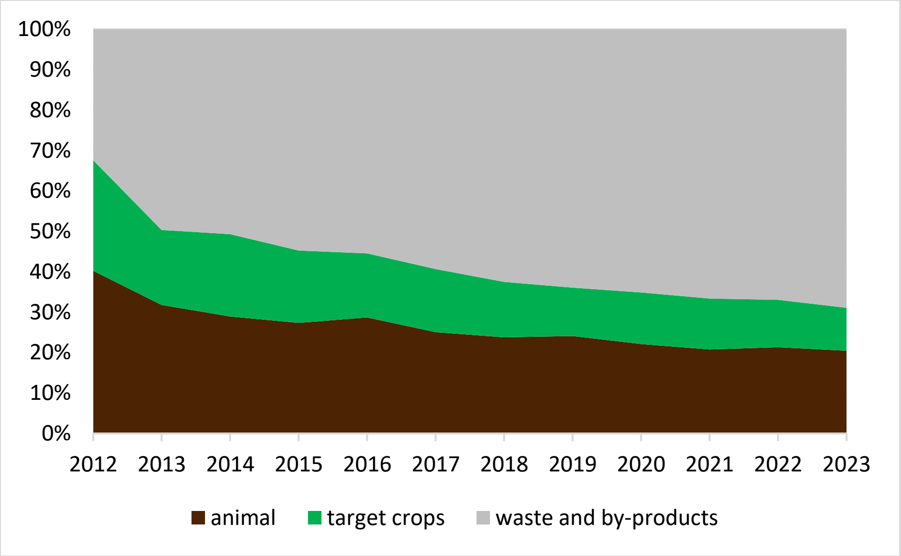

***Figure 1.*** *Structure of substrate using in agricultural biogas plants in Poland depending on origin.*

Comparing theoretical and actual biogas plant performance reveals optimization potential. Literature data indicate that biogas yield from some substrates (e.g., fats, expired food) can be higher than that achieved in practice, which may be the result of insufficient mixture homogenization or suboptimal fermentation conditions. Furthermore, the results show that relying on theoretical calculations can lead to underestimation or overestimation of actual biogas yield.

***Table 1.*** *Data on the operation of a biogas plant (sample year 2019).*

| Parameter | Unit | Amount |
|---|---|---|
| **Substrate consumption** | t | 34,747 |
| **Biogas production** | $m^3$ | 3,048,026 |
| **Electricity production** | MWh | 6,768.6 |
| **Electricity sales** | MWh | 6,356.9 |
| **Electricity consumption for own needs** | MWh | 411.7 |
| **Theoretical biogas yield (calculated)** | $m^3$ | 3,130,517 |

## Conclusions

Biogas plants are becoming not only a source of energy but also an effective waste processing system. The significant share of waste and by-products indicates a positive trend towards a circular economy. Further optimization of substrate formulations and adaptation of fermentation parameters to feedstock characteristics are recommended to increase biogas and methane production efficiency. This can improve the economic and environmental efficiency of biogas plants.

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## References

KOWR, 2025. List of raw materials used to produce agricultural biogas (in Polish), Available online (10 April 2025): https://www.gov.pl/web/kowr/dane-dotyczace-dzialalnosci-wytworcow-biogazu-rolniczego.

Podkówka, W., Podkówka, Z., Kowalczyk-Juśko, A., Pasyniuk, P., 2012. *Agriculture biogas. Renewable energy source* (in Polish); Agricultural and Forestry Publishing House, Warsaw, Poland.

# On the way to circular economy: Valorization of Brewery Waste for added-value bioproducts from Black Soldier Fly Larvae

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***Key words:*** *Hermetia illucens, bioproducts, proteins, chitin, amino acids.*

## Introduction

The solid organic waste, such as kitchen residues and crop-by products, represents an opportunity for valorization though bioconversion. Insects, particularly the larvae of *Hermetia illucens* (Black Soldier Fly Larvae, BSFL), are highly efficient in converting organic matter into value-added by-products. This insect could adapt to organic residues and grow rapidly under optimal conditions. Thus, the by-products that can be obtained from BSFL are oil for the production of biodiesel and green diesel, as well as proteins, amino acids and chitin [1]–[4] products with different uses in the industrial and food sectors. This by-products recovery encourages the principles of circular economy [5]. This work analyses the performance in the extraction of chitin and total proteins, furthermore the qualitative analysis of amino acids. In addition, the spectrum of BSFL chitin was qualitatively analyzed by FTIR.

## Methodology

The extraction of chitin was carried following a methodology similar to the one described in [4], using the centrifugation method for filtration after demineralization and deproteinization until to neutralize pH. The determination of total proteins it was used in the Kjeldahl method using the conversion factor (4.67) for insects [4], [6]. Finally, the prepare of amino acids was carried following the hydrolysis process [4]. Then, the technique Thin-Layer Chromatography (TLC) using three standards (phenylalanine, alanine and glycine) [7].

## Results

The filtration process yielded chitin with a significantly higher efficiency compared to the yield reported by [4] using prepupal stage larvae of BSFL, with a yield of 13.9 ± 0.12 % chitin. On the other hand, in the FTIR analysis was used to qualitatively analyze the chitin structure, with spectral similarity to those reported by [4], [8], [9]. Differently, the yield of total protein was of 48.09 ± 0.64 %, this result means a higher yield in contrast of reported in the literature [2], [4], [10]. Moreover, the TLC test slightly identifies the presence of phenylalanine in the triplicate of biomass samples, this amino acid coincides with others reports [4], [11].

## Conclusions

These findings highlight the potential for comprehensive use of the BSFL within a circular economy framework, including the development of value-added products for both the industrial and food sectors. Likewise, this work has areas of opportunity include quantitative analysis of the chitin and amino acids, and a life cycle assessment to estimate potential reductions in greenhouse gas emissions from future BSFL-based biorefineries. Experimental work for the further valorisation of spent BSFL is also underway.

## References

[1] S. Y. Leong, S. R. M. Kutty, A. Malakahmad, and C. K. Tan, "Feasibility study of biodiesel production using lipids of Hermetia illucens larva fed with organic waste," *Waste Manag.*, vol. 47, pp. 84–90, 2016, doi: 10.1016/j.wasman.2015.03.030.

[2] M. Meneguz *et al.*, "Effect of rearing substrate on growth performance, waste reduction efficiency

and chemical composition of black soldier fly (Hermetia illucens) larvae," *J. Sci. Food Agric.*, vol. 98, no. 15, pp. 5776–5784, 2018, doi: 10.1002/jsfa.9127.

[3] R. Menino *et al.*, "Agricultural value of Black Soldier Fly larvae frass as organic fertilizer on ryegrass," *Heliyon*, vol. 7, no. 1, 2021, doi: 10.1016/j.heliyon.2020.e05855.

[4] R. Smets, B. Verbinnen, I. Van De Voorde, G. Aerts, J. Claes, and M. Van Der Borght, "Sequential Extraction and Characterisation of Lipids, Proteins, and Chitin from Black Soldier Fly (Hermetia illucens) Larvae, Prepupae, and Pupae," *Waste and Biomass Valorization*, vol. 11, no. 12, pp. 6455–6466, 2020, doi: 10.1007/s12649-019-00924-2.

[5] S. Ojha, S. Bußler, and O. K. Schlüter, "Food waste valorisation and circular economy concepts in insect production and processing," *Waste Manag.*, vol. 118, pp. 600–609, 2020, doi: 10.1016/j.wasman.2020.09.010.

[6] A. Jonas-Levi and J. J. I. Martinez, "The high level of protein content reported in insects for food and feed is overestimated," *J. Food Compos. Anal.*, vol. 62, no. June, pp. 184–188, 2017, doi: 10.1016/j.jfca.2017.06.004.

[7] P. K. Sonkar, Narvdeshwar, and A. K. Verma, "Analysis of Amino acids using thin layer chromatography," *Lab. Man. Sch. Proj.*, no. August, pp. 56–59, 2022.

[8] K. Mohan *et al.*, "Recent insights into the extraction, characterization, and bioactivities of chitin and chitosan from insects," *Trends Food Sci. Technol.*, vol. 105, no. September, pp. 17–42, 2020, doi: 10.1016/j.tifs.2020.08.016.

[9] A. Xiong, L. Ruan, K. Ye, Z. Huang, and C. Yu, "Extraction of Chitin from Black Soldier Fly (Hermetia illucens) and Its Puparium by Using Biological Treatment," *Life*, vol. 13, no. 7, pp. 1–12, 2023, doi: 10.3390/life13071424.

[10] G. Arabzadeh *et al.*, "Diet Composition Influences Growth Performance, Bioconversion of Black Soldier Fly Larvae: Agronomic Value and In Vitro Biofungicidal Activity of Derived Frass," *Agronomy*, vol. 12, no. 8, 2022, doi: 10.3390/agronomy12081765.

[11] L. Loho, D. Lo, and A. Romulo, "Amino acid analysis and physiological properties of protein concentrate made from Black Soldier Fly Larvae (Hermetia illucens)," *IOP Conf. Ser. Earth Environ. Sci.*, vol. 1200, no. 1, 2023, doi: 10.1088/1755-1315/1200/1/012028.

# Integrated Microsieving and Gasification for Energy-Neutral Municipal Wastewater Treatment

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***Kew worlds***: *wastewater, microsieve, gasification, energy saving, waste to energy*

## Introduction

The treatment of urban and industrial wastewater leads to the production of sludge which contains organic matter, nutrients, and hazardous substances that makes difficult to dispose of. The treatment method used are anaerobic digestion, incineration, and pyrolysis, which are conventional and characterized by high energy costs, large facilities and greenhouse gas emissions. Treatment plants consume large amounts of energy with the aeration process being the most energy-intensive, accounting for 53% of total energy consumption. The increase in global wastewater production and rising energy costs make optimization necessary.

The European Union's goal is to convert WWTPs into energy-autonomous units by 2030, with a 55% reduction in emissions. In this context, energy recovery technologies such as gasification are being promoted. A pilot microsieving- gasification system was implemented at the Rethymnon plants as part of the LIFEB2E4SUSTAINABLE-WWTP project. The results of the implementation showed a significant reduction in energy consumption and the production of synthesis gas (syngas) capable of covering a large amount of the plant's needs. Finally, we note that the use of this technology can contribute to the conversion of plants to carbon neutrality, thereby enhancing sustainability.

## Materials and methods

Energy consumption in wastewater treatment plants is an important issue, and innovative solutions are being explored to achieve energy- neutral facilities. A pilot industrial- scale unit has been installed at the Rethymnon WWTP, which includes microsieving, drying, and gasification with an internal combustion engine. The aim is to remove biosolids before the aeration tank, reducing energy consumption, and to use as fuel for the production of syngas.

The dried biosolids with moisture content of 10-15% are formed into briquettes and fed into downdraft gasification reactor, which include drying, pyrolysis, combustion, reduction and ash removal zones. The syngas produced consists mainly of CO, $H_2$, and $CH_4$, but also contains pollutants (particles, tar, sulfur, chlorine), which are removed by a cyclone. Finally purified syngas is fed into the engine to produce heat and electricity.

The system is equipped with non-return valves and safety measures to prevent malfunctions. The integrated process is expected to reduce sludge production, improve plant performance, and offer a positive environmental footprint through energy recovery form biosolids.

## Results and discussion

The study evaluated the performance of a pilot microsieving-aeration system at the Rethymno WWTP. Microsieving achieved an average removal of 35% TSS, BOD 16% and COD 20%, significantly reducing the organic load and energy requirements for aeration. The average dry biosolids production was 3.5 kg/h with a solids content of up to 45%, suitable for gasification. The syngas produced ($H_2$ 15.5%, CO 16.4%, $CH_4$ 3.3%, $CO_2$ 7.5%) had a calorific value of 4.9 MJ/Nm³ and a yield of 1.92 Nm³/kg of fuel. The Cold Gas Efficiency calculation (54-60%) confirms high efficiency, in line with international literature. The results show that integrated technology can contribute significantly to the transition of WWTPs to energy neutral facilities

## Conclusions

The microsieving-gasification system at the Rethymno WWTP (2023-2024) with the aim of reducing energy consumption and recovering energy from biosolids. Microsieving achieved an average removal of 35% TSS,16% $BOD_5$, and 20% COD, leading to a 7.4% annual reduction in the plant's electricity consumption. The collected biosolids, after drying were used in the gasifier, with the clean PSS yielding high-quality syngas ($H_2$ 15.5%, CO 16.4%, $CH_4$ 3.3%, $CO_2$ 7.5%). Cogeneration reached a maximum electrical power of 9 kW and an average of 4.9 kW, significantly enhancing the unit's energy self-sufficiency. The results are in line with the EU's objectives (Directive 2022/0345) for energy-neutral facilities, proposing the system as a sustainable and scalable model for medium and large W WWTPs. The study demonstrates that integrated technology can transform WWTPs from energy consumers to producers, promoting circular and climate-neutral wastewater management.

## References

Alizadeh, S., Chowdhury, P., Ghodsi, V., Giaccherini, F., Sarathy, S., Santoro, D., Comeau, Y., 2023. Physico-chemical characteristics and biodegradability of primary effluent and particulate matter removed by microscreens. Water Environment Research 95. https://doi.org/10.1002/wer.10854

Cieślik, B.M., Namieśnik, J., Konieczka, P., 2015. Review of sewage sludge management: standards, regulations and analytical methods. J Clean Prod 90, 1–15. https://doi.org/10.1016/J.JCLEPRO.2014.11.031

Gao, N., Li, J., Qi, B., Li, A., Duan, Y., Wang, Z., 2014. Thermal analysis and products distribution of dried sewage sludge pyrolysis. J Anal Appl Pyrolysis 105, 43–48. https://doi.org/10.1016/J.JAAP.2013.10.002

Gikas, P., 2017. Towards energy positive wastewater treatment plants. *J. Environ. Manage.*, 203, 621–629.

Hao, X., Chen, Q., van Loosdrecht, M.C.M., Li, J., Jiang, H., 2020. Sustainable disposal of excess sludge: Incineration without anaerobic digestion. Water Res. https://doi.org/10.1016/j.watres.2019.115298

Marani, D., Braguglia, C.M., Mininni, G., Maccioni, F., 2003. Behaviour of Cd, Cr, Mn, Ni, Pb, and Zn in sewage sludge incineration by fluidised bed furnace. Waste Management 23, 117–124. https://doi.org/10.1016/S0956-053X(02)00044-2

Ruiz, J.A., Juárez, M.C., Morales, M.P., Muñoz, P., Mendívil, M.A., 2013. Biomass gasification for electricity generation: Review of current technology barriers. Renewable and Sustainable Energy Reviews 18, 174–183. https://doi.org/10.1016/J.RSER.2012.10.021

Wang, Ziyi, Gong, Z., Wang, Zhenbo, Li, X., Chu, Z., 2021. Application and development of pyrolysis technology in petroleum oily sludge treatment. Environmental Engineering Research 26, 1–15. https://doi.org/10.4491/eer.2019.460

# Optimization of trickling filters operation parameters for the removal of BOD and ammonic nitrogen from municipal wastewater

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***keywords:*** *trickling filters; wastewater; low energy*

Trickling filters (TFs) have long been used for municipal wastewater treatment. They consist of a permeable bed packed with rocks or specially designed plastics, on which microorganisms attach and form biofilms. Wastewater is distributed over the bed and treated through microbial oxidation of the organic carbon and ammonia, with limited denitrification in the deeper layers. In general, tickling filtration requires significantly less energy for wastewater treatment, compared with the activated sludge process, with the weakest point of TFs being the relative difficulty in removing particulate impurities. However, trickling filtration, combined with upfront partial removal of suspended solids may effectively compete with the activated sludge process and is re-emerging as a reliable and consistent, low-cost and energy-efficient alternative for municipal wastewater treatment. In this study, two different packing materials from polypropylene were tested, a random flow high voidance type (“R”) and a classical crossflow type (“C”) (Fig. 1), manufactured by GEA 2H Water Technologies, GmbH, Germany. The experiments were carried out in two identical cylindrical filters with height of 2 m and diameter of 0.2 m, operated at hydraulic loading of 0.08 m/h, using municipal wastewater pretreated by a coagulation-sedimentation process.

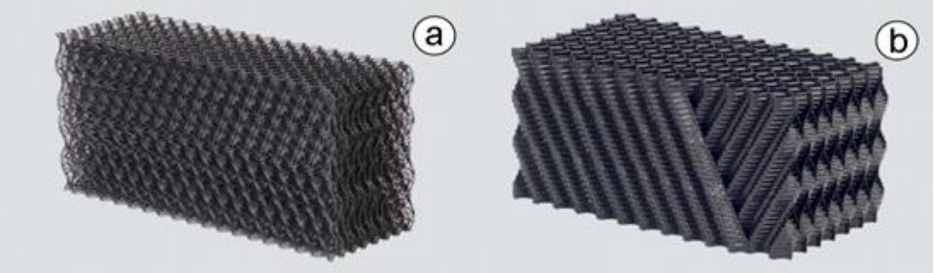

*Fig. 1. Photos of the support materials used in trickling filters. (a) Random flow high voidance (“R”), (b) Classical cross flow (“C”).*

The concentration of several parameters were monitored ($BOD_5$, COD, TSS, $N\text{-}NH_4^+$) at both inlet and outlet, at various recirculation rates and under natural or forced ventilation. In all cases, filter “R” performed better than filter “C”. Forced aeration improved treatment efficiency compared to natural ventilation. Recirculation of up to 100% (of the inlet flowrate) gave only marginal benefits, while increasing it further to 250% reduced the treatment performance. The random flow medium (“R”) demonstrated superior removal efficiency, particularly under forced aeration, highlighting the role of packing material and operational control. Based on the experimental results, TFs, combined with upfront removal of particulate matter rise as a viable, low energy alternative to activated sludge process.

# Full Papers

# Anaerobic production of biosurfactants from contaminated soils a waste valorization approach to soil remediation

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**keywords:** *Biosurfactants, Bioemulsifiers, Soil remediation, Food waste valorization*

## Abstract

This study investigated the anaerobic production of biosurfactants (BSs) and bioemulsifiers (BEs) by indigenous microbial communities in hydrocarbon-contaminated soils using waste-derived carbon sources as part of a circular economy approach. Sixty microcosms were prepared with real polluted soil, a microemulsion of waste frying oil and chickpea powder, and varying concentrations of nitrate, sulphate, and salinity to explore the influence of environmental conditions on BS/BE biosynthesis under oxygen-limited conditions. Mild oxidative stress was induced by hydrogen peroxide to enhance enzymatic activity. After nine months of incubation, the surface activity of the supernatant was assessed using oil displacement and emulsification index assays, and phytotoxicity was evaluated using germination tests. The results showed that mild salinity and sufficient electron acceptors significantly improved biosurfactant activity, with promising implications for in situ remediation. This low-cost, low-toxicity method valorizes food waste and supports sustainable soil remediation, providing a scalable alternative to synthetic surfactants. Further research is required to optimize production and assess field performance.

## Introduction

The use of biosurfactants (BSs) and bioemulsifiers (BEs) in environmental remediation has gained considerable interest in recent years owing to their natural origin, biodegradability, and effectiveness in enhancing the solubility and bioavailability of hydrophobic organic pollutants. Produced by various microorganisms, BSs, reducing surface tension and promoting oil spreading, and BEs, stabilizing emulsions without necessarily lowering surface tension, serve as metabolic by-products or extracellular compounds that facilitate hydrocarbon degradation by improving contact between microbial cells and hydrophobic contaminants.

In hydrocarbon-contaminated soils, especially those affected by petroleum-based pollution, leveraging indigenous microbial communities for in situ production of these compounds presents a promising and sustainable remediation strategy. Traditional bioremediation methods often rely on aerobic microbial processes and the addition of purified biosurfactants or synthetic surfactants, which can be costly, environmentally persistent, and occasionally toxic to non-target organisms.

The approach explored in this study diverges by focusing on anaerobic conditions, which are more representative of contaminated subsurface environments, and by using food-derived waste as carbon sources. This study investigated whether the microbial consortia present in real contaminated soils can be stimulated to produce BSs and BEs using a circular economy framework that emphasizes resource recovery and waste minimization.

In particular, this study evaluated the influence of electron acceptor (EA) availability, salinity, and mild oxidative stress on biosurfactant and bioemulsifier productivity. These factors are hypothesized to modulate microbial metabolism and stress responses, potentially enhancing the synthesis of surface-active compounds in the process. The ultimate goal is to develop low-toxicity, scalable formulations that can be directly applied to contaminated matrices without extensive downstream processing.

## Materials and methods

The experimental system was designed to simulate anaerobic bioremediation conditions using microcosms constructed with weathered hydrocarbon-contaminated soil (total petroleum hydrocarbons (TPH) = 4500 mg/kg dry weight) as the microbial inoculum. Sixty microcosms were established in 250 mL flasks, each containing 40 g of air-dried soil and 200 mL of amendment solution tailored to stimulate biosurfactant and bioemulsifier production under controlled conditions.

To mimic realistic low-cost amendment strategies, a microemulsion composed of waste frying oil (1.5%) and chickpea powder (6.0%) was used as the main carbon source. Urea was added as a nitrogen source (0.1%), while nitrate and sulphate were supplied at low (5 mg/L $KNO_3$, 0.1 g/L $MgSO_4$) and high (40 mg/L $KNO_3$, 0.5 g/L $MgSO_4$) concentrations to explore the impact of electron acceptor abundance on microbial metabolic pathways. Methanogenesis was selectively inhibited using 50 mM 2-bromoethanesulfonate to redirect metabolism toward non-methanogenic, potentially BS/BE-producing pathways. Additionally, hydrogen peroxide (0.35 g/g TPH) was added to induce mild oxidative stress, which was hypothesised to stimulate the enzymatic activity involved in hydrocarbon degradation and biosurfactant synthesis.

Salinity was investigated as a regulatory factor by comparing systems amended with and without NaCl (0.5 g/L). The final composition of the amendment solution is presented in Table 1.

Microcosms under anaerobic conditions were maintained for nine months in the dark at a controlled temperature (18 ± 2 °C). Samples were collected periodically to monitor the pH, redox potential, and concentrations of nitrate, sulphate, and dissolved organic carbon.

***Table 6***: *Amendment solution*

| | **Concentration** |
|---|---|
| NaCl | 0.0 or 0.5 g/L |
| $MgSO_4$ | 0.1 or 0.5 g/L |
| $KNO_3$ | 5 or 40 mg/L |
| Urea | 0.1% |
| Chickpea Powder | 6.0% |
| Waste Frying Oil | 1.5% |
| $H_2O_2$ 3% | 0.35g/1g TPH |
| 2-Bromoethanesulfonate | 50 mM |

The supernatants (both crude and microfiltered) were analysed for the presence of biosurfactants and/or bioemulsifiers using standard oil displacement tests and emulsification index (EI24h) assays using four representative hydrocarbon substrates: gasoline, diesel oil, fuel oil, and n-hexadecane. These tests evaluated the ability of the culture fluids to reduce surface tension and form stable emulsions.

Oil displacement experiments were conducted following the procedure described by Morikawa et al. (2000). In summary, for each combination of hydrocarbon mixture and supernatant, glass beakers with a diameter of 50 mm were filled with 20 ml of distilled water, and 1 ml of hydrocarbon substrate was added to the water's surface. Subsequently, 100 μl of the supernatant was carefully introduced at the centre of the oil layer on the water. The presence of biosurfactants in the supernatant would cause the oil to be displaced, creating a clear zone without oil. The diameter of this zone was measured to indicate surfactant or oil displacement activity. Negative controls were performed using distilled water, where no oil displacement or clear zone was observed.

The emulsification index at 24 hours (EI24h), used to evaluate emulsification capacity, was determined by vortexing equal volumes (5 mL each) of the biosurfactant solution—either microfiltered or in its crude extract form—and hydrocarbons in a 15 mL Falcon tube. After 24 h of static incubation, the ratio of the emulsion layer thickness to the total height of the solution was calculated.

The phytotoxicity of the most promising biosurfactant solutions was assessed using germination index (GI) assays on Zea mays and Lepidium sativum to determine whether the biosurfactant-rich extracts were compatible with plant growth and suitable for environmental application.

## Results and Discussion

The results of the oil displacement tests are reported in Table 2 and indicate that biosurfactant activity was more frequently observed under mild salinity (NaCl 0.5 g/L), suggesting that appropriate osmotic conditions are beneficial for BS/BE biosynthesis. However, oil dependency is relevant, with fuel oil consistently showing lower displacement performance than gasoline and mineral oil, potentially due to its higher viscosity, which could limit the spread of the displacement halo.

***Table 7***: *Results of oil displacement tests performed with gasoline, diesel oil, mineral and fuel oil, 12 tests for each condition as number of tests with no detected oil displacement (NEG), with oil displacement <1 cm (in diameter) (PART), and oil displacement ≥1 cm (in diameter) (POS).*

| **Test conditions** | **EAs** | **Oil displacement test** | | | | |
|---|---|---|---|---|---|---|
| | | | Gasoline | Diesel Oil | Fuel Oil | Mineral Oil |
| **0.5 g/l NaCl ("saline")** | **$MgSO_4$ 0.5 g/L + $KNO_3$ 40 mg/L** | NEG (%) | 8.3 | 16.7 | 25.0 | 8.3 |
| | | PART (%) | 33.3 | 25.0 | 33.3 | 16.7 |
| | | POS (%) | 58.3 | 58.3 | 41.7 | 75.0 |
| | **$MgSO_4$ 0.1 g/L + $KNO_3$ 5 mg/L** | NEG (%) | 8.3 | 8.3 | 25.0 | 8.3 |
| | | PART (%) | 0.0 | 25.0 | 25.0 | 8.3 |
| | | POS (%) | 91.7 | 66.7 | 50.0 | 83.3 |
| **No added NaCl ("non saline")** | **$MgSO_4$ 0.5 g/L + $KNO_3$ 40 mg/L** | NEG (%) | 75.0 | 75.0 | 75.0 | 75.0 |
| | | PART (%) | 16.7 | 8.3 | 0.0 | 0.0 |
| | | POS (%) | 8.3 | 16.7 | 25.0 | 25.0 |
| | **$MgSO_4$ 0.1 g/L + $KNO_3$ 5 mg/L** | NEG (%) | 25.0 | 25.0 | 33.3 | 25.0 |
| | | PART (%) | 0.0 | 8.3 | 33.3 | 0.0 |
| | | POS (%) | 75.0 | 66.7 | 33.3 | 75.0 |

Table 3 summarises the results of the 24-hour emulsification index (EI24h) assays under different test conditions across various hydrocarbon substrates. The data include the percentage of extracts showing any emulsifying activity (POS%) and the mean EI24h ± standard deviation for both crude and microfiltered extracts. These indicators provide insights into the frequency, strength, and consistency of bioemulsifier production.

Under saline conditions, emulsifying activity was frequently detected, with POS% values as high as 100% (e.g. high EA microfiltered extract with gasoline) and generally above 80% for fuel and mineral oil. This suggests that salinity (NaCl 0.5 g/L) also supports the production of emulsifying compounds.

In contrast, under non-saline conditions, the POS% values were significantly lower (e.g. only 8–25% in high-EA systems and diesel), indicating less consistent emulsification. However, some non-saline-low-EA combinations still produced high POS% for certain hydrocarbons (e.g. 67% for gasoline and fuel oil), suggesting that limited EAs may trigger emulsifier synthesis in specific microbial subpopulations.

Regarding the emulsifying capacity measured by the EI24h index, crude extracts from saline conditions generally yielded higher values than those from non-saline conditions, exceeding 30% for both mineral and fuel oils. Most saline microfiltered extracts demonstrated similar or even improved performance in comparison to crude extracts. Preservation of emulsifying capacity after filtration in these extracts indicates that likely the active emulsifying agents are predominantly extracellular and soluble, rather than being cell-associated.

Conversely, under non-saline conditions, particularly with low low-EA availability, a notable reduction in EI24h was observed after microfiltration, probably because of the removal of larger, cell-associated, or colloidal emulsifying structures during filtration. These findings highlight the importance of environmental conditions, particularly salinity, in influencing not only the quantity but also the physical nature of the produced emulsifiers.

A crucial aspect to consider is the relative dispersion of the EI24h results in many tests (as indicated by the high standard deviation, sometimes approaching or exceeding the mean). This high variability suggests that although some samples perform very well, emulsifying capacity is not yet consistent across replicates, possibly due to batch-to-batch variability in substrate availability, microbial activity, or instability of the produced emulsifiers under certain conditions and/or time. This underscores the need for further optimization and replication to ensure consistent production, which is essential for reliable application.

Germination indexes to evaluate the environmental safety of the filtered mixtures, against the two selected model species, provided restrictions regarding their application "as made".

Concentration related effects were evident in the 15% mixtures of both biosurfactant mixtures tested where inhibition of the germination and growth of the specimens were assessed, while in 5% concentration mixtures the inhibition was lower and transitory.

The observed influence of concentration and stabilization highlights key formulation parameters and suggests avenues for optimization through improved preparation and component characterization; future research should further investigate concentration-dependent effects and assess the mixture's potential interactions with environmental pollutants to better understand its applicability.

***Table 8***: *Results of emulsification index on 24 hours (EI24h) assays performed with gasoline, diesel oil, mineral and fuel oil, 12 tests for each condition. The results are reported as the percentage of tests in which the extract (crude or microfiltered) showed emulsifying activity (POS) and the average EI24h (± standard deviation).*

| **Test conditions** | **Extract** | **Emulsification Index** | | | | |
|---|---|---|---|---|---|---|
| | | | Gasoline | Diesel Oil | Fuel Oil | Mineral Oil |
| **0.5 g/l NaCl ("saline") $MgSO_4$ 0.5 g/L + $KNO_3$ 40 mg/L** | **crude** | POS (%) | 83 | 17 | 83 | 92 |
| | | EI24h | 16.9 (21.9) | 20 (7.8) | 30.5 (23) | 35.5 (32.4) |
| | **microfiltered** | POS (%) | 100 | 50 | 83 | 83 |
| | | EI24h | 17.5 (18.8) | 29.4 (21.5) | 35.1 (13.6) | 25 (28.8) |
| **0.5 g/l NaCl ("saline") $MgSO_4$ 0.1 g/L + $KNO_3$ 5 mg/L** | **crude** | POS (%) | 83 | 33 | 83 | 50 |
| | | EI24h | 13.1 (19.5) | 30.7 (24.4) | 30.3 (18.6) | 13 (22.6) |
| | **microfiltered** | POS (%) | 83 | 50 | 83 | 50 |
| | | EI24h | 14.7 (14.6) | 11.1 (11) | 23.9 (20.4) | 29.3 (32.7) |
| **No added NaCl ("non saline") $MgSO_4$ 0.5 g/L + $KNO_3$ 40 mg/L** | **crude** | POS (%) | 25 | 8 | 33 | 25 |
| | | EI24h | 14.3 (15.2) | 3.3 (0) | 30.6 (25.1) | 3.2 (2.5) |
| | **microfiltered** | POS (%) | 25 | 17 | 33 | 17 |
| | | EI24h | 16.7 (16.1) | 10 (6.7) | 22.3 (21.4) | 20.5 (35) |
| **No added NaCl ("non saline") $MgSO_4$ 0.1 g/L + $KNO_3$ 5 mg/L** | **crude** | POS (%) | 67 | 25 | 67 | 33 |
| | | EI24h | 20.5 (12.8) | 10 (4.2) | 40.7 (21.2) | 44.2 (36.1) |
| | **microfiltered** | POS (%) | 67 | 25 | 67 | 42 |
| | | EI24h | 8.5 (7.8) | 8.1 (6.5) | 21.6 (23.9) | 18 (29.4) |

## Conclusions

This exploratory study illustrates that indigenous microbial communities in hydrocarbon-contaminated soils can be effectively stimulated for the production of biosurfactants and bioemulsifiers under oxygen-limited conditions through the application of food waste-derived amendments when methanogenesis is inhibited. This process is influenced by environmental parameters such as salinity and the availability of electron acceptors, with mild oxidative stress induced by $H_2O_2$ further enhancing the activity. These observed dependencies suggest that careful tuning of environmental conditions can enhance BS/BE yield.

Additional studies are necessary to more thoroughly define the properties and stability of biosurfactants and bioemulsifier compounds, and their effects on microbial community dynamics, pollutant bioavailability, and plant health. It is important to evaluate production kinetics and refine formulations for practical field use.

**References**

Shekoohiya S., Moussavi G., Naddafi K., (2016), The peroxidase-mediated biodegradation of petroleum hydrocarbons in a H2O2-induced SBR using in-situ production of peroxidase: Biodegradation experiments and bacterial identification, Journal of Hazardous Materials, 313, 170-178.

Moussavi G., Shekoohiya S., Naddafi K., (2017), The accelerated enzymatic biodegradation and COD removal of petroleum hydrocarbons in the SCR using active bacterial biomass capable of in-situ generating peroxidase and biosurfactants, Chemical Engineering Journal, 308, 1081-1089.

Morikawa M., Hirata Y., Imanaka T., (2000) A study on the structure–function relationship of lipopeptide biosurfactants. Biochimica et Biophysica Acta (BBA) - Molecular and Cell Biology of Lipids, Volume 1488, Issue 3, 15 November 2000, 211-218

# Development of a Decision Support System for Shallow Lakes Under the Impact of Eutrophication and Climate Change and Its Application to a Hypertrophic Lake

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## ABSTRACT

In this paper; a decision support system that is designed for shallow lakes under the impact of eutrophication and climate change is presented together with its application to a lake that is located in the northwestern part of the Republic of Türkiye, and is under the threat of aging in a time scale of decades due to the cultural eutrophication. The lake that is an important breeding area for many bird species as well as one of the major resting areas for migratory birds is under the impact of mainly diffuse emission sources of nutrients and is classified as hypertrophic according to the country's water quality regulations. The decision support system (DSS) developed is based on non-linear mathematical programing and aims the minimization of initial investments and continuous annual expenses and utilizes the trophic status and related water quality as the main constraints. The main results of this study are the successful development of the DSS and its successful application on the decision problem, aiming at feasible and sustainable trophic status of the case study area based on Carlson trophic status index (TSI). The main conclusion is that even though the related lake will stay eutrophic, the probability of a hypertrophic state can at least be reduced considerably.

**Keywords**: Shallow lakes, Eutrophication, Hypertrophy, Decision Making

## 1. INTRODUCTION

Eutrophication is a crucial problem, especially for shallow lakes, elevated by excess nutrient (nitrogen and phosphorus) inputs from human activities (Abell et al., 2022; Suresh et al., 2023). While eutrophication is a well-identified environmental problem since 1960s and 1970s, climate change is a newer issue as an environmental problem gaining on importance as of in the early 21st century.

The direct reason for eutrophication has clearly been identified as the excess amount of nutrient (mainly nitrogen and phosphorus) loads into waterbodies. The emission sources of nutrient loads can be of point or diffuse character, where the diffuse source-based pollution is expected mainly from rural areas and point source-based pollution is expected mainly from urban areas. The climate change may play indirect roles such as change in flushing time of waterbodies because of the water budget alterations of waterbodies or the changes in temperature regime of waterbodies affecting their ecological responses.

The aim of this study is to develop a decision support system (DSS) for shallow inland lakes under the combined threat of eutrophication and the climate change. Such a DSS should incorporate the capability of presenting solutions with minimal costs of related countermeasures for different trophic states along with the observed symptoms.

The DSS is applied to the Manyas Lake (Figure 1) that is located in the northwestern part of the Republic of Türkiye and is under the threat of aging in a time scale of decades due to the cultural eutrophication. Climate change is considered as another threat in addition to eutrophication. The lake that is an important breeding area for many bird species as well as one of the major resting area for migratory birds is under the impact of mainly diffuse emission sources of nutrients and is classified as hypertrophic according to the country's water quality regulations. The lake is fairly large with an average surface area of 166 $km^2$ and a watershed area of approximately 3000 $km^2$ but very shallow with an averaged depth of 1.8 meters. Moreover, it is important to note that even though the case study area Manyas Lake is mostly phosphorus limited, fish kills that may be related to nitrogen components, are also an important problem as reported by Dorak et al. (2023).

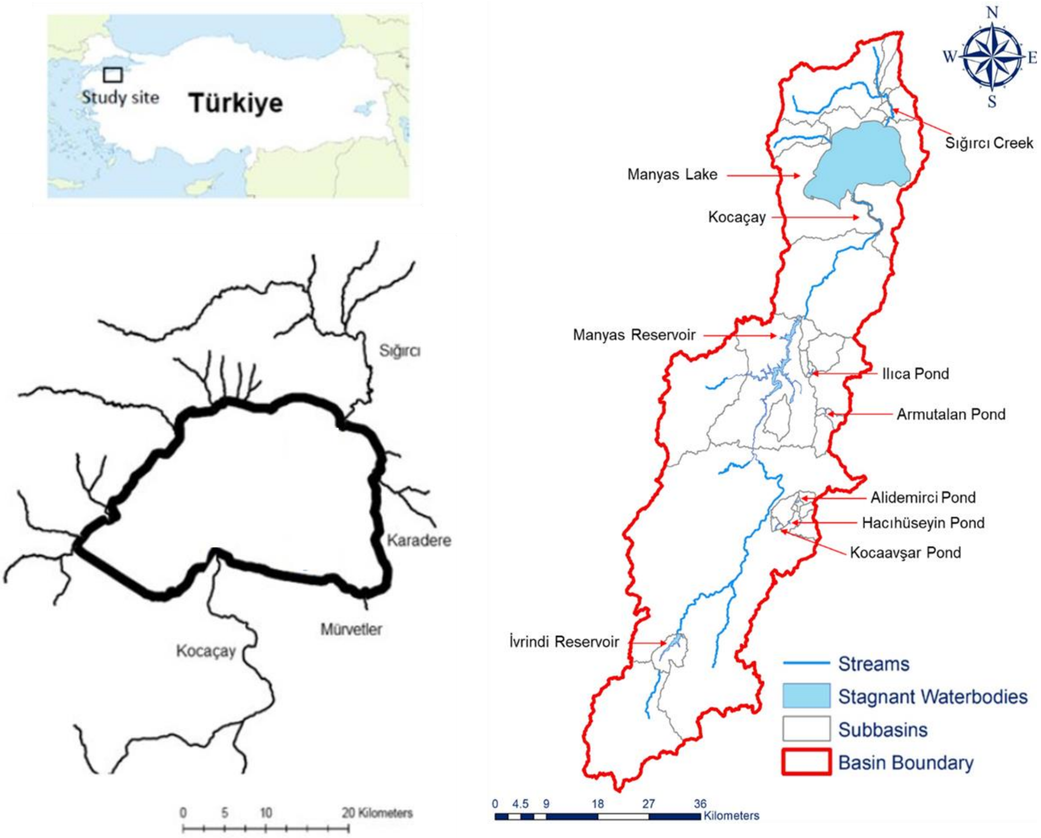
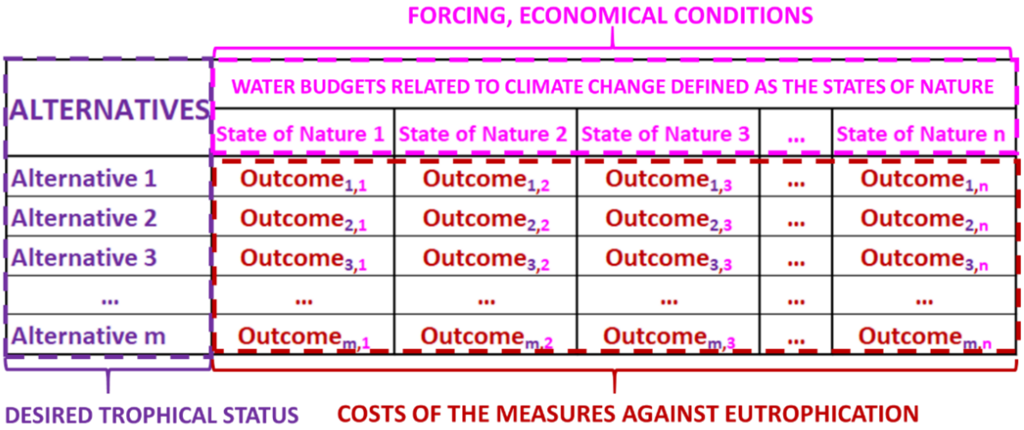


***Figure 1.*** *The Case study area.*

## 2. MATERIALS AND METHODS

As by any conventional decision support system (DSS), the DSS in this study is designed to provide the decision alternatives for the decision maker, defined as a group of relatively high-ranked bureaucrats who would formulate the suggestion for setting targets towards higher levels in the administrations eventually reaching the level of policy makers. Therefore, the decision problem in this study is defined as "aiming feasible and sustainable trophic status of an arbitrary shallow lake under the impact of cultural eutrophication and climate change".

Considering the relatively scarce financial resources allocated to solve environmental problems, the cost minimization of environmental measures is considered as the objective and the environmental quality is considered as the constraint that must be fulfilled for any acceptable decision. The output of the DSS is the so-called pay-off matrix as given in Figure 2, where each outcome is cost minimized group of diffuse nutrients pollution countermeasures using operation research methods.



FORCING, ECONOMICAL CONDITIONS

| ALTERNATIVES | WATER BUDGETS RELATED TO CLIMATE CHANGE DEFINED AS THE STATES OF NATURE | | | | |
|---|---|---|---|---|---|
| | State of Nature 1 | State of Nature 2 | State of Nature 3 | ... | State of Nature n |
| Alternative 1 | $\text{Outcome}_{1,1}$ | $\text{Outcome}_{1,2}$ | $\text{Outcome}_{1,3}$ | ... | $\text{Outcome}_{1,n}$ |
| Alternative 2 | $\text{Outcome}_{2,1}$ | $\text{Outcome}_{2,2}$ | $\text{Outcome}_{2,3}$ | ... | $\text{Outcome}_{2,n}$ |
| Alternative 3 | $\text{Outcome}_{3,1}$ | $\text{Outcome}_{3,2}$ | $\text{Outcome}_{3,3}$ | ... | $\text{Outcome}_{3,n}$ |
| ... | ... | ... | ... | ... | ... |
| Alternative m | $\text{Outcome}_{m,1}$ | $\text{Outcome}_{m,2}$ | $\text{Outcome}_{m,3}$ | ... | $\text{Outcome}_{m,n}$ |

DESIRED TROPHICAL STATUS

COSTS OF THE MEASURES AGAINST EUTROPHICATION

***Figure 2.*** *The structure of the pay-off matrix as the output of DSS.*

Following the operation research approach, the DSS aims the minimization of initial investments and continuous annual expenses defining the total annual cost as the objective function and utilizes the trophic status and related water quality as the main constraints, defining the Carlson trophic state index (TSI) (Carlson, 1977) as the constraint function along with the basic design parameters for pollution countermeasures as the decision variables.

The countermeasures for nutrient loads in this study were determined according to the relevant regulations of the Republic of Türkiye, namely the substitution of fertilizers with animal manure including manure storage and management, natural treatment systems for unsewered areas with septic tanks, terracing on land subject to erosion, filter strips with land slope adjustment, transfer of excess manure out of the watershed, limitation of aquaculture in the reservoirs in watershed. The corresponding decision variables are namely filter strip width, deviation from ideal slope for filter strip, ratio of terracing for potentially terraceable areas, success rate of applying animal manure to the field, ratio of animal manure removal to outside of the watershed and the limitation ratio of aquacultural production.

The infrastructure calculating the values of the objective function is based on the algorithmic sizing of the engineering structures related to the countermeasures in the paragraph above and using the unit costs of non-negligible cost items for initial investment (concrete, construction related labor, construction steel, clay coating, excavation and soil work, labor cost for initial planting, land cost, piping, seedling costs for initial filter strip planting, terracing cost as a single item including all related services), operation/maintenance (excavation of consolidated sediments in the ponds, harvesting and disposing of wetland macrophytes, operational costs covering periodic replanting of filter strip plants and removal of filter strip plants from previous period, loss of agricultural revenue corresponding to field areas covered by filter strips) and macroeconomic parameters such as the discount rates.

The value of the constraint function is calculated using a mass-balance model with total nitrogen (TN), total phosphorus (TP), chlorophyll-A (CHL) and detrital organic carbon (OC) as the state variables and Secchi disc depth (SD) as the derived variable. The outputs from the mass balance model (TN, TP, CHL and SD) are used to calculate the Carlson values of the lake as instructed by the latest updated “Regulation of Surface Water Quality” published in the Official Gazette of the Republic of Türkiye, Number: 32091 (Figure 3).

| Trophic State Index (TSI) Value | | Trophic State |
|---|---|---|
| >62 | | Hypertrophic |
| 62 | | Eutrophic |
| 60<br>(for reservoirs) | 52<br>(for natural lakes) | Mesotrophic |
| 44 | | Oligotrophic |
| ≤ 29 | | Ultraoligotrophic |

$$TSI(SD) = 60 - 14.41 \cdot ln(SD) \quad , SD: Secchi\ depth\ (m)$$

$$TSI(CHL) = 30.6 + 9.81 \cdot ln(CHL), CHL: Chlophyll - A\ (\mu g/L)$$

$$TSI(TP) = 4.15 + 14.42 \cdot ln(TP) \quad , TP: Total\ phosphorus\ (\mu g/L)$$

$$TSI(TN) = 54.45 + 14.43 \cdot ln(TN) \quad , TN: Total\ nitrogen\ (mg/L)$$

$$TSI = \frac{TSI(SD) + TSI(CHL) + TSI(TP) + TSI(TN)}{4}$$

***Figure 3.*** *TSI based Trophic classification according to the regulations in the Republic of Türkiye.*

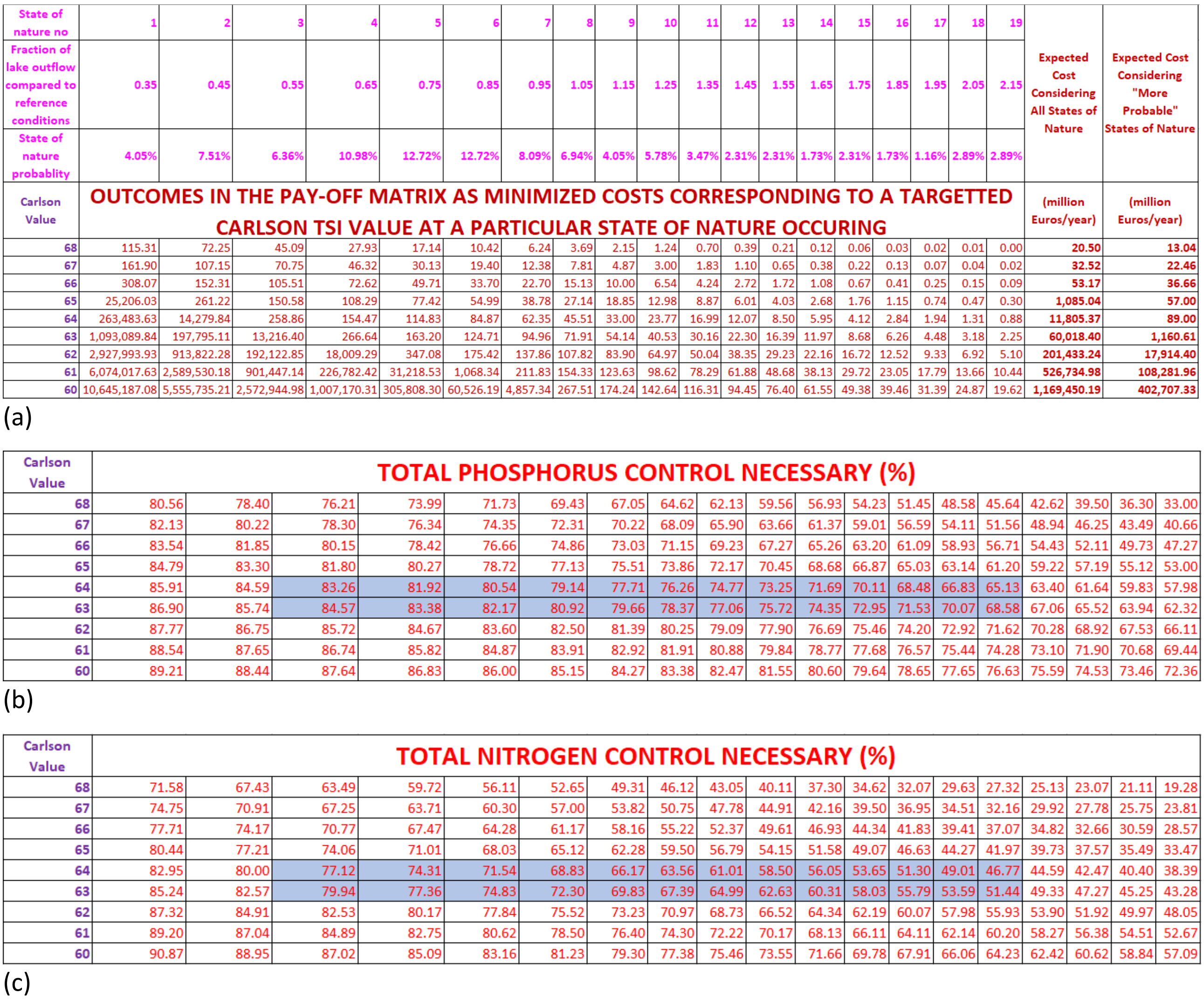
The non-linear nature of response of both, the objective and the constraint functions to decision variables necessitated the utilization of the non-linear mathematical programming to solve the operation research-based minimization problem to form the pay-off matrix illustrated in Figure 2.

The entire DSS is developed using Microsoft Excel as a spreadsheet platform to support the operation research infrastructure as it is useful to conduct simple formula-based calculation as well as non-linear programming embedded in its solver add-in. The rest, related to organization of the pay-off matrix is handled by MATrix LABoratory (MATLAB), version 2023 (Mathworks, 2023).

As stated in the introduction, the case study area on which the decision support system was applied is a shallow lake classified as hypertrophic by the "Regulation of Surface Water Quality". The outflows from the lake related to water budgets for different climate scenarios as defined by the states of nature in the pay-off matrix (Figure 2) using the outputs of a previous study (Öztürk et al., 2013), where all the hydrological processes were calculated for different climate scenarios to construct water budgets of Manyas Lake.

## 3. RESULTS AND DISCUSSION

The main results of this study are the successful development of the DSS and its successful application on the decision problem of aiming at feasible and sustainable trophic status of the case study area based on Carlson TSI. The outputs of the DSS were used to develop the cost curves for phosphorus and nitrogen reduction. The pay-off matrix is given in Figure 4. As previously discussed, the states of nature were generated using the climate change analysis results of Öztürk et al. (2013) correspond to different states of nature.



| State of nature no | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | Expected Cost Considering All States of Nature | Expected Cost Considering "More Probable" States of Nature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fraction of lake outflow compared to reference conditions | 0.35 | 0.45 | 0.55 | 0.65 | 0.75 | 0.85 | 0.95 | 1.05 | 1.15 | 1.25 | 1.35 | 1.45 | 1.55 | 1.65 | 1.75 | 1.85 | 1.95 | 2.05 | 2.15 | | |
| State of nature probablity | 4.05% | 7.51% | 6.36% | 10.98% | 12.72% | 12.72% | 8.09% | 6.94% | 4.05% | 5.78% | 3.47% | 2.31% | 2.31% | 1.73% | 2.31% | 1.73% | 1.16% | 2.89% | 2.89% | | |
| Carlson Value | OUTCOMES IN THE PAY-OFF MATRIX AS MINIMIZED COSTS CORRESPONDING TO A TARGETTED CARLSON TSI VALUE AT A PARTICULAR STATE OF NATURE OCCURING | | | | | | | | | | | | | | | | | | | (million Euros/year) | (million Euros/year) |
| 68 | 115.31 | 72.25 | 45.09 | 27.93 | 17.14 | 10.42 | 6.24 | 3.69 | 2.15 | 1.24 | 0.70 | 0.39 | 0.21 | 0.12 | 0.06 | 0.03 | 0.02 | 0.01 | 0.00 | **20.50** | **13.04** |
| 67 | 161.90 | 107.15 | 70.75 | 46.32 | 30.13 | 19.40 | 12.38 | 7.81 | 4.87 | 3.00 | 1.83 | 1.10 | 0.65 | 0.38 | 0.22 | 0.13 | 0.07 | 0.04 | 0.02 | **32.52** | **22.46** |
| 66 | 308.07 | 152.31 | 105.51 | 72.62 | 49.71 | 33.70 | 22.70 | 15.13 | 10.00 | 6.54 | 4.24 | 2.72 | 1.72 | 1.08 | 0.67 | 0.41 | 0.25 | 0.15 | 0.09 | **53.17** | **36.66** |
| 65 | 25,206.03 | 261.22 | 150.58 | 108.29 | 77.42 | 54.99 | 38.78 | 27.14 | 18.85 | 12.98 | 8.87 | 6.01 | 4.03 | 2.68 | 1.76 | 1.15 | 0.74 | 0.47 | 0.30 | **1,085.04** | **57.00** |
| 64 | 263,483.63 | 14,279.84 | 258.86 | 154.47 | 114.83 | 84.87 | 62.35 | 45.51 | 33.00 | 23.77 | 16.99 | 12.07 | 8.50 | 5.95 | 4.12 | 2.84 | 1.94 | 1.31 | 0.88 | **11,805.37** | **89.00** |
| 63 | 1,093,089.84 | 197,795.11 | 13,216.40 | 266.64 | 163.20 | 124.71 | 94.96 | 71.91 | 54.14 | 40.53 | 30.16 | 22.30 | 16.39 | 11.97 | 8.68 | 6.26 | 4.48 | 3.18 | 2.25 | **60,018.40** | **1,160.61** |
| 62 | 2,927,993.93 | 913,822.28 | 192,122.85 | 18,009.29 | 347.08 | 175.42 | 137.86 | 107.82 | 83.90 | 64.97 | 50.04 | 38.35 | 29.23 | 22.16 | 16.72 | 12.52 | 9.33 | 6.92 | 5.10 | **201,433.24** | **17,914.40** |
| 61 | 6,074,017.63 | 2,589,530.18 | 901,447.14 | 226,782.42 | 31,218.53 | 1,068.34 | 211.83 | 154.33 | 123.63 | 98.62 | 78.29 | 61.88 | 48.68 | 38.13 | 29.72 | 23.05 | 17.79 | 13.66 | 10.44 | **526,734.98** | **108,281.96** |
| 60 | 10,645,187.08 | 5,555,735.21 | 2,572,944.98 | 1,007,170.31 | 305,808.30 | 60,526.19 | 4,857.34 | 267.51 | 174.24 | 142.64 | 116.31 | 94.45 | 76.40 | 61.55 | 49.38 | 39.46 | 31.39 | 24.87 | 19.62 | **1,169,450.19** | **402,707.33** |

(a)

| Carlson Value | TOTAL PHOSPHORUS CONTROL NECESSARY (%) | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 68 | 80.56 | 78.40 | 76.21 | 73.99 | 71.73 | 69.43 | 67.05 | 64.62 | 62.13 | 59.56 | 56.93 | 54.23 | 51.45 | 48.58 | 45.64 | 42.62 | 39.50 | 36.30 | 33.00 |
| 67 | 82.13 | 80.22 | 78.30 | 76.34 | 74.35 | 72.31 | 70.22 | 68.09 | 65.90 | 63.66 | 61.37 | 59.01 | 56.59 | 54.11 | 51.56 | 48.94 | 46.25 | 43.49 | 40.66 |
| 66 | 83.54 | 81.85 | 80.15 | 78.42 | 76.66 | 74.86 | 73.03 | 71.15 | 69.23 | 67.27 | 65.26 | 63.20 | 61.09 | 58.93 | 56.71 | 54.43 | 52.11 | 49.73 | 47.27 |
| 65 | 84.79 | 83.30 | 81.80 | 80.27 | 78.72 | 77.13 | 75.51 | 73.86 | 72.17 | 70.45 | 68.68 | 66.87 | 65.03 | 63.14 | 61.20 | 59.22 | 57.19 | 55.12 | 53.00 |
| 64 | 85.91 | 84.59 | 83.26 | 81.92 | 80.54 | 79.14 | 77.71 | 76.26 | 74.77 | 73.25 | 71.69 | 70.11 | 68.48 | 66.83 | 65.13 | 63.40 | 61.64 | 59.83 | 57.98 |
| 63 | 86.90 | 85.74 | 84.57 | 83.38 | 82.17 | 80.92 | 79.66 | 78.37 | 77.06 | 75.72 | 74.35 | 72.95 | 71.53 | 70.07 | 68.58 | 67.06 | 65.52 | 63.94 | 62.32 |
| 62 | 87.77 | 86.75 | 85.72 | 84.67 | 83.60 | 82.50 | 81.39 | 80.25 | 79.09 | 77.90 | 76.69 | 75.46 | 74.20 | 72.92 | 71.62 | 70.28 | 68.92 | 67.53 | 66.11 |
| 61 | 88.54 | 87.65 | 86.74 | 85.82 | 84.87 | 83.91 | 82.92 | 81.91 | 80.88 | 79.84 | 78.77 | 77.68 | 76.57 | 75.44 | 74.28 | 73.10 | 71.90 | 70.68 | 69.44 |
| 60 | 89.21 | 88.44 | 87.64 | 86.83 | 86.00 | 85.15 | 84.27 | 83.38 | 82.47 | 81.55 | 80.60 | 79.64 | 78.65 | 77.65 | 76.63 | 75.59 | 74.53 | 73.46 | 72.36 |

(b)

| Carlson Value | TOTAL NITROGEN CONTROL NECESSARY (%) | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 68 | 71.58 | 67.43 | 63.49 | 59.72 | 56.11 | 52.65 | 49.31 | 46.12 | 43.05 | 40.11 | 37.30 | 34.62 | 32.07 | 29.63 | 27.32 | 25.13 | 23.07 | 21.11 | 19.28 |
| 67 | 74.75 | 70.91 | 67.25 | 63.71 | 60.30 | 57.00 | 53.82 | 50.75 | 47.78 | 44.91 | 42.16 | 39.50 | 36.95 | 34.51 | 32.16 | 29.92 | 27.78 | 25.75 | 23.81 |
| 66 | 77.71 | 74.17 | 70.77 | 67.47 | 64.28 | 61.17 | 58.16 | 55.22 | 52.37 | 49.61 | 46.93 | 44.34 | 41.83 | 39.41 | 37.07 | 34.82 | 32.66 | 30.59 | 28.57 |
| 65 | 80.44 | 77.21 | 74.06 | 71.01 | 68.03 | 65.12 | 62.28 | 59.50 | 56.79 | 54.15 | 51.58 | 49.07 | 46.63 | 44.27 | 41.97 | 39.73 | 37.57 | 35.49 | 33.47 |
| 64 | 82.95 | 80.00 | 77.12 | 74.31 | 71.54 | 68.83 | 66.17 | 63.56 | 61.01 | 58.50 | 56.05 | 53.65 | 51.30 | 49.01 | 46.77 | 44.59 | 42.47 | 40.40 | 38.39 |
| 63 | 85.24 | 82.57 | 79.94 | 77.36 | 74.83 | 72.30 | 69.83 | 67.39 | 64.99 | 62.63 | 60.31 | 58.03 | 55.79 | 53.59 | 51.44 | 49.33 | 47.27 | 45.25 | 43.28 |
| 62 | 87.32 | 84.91 | 82.53 | 80.17 | 77.84 | 75.52 | 73.23 | 70.97 | 68.73 | 66.52 | 64.34 | 62.19 | 60.07 | 57.98 | 55.93 | 53.90 | 51.92 | 49.97 | 48.05 |
| 61 | 89.20 | 87.04 | 84.89 | 82.75 | 80.62 | 78.50 | 76.40 | 74.30 | 72.22 | 70.17 | 68.13 | 66.11 | 64.11 | 62.14 | 60.20 | 58.27 | 56.38 | 54.51 | 52.67 |
| 60 | 90.87 | 88.95 | 87.02 | 85.09 | 83.16 | 81.23 | 79.30 | 77.38 | 75.46 | 73.55 | 71.66 | 69.78 | 67.91 | 66.06 | 64.23 | 62.42 | 60.62 | 58.84 | 57.09 |

(c)

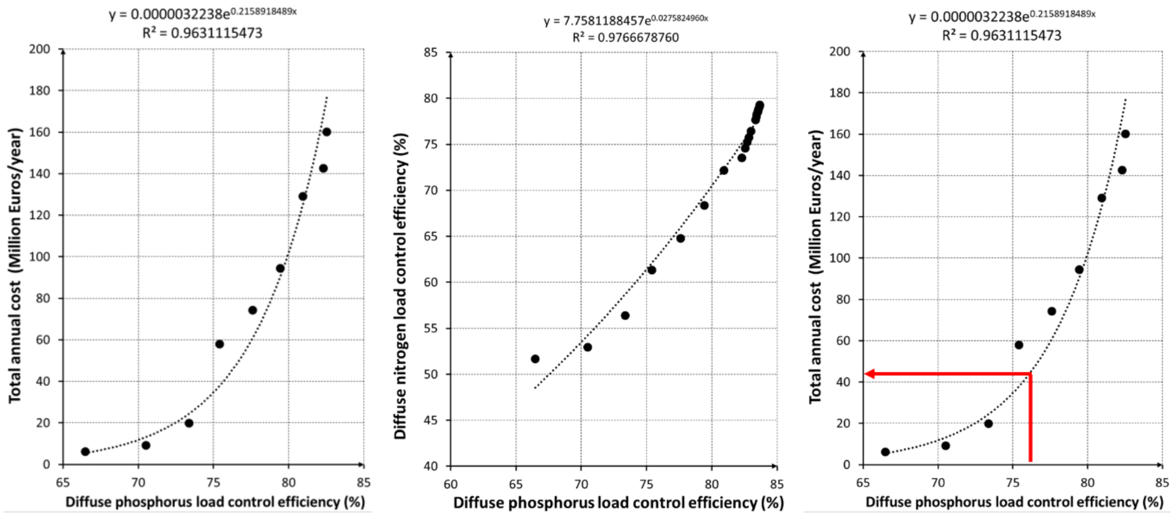
***Figure 4.*** *The pay-off matrix as the screen output of DSS together with nutrient reduction necessary to reach certain Carlson TSI*

As seen in Figure 4a, there is a wide range of expected total annual costs for any particular targeted Carlson TSI value, some of which only being unrealistic due to their extreme extensions corresponding to very low probabilities of realization. Such marginal values can be observed as two types from very low total annual costs not exceeding few tens of thousands of Euros to very high reaching trillions of euros. These are obviously due to steep changes in the cost curves indicating that the limits of the countermeasures are reached and further efforts would have been futile under the circumstances in case of extremely high estimated costs or that as a very low probability the nature being on the managers side by providing extremely high flows from time to time flushing the lake and improving its water quality. The latter one is clearly unreliable from the eutrophication management point. Therefore, the states of nature corresponding to such events were neglected during the calculation of expected costs, which was conducted according to the best expected value for cost considering simple decision modeling under the risk environment as given with the equation below.

$$Best\ Expected\ Value = \sum_{j=1}^{m} P_j \cdot S_{i,j}$$

where m is the number of alternatives (number of targeted Carlson TSIs in this study), i and j are the indexes for the rows (alternative targeted Carlson TSIs) and columns (states of nature) for the pay-off matrix respectively, $P_j$ is the probability of a particular state of nature and $S_{i,j}$ is the value of outcome (the minimized total annual cost for the combination of a particular alternative Carlson TSI and a particular state of nature as defined in this study). The nutrient control results corresponding to each outcome were given in Figure 5b and Figure 5c. From the point of feasibility and sustainability the nutrient reductions highlighted in Figure 5b and Figure 5c are recommended.

Because the lake was phosphorus limited the system designs were focused on phosphorus control (Figure 5a), where the nitrogen control efficiency was a secondary result depending on phosphorus control efficiency (Figure 5b), eventually reaching total phosphorus and total nitrogen controls of 76% and 63%, respectively, with a expected Carson TSI value of 63-64 with an annual cost of 42 million of Euros (Figure 5c).



**(a)** **(b)** **(c)**

***Figure 5.*** *Summarized results*

## 4. CONCLUSIONS

The main conclusion is that even though the related lake will stay highly eutrophic, at least the probability of a trophic state of a lake with hypertrophic symptoms can be reduced considerably. Setting a target TSI range of 63-64 can be recommended. This range is still eutrophic; however, it corresponds to a much higher ecological state compared to TSI 78 keeping in mind that the TSI value is based on logarithms meaning that each unit increase occurs by an exponential increase of relevant nutrient and chlorophyll-a concentrations. Another important point to note is that, the DSS infrastructure developed in this study can be applied to different lakes of similar type, provided that adequate information can be supplied by the users who need to operate this system.

## 5. ACKNOWLEDGEMENTS

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## REFERENCES

Abell, J.M., Özkundakci, D., Hamilton, D.P., Reeves, P. 2022. Restoring shallow lakes impaired by eutrophication: Approaches, outcomes, and challenges. *Crit. Rev. Environ. Sci. Technol.,* 52, 1199–1246. https://doi.org/10.1080/10643389.2020.1854564

Carlson, R.E. 1977. A trophic state index for lakes. *Limnol. Oceanogr.,* 22, 361–369. https://doi.org/10.4319/lo.1977.22.2.0361

Dorak, Z., Köker, L., Gürevin, C., Saç, G. 2023. How do environmental variables affect the temporal dynamics of zooplankton functional groups in a hyper-eutrophic wetland? *Environmental Science and Pollution Research*, 30, https://doi.org/10.1007/s11356-023-29252-8

Mathworks, 2023. Natick, Massachusetts: The MathWorks Inc.

Ozturk, I., Gurel, M., Erturk, A. 2013. Effects of Climate Change on Water Resources in Turkey, Proceedings of *AASSA Regional Workshop on Sustainable Development of Asian Countries, Water Resources and Biodiversity Under Climate Change*, Compilation by D.M. Bezmaternykh, D.N.Troshkin, Institute for Water and Environmental Problems, Siberian Branch of the Russian Academy of Sciences (IWEP SB RAS), August 19-23, 2013, Barnaul, Russia.

Suresh, K., Tang, T., van Vliet, M.T.H., Bierkens, M.F.P., Strokal, M., Sorger-Domenigg, F., Wada, Y. 2023. Recent advancement in water quality indicators for eutrophication in global freshwater lakes. *Environmental Research Letters*, 18, 063004. https://doi.org/10.1088/1748-9326/acd071

# Copper recovery from printed circuit boards: Alkaline glycine-peroxide leaching system

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## ABSTRACT

The rapid evolution of electronic technologies has led to a growing accumulation of waste printed circuit boards (WPCBs), which are rich in hazardous substances and valuable metals—particularly copper, a critical raw material in green and digital transitions. This study focuses on recovering copper from WPCB using glycine-peroxide leaching solutions, a biodegradable and non-toxic amino acid, as an alternative leaching agent. Factors that influence recovery, such as glycine concentration and pH were assessed. The results show the influence of glycine concentration and pH, identifying optimal conditions at 2 $mol/dm^3$ glycine under which copper dissolution reached 44%, and pH 10. Cementation with zinc achieved a high recovery efficiency of 99.6% within 10 minutes to recover copper from the leachate. These results demonstrate the potential of glycine-based leaching, combined with cementation, as a safer, scalable, and more environmentally alternative to traditional hydrometallurgical processes for copper recovery from electronic waste.

**Keywords:** *printed circuit boards; leaching; glycine; copper; recovery.*

## 1. INTRODUCTION

The fast development of technology, the high-performance requirements, and the great demands in electrical and electronic equipment (EEE) make the replacement of printed circuit boards (PCBs) more frequent, resulting in large quantities of waste printed circuit boards (WPCBs) that need to be disposed of.

WPCBs contains a variety of hazardous substances and heavy metals, namely halogenated flame retardants, cadmium, lead, and other metals that, from environmental point of view, should be adequately managed, preferably recycled. On the other hand, WPCBs are composed of base metals and precious metals, mainly copper, aluminium, tin, lead, zinc, silver, and gold being copper the major metal with 10 − 30 %, representing a high economic value (Oishi et al., 2007; Koyama et al, 2006). Copper is considered a strategic raw material due to its wide application, particularly concerning ecological and digital transitions, so its recovery and incorporation into the production chain is imperative.

Hydrometallurgical processes are commonly used to recover metals and are recognized as having the advantage of being easily controlled, having high leaching efficiencies, being predictable, having low capital cost, and may be viable under small-scale operations (Oishi et al., 2007). Various researchers studied copper leaching from WPCBs using different leaching agents, such as mineral acids, including sulphuric acid (Kumari et al., 2016; Oh et al., 2003), nitric acid (Choubey et al., 2015; Maguyon et al, 2012) and a mixture of acids (Arshadi et al., 2020; Tunali et al., 2020). However, these acids are not very selective concerning the leachable metals. Furthermore, nitric acid and aqua regia, due to their corrosive and highly toxic nature, may bring environmental risks. Thus, some authors have studied environmentally benign alternative reagents to recover metals such as glycine. These studies reported that amino acid has a high affinity for copper (Oraby et al., 2020; Tanda et. al, 2017). The glycine forms stable complexes with copper over a pH range between 2.6 and 12.0, being the regions of stability for the species in the coper-water-glycine system are defined on

Eh-pH diagrams. The main copper (II) glycine complexes are: $Cu(H_3NCH_2COO)^{2+}$, $Cu(H_2NCH_2COO)^{+}$ and $Cu(H_2NCH_2COO)_2$ , and for copper(I) the predominant complex is $Cu(H_2NCH_2COO)_2^{-}$ (Tanda et al., 2017).

This work evaluates copper recovery using glycine solutions to leach WPCBs samples followed by reductive precipitation. Factors that influence recovery, such as glycine concentration and pH were assessed.

## 2. MATERIALS AND METHODS

All the WPCBs samples used in this research were from obsolete computers. First, the large components as the universal serial bus (USB) and the high-definition multimedia interface (HDMI) were removed from the WPCBs. The samples were previously ground with a particle size of 1 mm to < 1.4 mm. For metals quantification, WPCBs samples were subjected to chemical attack with aqua regia, according to the ISO 11466:1995 standard. The quantification was carried out in triplicate and copper was determined in the solutions by atomic absorption spectrometry (AAS) analysis using a UNICAM 969 AA spectrometer.

The leaching tests were performed at room temperature during 48 h in Erlenmeyer flasks using 0.5 or 2 mol $dm^{-3}$ glycine solution, 1 mol $dm^{-3}$ hydrogen peroxide solution, with an L/S 40 under pH 8, 9 or 10, and a mechanical stirring of 500 rpm. Samples of 1 mL were taken at regular time intervals to follow the dissolution of copper.

Copper was recovered directly from the leaching solutions by reductive precipitation using zinc with 2 times the stoichiometric amount that copper.

## 3. RESULTS AND DISCUSSION

### 3.1 Chemical composition of samples

The XRF semi-quantitative analysis showed that copper was the most abundant metal in the samples tested (data not shown). The copper content of WPCB samples obtained after aqua regia digestion and AAS analysis was 17,8 ± 1,3 % confirming XRF evaluation.

### 3.2 Leaching tests

***Effect of glycine concentration***

The glycine concentrations chosen were based on copper present in the WPCB amount since the stable copper-glycine complex predominant is $Cu(H_2NCH_2COO)_2$, at a range of pH studied, implying that a minimum of two moles of glycine are needed per mole of copper for complex formation.

The results showed that the glycine concentration influenced leaching, and increasing glycine concentration increased copper dissolution (Figure 1). The most significant dissolution of copper, 44 %, was achieved using a solution of glycine concentration 2 mol/$dm^3$ after 48 h of leaching.

To obtain the highest copper leaching levels, it is necessary to use a solution of glycine concentration 2 mol/$dm^3$ due to the competitiveness of other metals existing in the plates (such as zinc) which also form complexes with glycine.

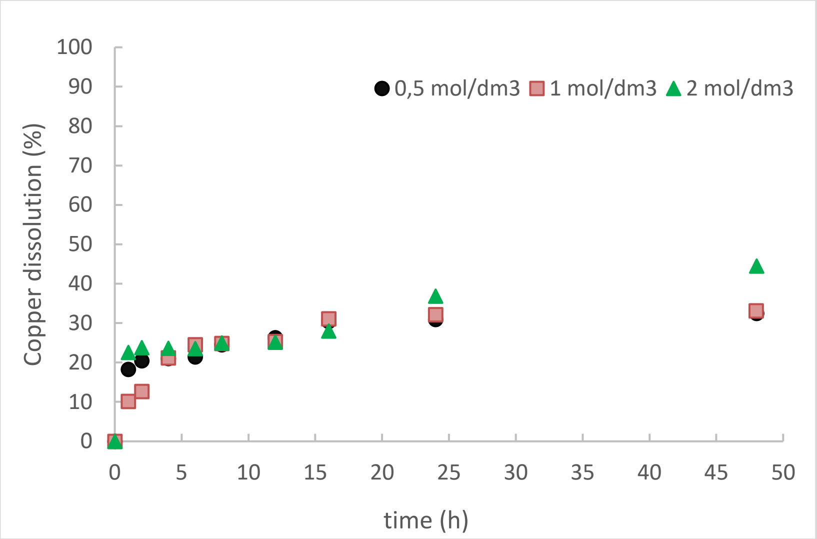

***Figure 1.*** *Effect of glycine concentration on copper leaching from the WPCB (experimental conditions: L/S ratio of 40; 1 mol dm$^{-3}$ of hydrogen peroxide; pH=8).*

***Effect of pH***

The effects of pH on copper dissolution from WPCB is shown in Figure 2. For all experiments, the glycine and peroxide concentration was kept constant at 1 mol dm$^{3}$. The initial pH of the leaching solution was adjusted with sodium hydroxide, and no further pH control was performed. The time profile shows that the copper dissolution is lower at a pH 8 being that at pH 9 and pH 10 the leaching percentages are not significant. For

the three pH values, copper leaching occurs mainly in the first 4 hours, after which the copper dissolution rate is lower. The results indicate that the highest copper dissolution of 31 % was achieved at pH 10.

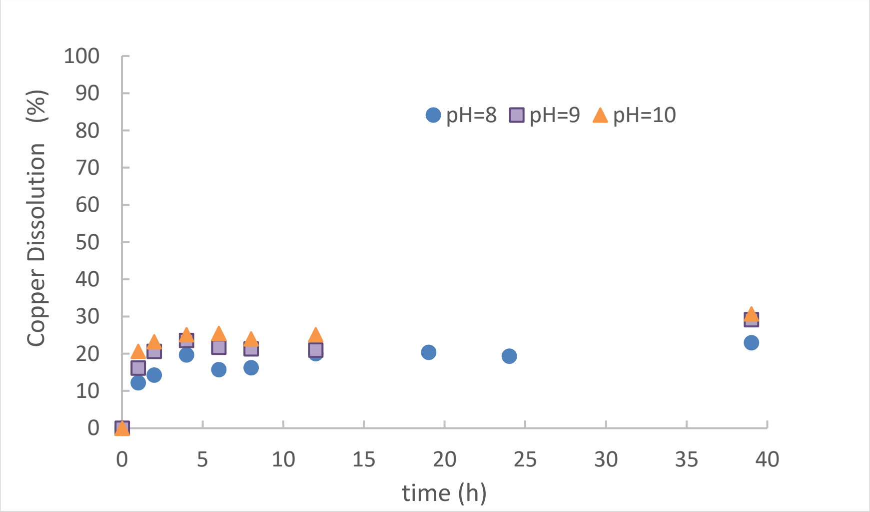

***Figure 2.*** *Effect of pH on copper leaching from the WPCB (experimental conditions: L/S ratio of 40; 1 mol dm$^{-3}$ of glycine; 1 mol dm$^{-3}$ of hydrogen peroxide).*

### 3.3 Copper cementation

The cementation was carried out in solution resulting from leaching WPCB at pH 8, L/S ratio of 40; 1 mol dm$^{-3}$

of glycine; 1 mol dm$^{-3}$ of hydrogen peroxide. Zinc was the metal chosen for the recovery of copper in metallic form because it has a lower reduction potential than copper and is probably present in the solution, as this metal also forms stable complexes with glycine. The results showed that zinc is a good cement agent for glycine peroxide leaching solutions, as shown in the Table 1.The copper recovery from leaching solutions using zinc was 99.6 % after 10 min.

***Table 1.*** *Copper concentration on solution before and after cementation*

| **Solution** | **Cu (mg/L)** |
|---|---|
| **before cementation** | 3783,0 |
| **after cementation** | 13,6 |

## 4. CONCLUSIONS

Glycine-peroxide solutions leach copper at room temperature, but the dissolution depends on the glycine concentration and pH. The dissolution obtained was not very high, probably due to the sample's particle size. This could be improved by using a smaller particle size to ensure sufficient liberation of the metals and increase the contact area between the metals and the solution.

Cementation can be seen as a very effective method to remove metals from solutions, given that its implementation can achieve very low concentrations. Compared with other processes, cementation is a straightforward and quick process to recover metals; therefore, it is a good alternative to electrowinning for copper extraction from alkaline glycine solutions.

This leaching agent can be a great alternative to the classic leaching agents mainly due to its high stability and environmentally friendly nature.

## REFERENCES

Arshadi, M., Yaghmaei, S., Esmaeili, A., 2020. Evaluating the optimal digestion method and value distribution of precious metals from different waste printed circuit boards. J. Mater. Cycles Waste Manag., 22,
1690–1698.

Choubey, P.K., Panda, R., Jha, M. K., Lee, J.C., Pathak, D., 2015. Recovery of copper and recycling of acid from the leach liquor of discarded Printed Circuit Boards (PCBs). Sep. Purif. Technol. 156, 269–275.

Koyama, K., Tanaka, M., Lee, J., 2006. Copper Leaching Behavior from Waste Printed Circuit Board in Ammoniacal Alkaline Solution. Mater. Trans. 47 (7), 1788–1792.

Kumari, A., Jha, M.K., Lee, J., Singh, R.P., 2016. Clean process for recovery of metals and recycling of acid from the leach liquor pf PCBs. J. Clean. Prod. 112, 4826–4834.

Maguyon, M.C., Catalino, G., Alfafara, G., Migo, V.P., Movillon, J.L., Rebancos, C.M., 2012. Recovery of copper from spent solid printed circuit board (PCB) wastes of a PCB manufacturing facility by two-step sequential acid extraction and electrochemical deposition. J. Environ. Sci. Manag. 15 (1).

Oh, C.J., Lee, S.O., Yang, H.S., Ha, T.J., Kim, M.J., 2003. Selective leaching of valuable metals from waste printed circuit boards. J. Air Waste Manag. Assoc. 53 (7), 897–902.

Oishi, T., Koyama, K., Alam, S., Tanaka, M., Lee, J.C., 2007. Recovery of high purity copper cathode from printed circuit boards using ammoniacal sulfate or chloride solutions. Hydrometallurgy, 89 (1–2), 82–88.

Oraby, E.A., Huan, L., Eksteen, J.J., 2020. An alkaline glycine-based leach process of base and precious metals from powered waste printed circuit boards. Waste and Biomass Valorization, 11, 3897–3909.

Tanda, B.C., Eksteen, J.J., Oraby, E.A., 2017. An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions. Hydrometallurgy, 167, 153–162.

Tunali, M., Tunali, M.M., Yenigun, O., 2020. Characterization of different types of electronic waste: heavy metal, precious metal and rare earth element content by comparing different digestıon methods. J. Mater. Cycles Waste Manag, 23, 149–157.

# Influence of Operational Parameters on Lead Hydrometallurgical Leaching of Lead-Acid Batteries with Sodium Chloride

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## ABSTRACT

The increasing demand for sustainable energy technologies and the need for environmentally sound disposal of hazardous waste have made the recycling of lead-acid batteries (LABs) a strategic priority. Although pyrometallurgical processes dominate the industry, they involve high energy consumption, emission of toxic gases, and generation of hazardous slag, limiting their environmental and economic sustainability. Hydrometallurgical approaches offer a cleaner, more selective alternative for metal recovery under milder conditions. This study evaluated the leaching of lead (Pb) from thermally desulfated LAB paste using sodium chloride (NaCl) solutions. The influence of NaCl concentration (2–6 mol·L$^{-1}$), solid-to-liquid ratio (2–10 g/200 mL), and temperature (25–75 °C) on Pb recovery was systematically investigated. Pb concentration in the leachate was quantified using flame atomic absorption spectrometry (AAS). The optimal condition—32.3% Pb recovery in 6 hours—was achieved with 5 mol·L$^{-1}$ NaCl, S/L ratio of 2/200, and temperature of 60 °C. Higher concentrations and temperatures offered no further improvement and may have promoted the formation of passivating or insoluble phases such as Pb(OH)Cl. Increased solid loading negatively affected ion diffusion and chloride availability, limiting extraction efficiency. These findings highlight the potential of NaCl as an environmentally benign lixiviant, with notable operational advantages over conventional acid-based systems. The results provide a technical foundation for the development of sustainable hydrometallurgical processes tailored for decentralized lead recycling applications.

**Keywords:** processes; leaching; hydrometallurgy; battery recycling.

## 1. INTRODUCTION

Lead-acid batteries (LABs) remain a globally dominant electrochemical storage technology, extensively used in automotive, industrial, telecommunications, and backup energy systems. Over 85% of the global refined lead supply is directed to LAB manufacturing (Sun et al., 2017). However, their widespread use and limited lifespan generate substantial amounts of hazardous waste, primarily composed of metallic lead and toxic compounds such as lead sulfate ($PbSO_4$), posing significant environmental and health risks due to the persistence and toxicity of Pb (Chen et al., 2014).

Current recycling practices rely heavily on pyrometallurgical processes, which, despite high Pb recovery (>95%), operate at elevated temperatures (>1000 °C), emitting toxic gases and generating hazardous slag (Espinosa et al., 2004; Ellis & Mirza, 2010; Nowińska & Adamczyk, 2023).

Hydrometallurgy offers a cleaner alternative, enabling selective metal recovery under milder conditions with lower energy consumption and emissions (Ferracin et al., 2002; Rao et al., 2021). Nonetheless, the low solubility of LAB paste components ($PbSO_4$, PbO, $PbO_2$) in aqueous media limits direct leaching (Zhang et al., 2010; Shu et al., 2015).

Thermal desulfation is commonly applied to enhance reactivity by converting $PbSO_4$ into PbO (Yang et al., 2014). Among potential lixiviants, sodium chloride (NaCl) has gained attention for its low cost, environmental compatibility, and ability to form soluble lead complexes such as $PbCl^+$, $PbCl_2$, $PbCl_3^-$, and $PbCl_4^{2-}$ (Xie et al., 2019; Dutrizac, 1992).

This study investigates the effects of NaCl concentration, solid-to-liquid ratio (S/L), and temperature on Pb leaching efficiency from desulfated LAB pastes, aiming to support the development of selective, low-impact hydrometallurgical processes suitable for decentralized recycling applications.

## 2. CONTEXTUALIZATION - LITERATURE

The recycling of lead (Pb) from lead-acid batteries (LABs) has attracted increasing attention due to the global demand for strategic metals and growing environmental concerns related to the improper disposal of hazardous residues (Margallo et al., 2019; Wang et al., 2023). Pb is a persistent and toxic element, frequently associated with soil and groundwater contamination, especially in industrial and urban areas (Chen et al., 2014).

Pyrometallurgical methods, though widely used and capable of achieving high recovery rates (>95%), involve temperatures above 1000 °C and require complex infrastructure for managing gaseous and solid emissions. These processes also generate slag containing trace metals and sulfur compounds, posing additional environmental challenges (Ellis & Mirza, 2010; Prengaman, 1995; Nowińska & Adamczyk, 2023).

As an alternative, hydrometallurgical processes offer greater selectivity, reduced energy demand, and the possibility of operation in smaller, modular facilities with lower environmental impact (Espinosa et al., 2004; Ferracin et al., 2002). However, in the case of LABs, leaching remains a technical bottleneck due to the low solubility of key active compounds ($PbSO_4$, PbO, $PbO_2$) in aqueous media (Zhang et al., 2010; Shu et al., 2015).

### 2.1. Leaching of lead compounds

LAB active paste primarily contains $PbSO_4$, PbO, and $PbO_2$, all of which are poorly soluble and exhibit limited reactivity in neutral or mildly acidic solutions. $PbSO_4$, in particular, is the dominant phase after battery discharge and requires transformation to more reactive forms for effective leaching (Zhang et al., 2010; Shu et al., 2015).

Thermal desulfation, through controlled calcination, converts $PbSO_4$ into PbO, enhancing leachability and reducing sulfate residues in solution (Yang et al., 2014; Li et al., 2012). Although mineral acids (e.g., $HNO_3$, HCl) have shown good laboratory performance, their corrosiveness, high cost, and environmental risks make them unsuitable for decentralized or sustainable applications (Pan et al., 2019; Liu et al., 2018).

### 2.2. Sodium chloride as a leaching agent

Sodium chloride (NaCl), traditionally viewed as inert, has shown promise as a low-risk, low-cost complexing agent. $Cl^-$ ions form soluble Pb complexes ($PbCl^+$, $PbCl_2$, $PbCl_3^-$, $PbCl_4^{2-}$), particularly under high concentrations and agitation (Xie et al., 2019; Dutrizac, 1992). This enables Pb mobilization at near-neutral pH, reducing corrosivity and improving compatibility with standard equipment (Zhang et al., 2017; Pan et al., 2019).

NaCl's abundance, affordability, and environmental safety make it attractive for small-scale or urban recycling setups. When combined with pretreatments and optimized conditions, NaCl-based systems have demonstrated Pb recoveries above 30% (Rao et al., 2021; Volpe et al., 2009).

### 2.3. Influence of operating parameters

The leaching efficiency in NaCl systems is governed by three key variables: salt concentration, temperature, and solid-to-liquid ratio (S/L). While increasing NaCl concentration initially enhances Pb complexation, exceeding 5–6 $mol \cdot L^{-1}$ may lead to precipitation of $PbCl_2$ or Pb(OH)Cl, decreasing system performance (Shu et al., 2015; Xia et al., 2017; Pan et al., 2013).

Moderate temperatures (~60 °C) improve reaction kinetics, but excessive heating (>70 °C) may promote passivation or destabilize complexes. Similarly, S/L ratios must be carefully balanced: high solid loads reduce diffusion and ion availability, whereas very low S/L ratios impair productivity due to excessive solvent use (Volpe et al., 2009; Rao et al., 2021).

### 2.4. Perspectives and challenges for lead hydrometallurgy

Despite its potential, NaCl-based hydrometallurgy still faces implementation challenges. Metallic Pb recovery requires compatible downstream processes (e.g., electro-winning, cementation), and concerns remain regarding lixiviant reuse, residue stability, and corrosion control in long-term operations (Ferracin et al., 2002;

Yu et al., 2019).

Nonetheless, ongoing advances in modular reactor design, in situ purification, and process automation strengthen the case for NaCl as a core technology in urban and decentralized Pb recycling. Compared to pyrometallurgy, this approach aligns better with the principles of circular economy, offering lower emissions, energy efficiency, and scalability (Liu et al., 2018; Pan et al., 2019).

## 3. MATERIALS AND METHODS

### 3.1. Sample preparation

Active paste from spent lead-acid batteries was collected from a battery disassembly facility. The material was oven-dried at 105 °C for 24 h to remove moisture, followed by thermal desulfation at 450 °C for 2 h in a muffle furnace (heating rate: 10 °C/min). This process converted $PbSO_4$ into reactive PbO (Yang et al., 2014; Li et al., 2012), as confirmed by FTIR analysis and visual inspection.

### 3.2. Reagents and leaching solutions

Analytical-grade sodium chloride (NaCl, PA, ≥99%, Sigma®) was dissolved in deionized water to prepare leaching solutions with concentrations of 2, 4, 5, and 6 $mol·L^{-1}$. All solutions were freshly prepared to prevent degradation or contamination.

### 3.3. Experimental design

Three operational variables were independently assessed: i) NaCl Concentration: 2–6 $mol·L^{-1}$ (S/L = 5/200, 25 °C); ii) Solid/Liquid Ratio (S/L): 2/200, 5/200, 10/200 (NaCl 4 $mol·L^{-1}$, 25 °C); iii) Temperature: 25 °C, 60 °C, 75 °C (NaCl 4 $mol·L^{-1}$; S/L = 5/200).

Each leaching test lasted 24 h under continuous agitation (300 rpm), with sampling at 1, 2, 4, 6, 8, and 24 h. Tests were conducted in triplicate to ensure reproducibility. Temperature-controlled systems-maintained stability within ±1 °C.

### 3.4. Chemical analysis of leachate solution

Filtered leachates (0.45 µm membranes) were stored in pre-cleaned polyethylene vials. Lead concentrations were determined by flame atomic absorption spectrometry (AAS) using a certified Pb standard in nitric acid. Calibration curves (0–5 $mg·L^{-1}$) showed $R^2 > 0.999$, and measurements were performed at 217.0 nm with background correction.

### 3.5. Calculation of recovery efficiency

The Pb recovery efficiency was calculated based on the dissolved mass in relation to the initial mass present in the sample, according to the equation Eq. (1):

$$\%Pb\ Recovery = \left(\frac{[Pb]leachate\ x\ V}{mPb\ initial}\right) x\ 100 \qquad \text{Eq. (1)}$$

Where:
$[Pb]_{leachate}$ = concentration of Pb in solution ($mg·L^{-1}$)
V = volume of leaching solution (L)
$m_{Pb\ initial}$ = Pb mass in solid sample (g), previously determined by total acid digestion

## 4. RESULTS AND DISCUSSION

The analysis of the experimental data allowed us to understand the behavior of lead (Pb) leaching from the desulfated paste of Labs under different operating conditions. Three parameters were evaluated: NaCl concentration, solid/liquid ratio (S/L) and solution temperature. The following graphs summarize the results obtained and support the technical-scientific interpretation of the observed trends.

### 4.1. Influence of NaCl concentration

Figure 1 shows the effect of the concentration of NaCl (2, 4, 5 and 6 mol· L⁻¹) on Pb recovery over time, with room temperature and S/L ratio of 5/200.

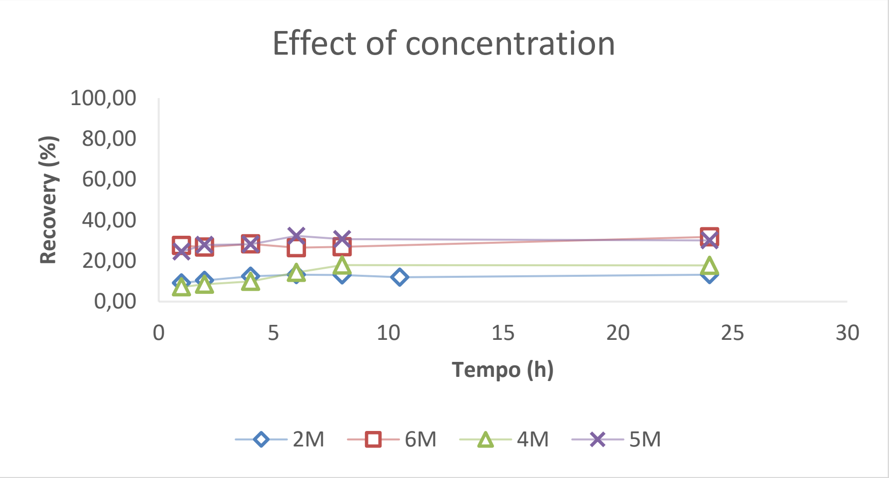

***Figure 1.*** *Effect of NaCl concentration on Pb recovery (%) over time.*

Recovery progressively increased between 2 and 5 mol· L⁻¹, reaching 32.3 % with 5 mol· L⁻¹ in 6 hours. This behavior highlights the central role of Cl⁻ ions in the formation of soluble complexes (such as $PbCl_4^{2-}$), which promote metal mobilization (Dutrizac, 1992; Xie et al., 2019). However, the rise to 6 mol· L⁻¹ did not bring additional gain, possibly due to solution saturation and the formation of precipitates such as $PbCl_2$ (Shu et al., 2015), which reduce effective solubility.

### 4.2. Influence of solid/liquid ratio (S/L)

Figure 2 presents the results for different S/L ratios (2/200, 5/200, 10/200 and 20/200), with NaCl 4 mol· L⁻¹ and room temperature.

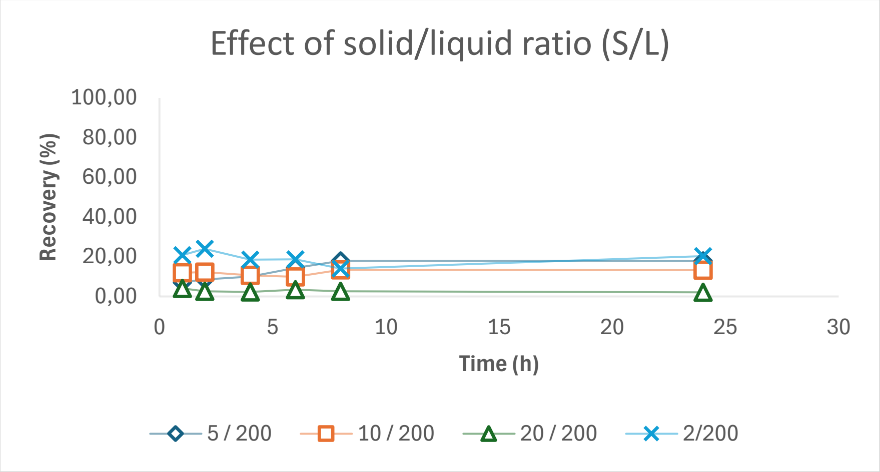

***Figure 2.*** *Effect of solid/liquid ratio (S/L) on Pb recovery with 4 mol· L⁻¹.*

The 2/200 ratio showed the best performance, with 24% of Pb extracted in just 2 hours. This result is associated with the high availability of Cl⁻ ions per solid mass and the reduction of diffusional strength in the liquid medium. In contrast, the 20/200 ratio showed significantly lower performance (max. ~3%), which can be explained by the early saturation of the system and limitation in the diffusion of leaching ions (Volpe et al., 2009; Rao et al., 2021).

### 4.3. Temperature Influence (°C)

Figure 3 shows the results obtained at temperatures of 25 °C, 60 °C and 75 °C, under NaCl 4 mol· $L^{-1}$ and S/L ratio of 5/200.

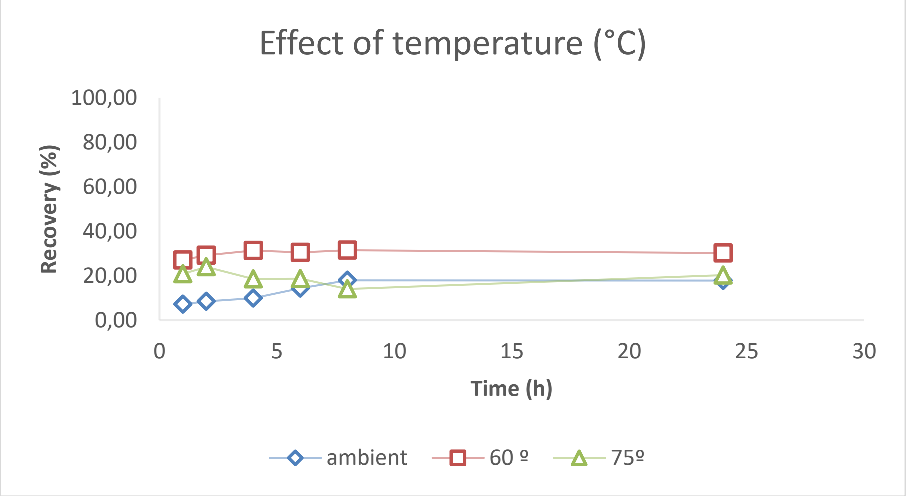

***Figure 3.*** *Effect of temperature on Pb recovery (%) with NaCl 4 mol·* $L^{-1}$*.*

The temperature of 60 °C provided the highest recovery (31.5% in 8 hours), attributed to the acceleration of chemical reactions and greater ionic mobility. On the other hand, at 75 °C, recovery dropped after 4 hours, suggesting the formation of passivating phases such as Pb(OH)Cl, which inhibit the continuity of the leaching process (Pan et al., 2013; Xia et al., 2017). These data demonstrate that there is an optimal thermal range for the process.

### 4.4. Síntese dos resultados e perspectivas

The data allows to establish optimal operating parameters to maximize Pb recovery:

***Table 1.*** *Summary of assay conditions and respective Pb recoveries*

| Assay | NaCl concentration (M) | S/L ratio (g/200 mL) | Temperature (°C) | Time (h) | Pb Recovery (%) |
|---|---|---|---|---|---|
| **Effect of concentration** | 5 | 5/200 | Ambient (~25 °C) | 6 | 32,3 |
| **Effect of S/L ratio** | 4 | 2/200 | Ambient (~25 °C) | 2 | 24,0 |
| **Effect of temperature** | 4 | 5/200 | 60 °C | 8 | 31,5 |

The results indicate that it is possible to achieve high levels of recovery without the use of aggressive acids, using a neutral, affordable and environmentally compatible agent such as NaCl. These findings pave the way for the development of safer, modular, and sustainable hydrometallurgical routes, applicable even in urban regions with limited infrastructure.

## 5. CONCLUSIONS

This study demonstrated the feasibility of hydrometallurgical leaching of lead (Pb) present in desulfated lead-acid battery slurries using aqueous solutions of sodium chloride (NaCl) as a leaching agent. The experiments conducted showed that the efficiency of the process is related to three critical operating parameters: NaCl concentration, solid/liquid ratio (S/L) and operating temperature.

The optimal condition was identified with 5 mol· $L^{-1}$ of NaCl, S/L ratio of 2/200 and temperature of 60 °C, resulting in a maximum recovery of 32.3 % of Pb in 6 hours, without the use of aggressive acids. From these observations, it can be seen that leaching with NaCl achieves a favorable balance between efficiency, operational safety and environmental compatibility. The superior performance under moderate conditions reveals that the process is strongly kinetically controlled, with limitations associated with the formation of stable complexes and the precipitation of secondary phases at excessive concentrations and temperatures.

In addition, the study highlights that higher solid/liquid ratios compromise metal recovery, reinforcing the need for fine-tuning the ratio between reactant mass and solution volume to avoid local saturation and promote effective diffusion of leaching ions. Likewise, thermal optimization proved to be fundamental, and temperatures above 60 °C did not represent additional benefits, and could even inhibit extraction due to the formation of passivating species.

From a practical point of view, the results obtained support the viability of NaCl as a leachant in smaller-scale lead recycling systems, with potential for implementation in urban, modular or decentralized plants, meeting the principles of circular economy and sustainable management of hazardous waste.

As future perspectives, it is recommended the investigation of complementary strategies for the recovery of metallic Pb, such as selective electro-obtainment, controlled precipitation or cementation, as well as the analysis of the reusability of the leachant and evaluation of the waste generated. The consolidation of hydrometallurgical routes based on NaCl can represent a relevant technical-environmental advance compared to conventional methods, contributing to a safer, cleaner and more efficient battery recycling chain.

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## REFERENCES

Chen A, Lin C, Wu C, Hong A (2014). Risk assessment and heavy metal accumulation in vegetables grown on Pb/Zn mine tailing soil in the vicinity of Dabaoshan, South China. Human and Ecological Risk Assessment, 20(6), 1510–1521.

Dutrizac JE (1992). The leaching of lead sulphate in chloride media. Hydrometallurgy, 29(1–3), 1–20.

Ellis TW, Mirza AH (2010). The refining of secondary lead for use in advanced lead-acid batteries. Journal of Power Sources, 195(15), 4525–4529.

Espinosa DCR, Bernardes AM, Tenório JAS (2004). An overview on the current processes for the recycling of batteries. Journal of Power Sources, 135(1–2), 311–319.

Ferracin LC, Testoni G, Tenório JAS, Espinosa DCR (2002). Obtenção de chumbo metálico a partir de baterias chumbo-ácido exauridas utilizando via hidrometalúrgica. Revista Escola de Minas, 55(2), 101–106.

Li G, Zhang W, Zhang X, Tang J, Xie H, Zhang L (2012). Effects of thermal pretreatment on $PbSO_4$ phase transformation and Pb leaching behavior in sulfuric acid solution. Journal of Power Sources, 214, 223–228.

Liu Y, Zhu D, Lu C, Li M, Tian S, Liu J (2018). Recovery of lead from lead paste in spent lead–acid battery by hydrometallurgical process. Journal of Cleaner Production, 202, 650–657.

Margallo M, Ziegler-Rodriguez K, Vázquez-Rowe I, Irabien A, Aldaco R (2019). Enhancing waste battery management in the context of a circular economy. Science of the Total Environment, 653, 1200–1209.

Nowińska K, Adamczyk A (2023). Recovery of valuable metals from spent batteries using pyrometallurgical and hydrometallurgical methods: a review. Minerals, 13(1), 75.

Pan Y, Wang L, Huang Y, Tan Q, Li J (2013). Leaching behavior and dissolution mechanism of lead from $PbO_2$ in hydrochloric acid solution. Hydrometallurgy, 139, 38–44.

Pan Y, Zhang Y, Wang L, Tan Q, Li J (2019). Hydrometallurgical recovery of valuable metals from spent lead-acid batteries: a review. Journal of Cleaner Production, 228, 1140–1153.

Prengaman RD (1995). Development of new technologies for the recycling of lead. Journal of Power Sources, 57(1–2), 27–33.

Rao S, Liu ZQ, Wang DX, Cao HY, Zhu W, Zhang KF, Tao JZ (2021). Hydrometallurgical process for recovery of Zn, Pb, Ga and Ge from Zn refinery residues. Transactions of Nonferrous Metals Society of China, 31(2), 555–564.

Rand DAJ, Moseley PT, Garche J, Parker CD (1996). Valve-regulated lead–acid batteries. Elsevier.

Shu Y, Xie H, Zhang L, Li H, Yin S, Zhu F (2015). Enhanced leaching behavior of $PbO_2$ from spent lead paste in NaCl–HCl media. Hydrometallurgy, 155, 27–32.

Sun Y, Xie H, Zhang L, Yin S, Zhu F (2017). Advances in lead–acid battery recycling: a review. Journal of Power Sources, 341, 361–369.

Volpe M, Ferella F, De Michelis I, Vegliò F (2009). Treatment of lead paste from spent lead acid batteries: development of a new hydrometallurgical process. Hydrometallurgy, 98(1–2), 24–32.

Xia H, Zhang L, Xie H, Yin S, Zhu F (2017). Effects of temperature and acid concentration on the leaching behavior of PbO in HCl solutions. Journal of Power Sources, 341, 198–205.

Xie H, Zhang L, Li H, Koppala S, Yin S, Li S, Zhu F (2019). Efficient recycling of Pb from zinc leaching residues by using the hydrometallurgical method. Materials Research Express, 6(7), 075505.

Yang D, Xie H, Zhang L, Yin S, Zhu F (2014). Leaching behavior of $PbSO_4$ in HCl–NaCl system. Journal of Power Sources, 248, 135–140.

Yu X, Wang J, Wu C, Zhu M, Liu H (2019). Selective recovery of lead from leach liquor by cementation in hydrochloric acid system. Hydrometallurgy, 185, 52–58.

Zhang W, Xie H, Zhang L, Yin S, Zhu F (2010). Kinetics of leaching lead from spent lead paste in NaCl-HCl system. Journal of Power Sources, 195(9), 2550–2556.

Zhang Y, Tan Q, Wang L, Li J (2017). Review of waste battery recycling technologies: limitations and recent developments. Journal of Hazardous Materials, 339, 91–102.

# Utilization of Agricultural By-Products and Waste Biomass for Energy Purposes

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***keywords:*** *lignocellulosic biomass; anaerobic digestion; pelleting; energy valorization; biogas feedstock storage.*

## Introduction

Large amounts of lignocellulosic agricultural residues and processing by-products remain unutilized despite their significant energy potential. In the context of climate change mitigation and rising energy demand, their sustainable transformation into bioenergy carriers is highly relevant. This study investigates the energy valorization potential of various agricultural waste materials including wheat straw pellets, oat husk pellets, cow manure pellets, sunflower husk pellets, lupine cleaning waste, and sunflower cake. The research focuses on two technological approaches: direct anaerobic digestion and pelletization followed by combustion. Additionally, the study aims to identify solid, energy-dense materials that can be easily stored and serve as a strategic energy buffer for biogas plants during interruptions in the supply of primary feedstocks.

## Materials and methods

The biomass samples were pelletized using a granulator (G-200, 7.5 kW, 150 kg/h) to produce uniform, compacted material suitable for both storage and energy conversion. The process parameters, including die temperature and motor load, were recorded. Physical and chemical characterization of each sample included dry matter content (EN ISO 18134-3:2015), volatile solids (BS EN 12879:2000), cellulose (Seifert method), and lignin (TAPPI T 222 om-06). Anaerobic digestion trials were conducted in batch bioreactors according to DIN 38414-8 and VDI 4630 standards to assess methane potential.

The quality of produced pellets was evaluated based on mechanical durability (PN-EN ISO 17831-1:2016-02), bulk density (PN-EN ISO 17828:2016-02), and size (PN-EN ISO 17829:2016-02). Higher heating value (HHV) was determined using a Leco AC600 calorimeter in accordance with PN-EN ISO 18125:2017-07. Energy inputs were monitored using a class S energy quality analyzer (MI 2883), enabling the estimation of net energy balance for both combustion and anaerobic digestion pathways.

## Results and discussion

Table 1 presents the cumulative methane and biogas yields of the tested pelletized substrates calculated on a fresh matter basis. Anaerobic digestion trials revealed considerable differences in methane yields among the materials, each of which was tested in triplicate under standardized conditions. The results demonstrate that agricultural by-products vary significantly in their biodegradability and bioenergy potential, which is essential for assessing their role as emergency or supplementary feedstocks in biogas plants..

***Table 1.****Cumulative methane and biogas yields of selected pelletized substrates based on fresh matter (FM)*

| **Substrate** | **Methane content [%]** | **Cumulative methane [m³/Mg FM]** | **Cumulative biogas [m³/Mg FM]** |
|---|---|---|---|
| **Wheat straw pellets** | 49.99 | 198.02 | 396.15 |
| **Oat husk pellets** | 49.36 | 235.60 | 477.35 |
| **Cow manure pellets** | 53.72 | 83.51 | 155.46 |
| **Sunflower husk pellets** | 52.33 | 105.11 | 200.86 |
| **Lupine cleaning waste** | 50.06 | 251.48 | 502.40 |

| | | | |
|---|---|---|---|
| **Sunflower cake** | 57.06 | 318.99 | 559.04 |

Among the samples, sunflower cake produced the highest cumulative methane volume (318.99 $m^3$/Mg FM), followed by lupine cleaning waste (251.48 $m^3$/Mg FM) and oat husk pellets (235.60 $m^3$/Mg FM). In contrast, cow manure pellets exhibited the lowest performance (83.51 $m^3$/Mg FM), indicating limited biogas potential despite relatively high organic content. These findings highlight the relevance of feedstock selection in ensuring process efficiency and energy output, especially in scenarios of disrupted primary substrate supply.

To ensure flexibility and continuity in biogas production, a strategy based on the pelletization of agricultural and waste biomass was proposed. Pelletized substrates can be stored for extended periods without significant quality loss and utilized when the supply of primary feedstocks is disrupted. This concept is illustrated in Figure 1.

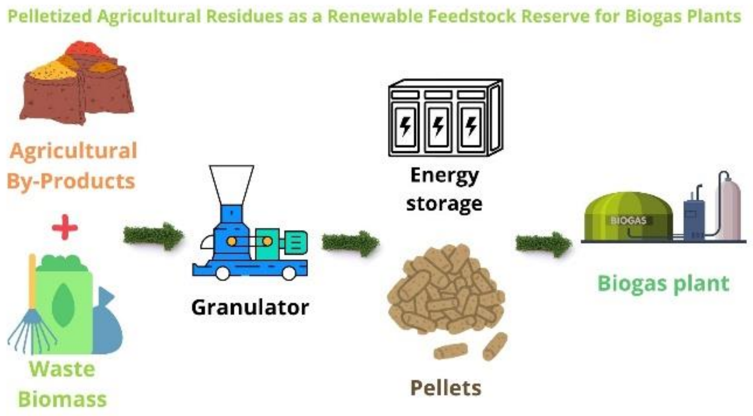

***Figure 1.*** *Conceptual scheme of biomass pelletization as a method of energy storage for biogas plants.*

## Conclusions

The study confirms that pelletized agricultural residues can serve as viable substrates for anaerobic digestion and bioenergy production. Among the tested materials, sunflower cake and lupine cleaning waste demonstrated the highest methane yields, indicating their strong potential as supplementary energy sources in biogas plants. The results also highlight the importance of substrate selection in optimizing biogas output, particularly during interruptions in the supply of primary feedstocks. Additionally, the pelletized form offers advantages in terms of storage, handling, and transport, making these materials strategically valuable for ensuring continuity and flexibility in biogas production systems.

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## References

1. Hendriks, A.T.W.M.; Zeeman, G. Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresour. Technol. 2009, 100, 10–18. https://doi.org/10.1016/j.biortech.2008.05.027
2. Witaszek, K.; Pilarski, K.; Niedbała, G.; Pilarska, A.A.; Herkowiak, M. Energy Efficiency of Comminution and Extrusion of Maize Substrates Subjected to Methane Fermentation. Energies 2020, 13, 1887. https://doi.org/10.3390/en13081887
3. VDI 4630. Fermentation of Organic Materials – Characterisation of the Substrate, Sampling, Collection of Material Data, Fermentation Tests. Verein Deutscher Ingenieure, Düsseldorf, Germany, 2006.
4. Kaparaju, P.; Serrano, M.; Thomsen, A.B.; Kongjan, P.; Angelidaki, I. Bioethanol, biohydrogen and biogas production from wheat straw in a biorefinery concept. Bioresour. Technol. 2009, 100, 2562–2568. https://doi.org/10.1016/j.biortech.2008.11.011

# The influence of substrate extrusion process on the energy and economic efficiency of biogas plant exploitation.

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***keywords:*** *biomass; extrusion; anaerobic digestion; energy efficiency.*

## Introduction

The agricultural sector currently underutilises organic waste in the form of so-called lignocellulosic biomass, which can include maize straw, rapeseed straw, leaves and hay (Panigrahi and Dubey, 2019). In recent years, technologies to manage these wastes have been increasingly developed. As an example, they can be used in agricultural biogas plants, where heat or electricity can be produced. By carrying out a methane fermentation process, it is possible to dispose of biodegradable substances that are a burden on the ecosystem. The full utilisation of these raw materials as a substrate for biogas production is only possible after pretreatment, which allows the lignocellulosic structures to be broken down. This has the effect of increasing the efficiency of biogas production, including methane (Tong et al. 1990; Kozlowski et al. 2018; Dach et al. 2014). One of the pre-treatment methods is extrusion. Extrusion is a HTST (High Temperature Short Time) type of process due to the fact that the material in the extruder stays in it from several seconds to several minutes and is exposed to high temperature. During this time, the material inside is mixed, compacted, compressed, sheared, liquefied and plasticized in the final zone (Oniszczuk et al., 2012). Specific processing conditions contribute to the disintegration of lignin, facilitating access to cellulose and hemicellulose for bacteria (Oniszczuk and Pilawka, 2013). The high pressure and temperature during extrusion contribute to the hydrolysis of lipids, proteins, carbohydrates, hemicellulose, cellulose and the disruption of the cell wall, thanks to which the material becomes plastic.

Agricultural biomass with an increased content of ligni-cellulose compounds is not normally used in biogas plants due to decomposition problems (straw has a structure that is difficult to access for fermentation bacteria). However, their use can bring a significant effect by increasing the energy efficiency and profitability of biogas plants. The methane fermentation process is highly dependent on conditions, availability and type of substrate. Depending on the raw materials used, the gas mixture resulting as a final product can have different contents of methane, carbon dioxide and other components. It is possible to use agricultural by-products such as cereal straw, corn and cotton waste, plant stalks, animal residues (manure, slurry, poultry manure, litter) and others (Gregersen and Raven 2007; Kalina and Skorek 2002; Lantza et al. 2007; Rasi et al. 2007). The production of methane in the anaerobic digestion process is a proven technology, but it is characterized by low profitability. Biogas installations without financial initiative in the form of green and yellow certificates or fixed feed-in tariffs for the sale of electricity and heat would not be cost-effective and could not compete with conventional fuels such as coal or natural gas. There are a lot of factors causing this state of affairs, e.g., the high costs of substrates for biogas production, a limited supply of local raw materials, and limited availability of innovations that would make biogas energy production cost-effective (Witaszek et al. 2020). Lignocellulose found in plant raw materials is a polymer consisting of three main fractions: cellulose (40-55% DM), hemicellulose (24-40% DM) and lignin (18-25% DM). Because they belong to long-chain polysaccharides that are hydrolysed to a mixture of pentoses and hexoses, they can be used as a substrate for biogas production (Tan et al. 2008). As research has shown (Rodiahwati and Sriariyanun, 2016), the use of the extrusion process in the preparation of raw materials for anaerobic digesion may be justified. Several factors influence the extrusion process: the degree of comminution of the raw materials, the speed of the extruder screw, the plasticising system used, the use of a suitable extruder (single-screw, twin-screw), the appropriate level of wetting of the raw material and the process temperature. An important parameter affecting the extrusion process is the degree of fineness of the substrates, which affects their more effective mixing and obtaining a homogeneous mixture (e.g. for chopped rye straw the lengths are assumed to be: 1-3 mm, 8-11 mm, 10-15 mm and 20-40 mm) (Kupryaniuk et al. 2020). The processing of the raw material, regardless of its structure, is only possible through the use of optimal wetting. A difference in the moisture content of the raw material of even 1% can increase the energy intensity of the process by up to 100%. In this case, additional pressure-thermal treatment of the lignocellulosic pulp may not be economically justified.

The aim of the work was to investigate the impact of extrusion of two types of straw (cereal and rapeseed) on increasing the efficiency of methane production and the energy and economic efficiency of the operation of a biogas plant with a capacity of 0.5 MW.

## Materials and methods

In the study, 2 types of extruded substrates were used to feed the biogas plant: cereal straw and rapeseed straw. Both types of straw were shredded using a CF420B flail shredder (Pavolt, Zrębice, Poland) to particle sizes below 10mm and then extruded using a TS-45 single-screw extruder (Z.M.Ch Metalchem, Gliwice, Poland), and then all substrates were tested for methane yield according to standard methodologies (DIN 38414/S8 and VDI 4630) (Dach et al. 2014) and contrasted with tests on straw without pretreatment. Biogas yield testing was conducted under standard methane fermentation conditions in sets of 3 tank biofermenters (Czekała 2017). The 2 dm3 fermentation reactors were first filled with inoculum (a dose of microorganisms from a working biogas plant) and raw materials processed under different conditions. The organic dry matter content of the inoculum varied from 1.5 to 2%. Dry matter and organic dry matter were checked before testing and the substrates were placed in an airtight digestion reactor. The reactors were placed in temperature-controlled water (approximately 39°C), which simulated the actual operating conditions of commercial biogas plants. The volume and qualitative composition of the gases produced were measured every 24 hours. The fermentation process was stopped when the daily biogas production was less than 1% of the total biogas production. Samples were tested in triplicate. Biogas yield (m3 Mg$^{-1}$) was expressed in terms of fresh matter, dry matter and dry organic matter, as described by Dach et al. (2014).

In the calculation of the efficiency of the biogas plant operation, two variants of biogas plant power supply were tested:

1. Variant 1: cereal straw + pig slurry and extruded cereal straw + pig slurry;
2. Variant 2: rapeseed straw + pig slurry and extruded rapeseed straw + pig slurry.

Energetic and economic calculations were carried out according to a standard methodology, based on market prices in Poland in May 2024 and taking into account the additional amount of electricity used during the extrusion of both types of straw.

## Results and discussion

The results of anaerobic digestion tests and preliminary energetic and economic analysis are presented in Table 1.

***Table 1.*** *Methane efficiency of the tested substrates and preliminary energetic and economic analysis for variants I and II*

| **Substrate** | **D.M.** | **Methane efficiency** | **Substrate use** | **Electric energy spent for extrussion** | **Electric energy to use** | **Substrate cost (straw)** | **Revenue from electricity sold** |
|---|---|---|---|---|---|---|---|
| **Variant I** | **%** | **$m^3 \cdot Mg^{-1}$** | **Mg/a** | **MWh** | **MWh** | **EUR** | **EUR** |
| Wheat straw | 88.51 | 197.18 | 5150 | 0 | 3854.50 | 301.678 | 879.450 |
| Wheat straw after extrusion | 91.96 | 213.72 | 4750 | 1220.75 | 2632.69 | 278.246 | 600.680 |
| **Variant II** | | | | | | | |
| Rapeseed straw | 90.70 | 205.07 | 4950 | 0 | 3853.14 | 289.962 | 879.141 |
| Rapeseed straw after extrusion | 90.62 | 228.79 | 4440 | 888.00 | 2967.84 | 260.087 | 677.148 |

In both variants, an increase in methane production from straw was observed, but this increase was relatively small (8.4% in the case of wheat straw and 11.6% in rapeseed straw). The increase in the efficiency of methane production from the same amount of straw resulted in a decrease in the mass necessary to power a biogas plant with a capacity of 0.5 MW, from 5150 to 4759 Mg/year in the case of wheat straw and from 4950 to 4400 Mg in the case of rapeseed straw, respectively. In this case, there are savings due to the smaller amount of straw needed, at the level of 23.4 kEUR in variant I and 29.9 kEUR in variant II.

However, during further calculations, it must be taken into account that the extrusion process requires additional electricity, which increases the cost of this technology. Therefore, taking into account the cost of electricity necessary for the extrusion process, it should be concluded that in both variant I and variant II, the revenue from the sale of electricity from a biogas plant powered by straw is higher in the variant without extrusion, respectively 278.7 kEUR in the case of wheat straw and 202 kEUR in the case of case of rapeseed straw.

## Conclusions

The research presented above confirms that it is possible to process lignocellulosic materials using a TS-45 single-screw extruder. On the basis of the research carried out, it was observed that the application of the extrusion technique to lignocellulosic raw materials had a differential effect on the properties of potential substrates for biogas plants. The extrusion process increases the efficiency of $CH_4$ production during anaerobic digestion of lignocellulosic substrates such as various types of straw. However, various parameters of the extrusion process influence the increase in productivity. Problems have been observed due to the dosage of raw material. In the studies discussed, the increase in $CH_4$ production was so low (8.4% in the case of cereal straw and 11.6% in rapeseed straw) that it did not cover the increase in electricity consumption resulting from the operation of the extruder. As a consequence, the use of the extrusion process in the analyzed variants of biogas plants gave a negative economic result. Therefore, it should be concluded that further research is necessary on the optimization of the extrusion process in order to increase the efficiency of $CH_4$ production from straw with reduced energy demand. It would be desirable to extend the scope to include further publicly available raw materials. A second direction for extending the research is the selection of appropriate process variables (temperature, extruder screw speed, raw material moisture content), as well as the selection of a suitable screw for the extruder. The next step could be the use of advanced technologies such as heat recovery systems (recuperators) or efficient cooling systems. The use of modern process monitoring technologies is crucial for their ability to provide precise control over the course of the esctrusion process. They enable the key parameters of the process to be monitored in real time, identify potential problems and respond quickly to any irregularities. As a result, they will contribute to the efficiency, quality and profitability of the process.

## References

1. Panigrahi, S.; Dubey, B.K. A critical review on operating parameters and strategies to improve the biogas yield from anaerobic digestion of organic fraction of municipal solid waste. *Renew. Energy* 2019, *143*, 779–797.
2. Tong M., Smith LH., McCarty PL. 1990. Methane fermentation of selected lignocellulosic materials. Biomass, 21: 239-255.
3. Kozłowski K., Dach J., Lewicki A., Cieślik M., Czekała W., Janczak D., Brzoski M. 2018. Laboratory simulation of an agricultural biogas plant start-up. Chem. Eng. Technol., 41(4): 711-716. https://doi.org/10.1002/ceat.201700390
4. Dach J., Czekała W., Boniecki P., Lewicki A., Piechota T. 2014. Specialised internet tool for biogas plant modelling and marked analysing. Adv. Mater. Res., 909, 305–310. https://doi.org/10.4028/www.scientific.net/AMR.909.305.
5. Gregersen K.H., Raven R.P.J.M. 2007. Biogas plants in Denmark: successes and setback. Renew. Sust. Energ. Rev., 11, 116-132. https://doi.org/10.1016/j.rser.2004.12.002
6. Kalina J., Skorek J. 2002: Paliwa gazowe dla układów kogeneracyjnych; Seminarium cykliczne „Elektroenergetyka w procesie przemian” - Generacja rozproszona, Politechnika Śląska, 11-26.

7. Lantza M., Svenssonb M., Bjornssonb L., Borjessona P. 2007. The prospects for an expansion of biogas systems in Sweden-Incentives, barriers and potentials. Energy Policy, 35, 1830-1843.
8. Rasi S., Veijanen A., Rintala J. 2007. Trace compounds of biogas from different biogas production plants. Energy, 32, 1375-1380.
9. Witaszek K., Pilarski K., Niedbała G., Pilarska A. A., Herkowiak M. Energy Efficiency of Comminution and Extrusion of Maize Substrates Subjected to Methane Fermentation. *Energies*. 2020; 13(8):1887. https://doi.org/10.3390/en13081887
10. Oniszczuk T., Wójtowicz A., Mitrus M., Mościcki L., Combrzyński M., Rejak A., Gładyszewska B. 2012. Influence of process conditions and fillers addition on extrusion-cooking efficiency and SME of thermoplastic potato starch. TEKA Commission of Motorization and Energetics in Agriculture, 12(1), 181-184.
11. Oniszczuk T., Pilawka R. 2013. Wpływ dodatku włókien celulozowych na wytrzymałość termiczną skrobi termoplastycznej. Przemysł Chemiczny, 2, 265-269.
12. Rodiahwati W., Sriariyanun M. 2016. Lignocellulosic biomass to biofuel production: integration of chemical and extrusion (screw press) pretreatment. KMUTNB Int. J. Appl. Sci. Technol., 9, 289-298. https://doi.org/10.14416/j. ijast.2016.11.001
13. Czekała W. 2017. Concept of in oil project based on bioconversion of by products from food processing industry. J. Ecol. Eng., 18, 180–185. https://doi.org/10.12911/22998993/76211.

# Spray Mode and Precursor Molarity as Key Parameters in Solution Spray Pyrolysis of Oxygen Electrodes for Low Temperature Reversible Solid Oxide Cells (SOCs)

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## ABSTRACT

Reversible Solid Oxide Cells (rSOCs) are considered to play a major role in the future energy sector as they offer both high energy efficiency and storage capacity by operating in both fuel cell (SOFC) and electrolysis (SOEC) modes. In SOFC mode, they convert even conventional fuels directly into electricity while in SOEC mode, they use electricity to produce hydrogen or syngas. Challenges however, remain that include high costs mainly due to material requirements, fabrication and reliability. Lowering operating temperatures (from 750–950°C to 500–750°C) is generally considered an advantage due to the relaxation of material selection requirements but it comes with the drawback of lowering overpotentials at the oxygen electrode. This necessitates the adoption of cost efficient fabrication methods for nanostructured oxygen electrodes. The technique of Solution Spray Pyrolysis constitutes a film deposition method in which the required soluble precursors are supplied at atomic level from a solution and deposited on a suitable substrate to form the required ceramic film. Film properties are suitably tailored by tuning the process parameters involved during the spraying of the solution as well as the substrate properties. The process offers low cost and potential for upscale for coating surfaces of any shape including the potential for nanostructured porous or dense thin films. Perovskites consisting of Strontium substituted lanthanum manganites (LSM) or ferrites (LSF) have been traditionally used as oxygen electrodes in these cells due to their enhanced electrocatalytic behavior under oxygen atmospheres and in contact with either Yttria Stabilized Zirconia (YSZ) or Gadolinia stabilized Ceria (CGO) electrolytes respectively. The latter combination has been proved more suitable for the lower temperature range so in this investigation, we examine the potential of the technique to yield suitable LSF films on CGO dense electrolytes using an air pressurized nozzle for reduced cost.

Keywords: spray pyrolysis; solid oxide cells; low temperature; cathode.

## 1. INTRODUCTION

Reversible Solid Oxide Cells (rSOCs) offer efficient energy conversion and storage by operating in both fuel cell (SOFC) and electrolysis (SOEC) modes. In SOFC mode, they convert a variety of conventional fuels or hydrogen into electricity while in SOEC mode, they use electricity from renewable sources to produce hydrogen or syngas. This dual functionality makes them ideal for sustainable energy systems, but challenges remain, including high costs emanating to a large extent from material limitations and reliability (Kopras et al., 2024).

Lowering operating temperatures (from 750–950°C to 500–750°C) could relax material selection requirements, but there exist the drawback of increasing overpotential especially at the oxygen electrode. This necessitates the need for nanostructured electrodes and ultra-thin electrolytes. Such structures are preferably obtained by molecular deposition methods (i.e. with precursors starting at atomic and/or molecular) instead of conventional particulate methods. This bottom up approach allows for control and optimization of the final film properties by suitably tuning the physicochemical and process parameters of the fabrication method.

Towards this end, the technique of Solution Spray Pyrolysis offers the advantages of simplicity and ease of upscaling of a low-cost molecular deposition method based on an air-pressurized nozzle that sprays a suitable composition of atomic precursors on a hot substrate surface that can be of any design and size (Krestou et al., 2021). Ceramic films of any composition stoichiometry can be obtained by adjusting accurately the cation atomic ratios at the solution level. Thus, final ceramic film properties can be controlled through tuning of the physicochemical properties of the starting solution and substrate, deposition temperature and profile and the process parameters operating during deposition. Despite the large number of these factors (that include air and solution flowrate, air pressure, nozzle to substrate distance and deposition time) experimental optimization can be done easily in order to identify a suitable parameter set for each desirable film morphology. Thin films of thicknesses of the order of 1 μm are easily obtainable in either porous or dense morphology. An additional step is usually required, that of post deposition sintering in order to obtain the suitable crystal structure. This step can be also done in situ to a certain extent (depending on the type of the heating plate used) and constitutes a crucial parameter for the final film. Combination operating protocols regarding spraying modes (such as continuous or on-off with intermediate in situ sintering) can be applied in order to check the effect on final morphology. Generally, however, the sintering temperatures required for obtaining the final crystal structure are much lower than conventional sintering temperatures of particulate based ceramic films as the precursor particles formed during deposition are more active just after solvent evaporation. It should be also pointed out, that these post deposition steps of precipitation, thermolysis (or calcination) and sintering can all be integrated into a single process, offering significant reductions in fabrication costs.

Oxygen electrodes, on the other hand, constitute the rate limiting polarization step for rSOCs. They are demanded to function in both oxidizing and reducing conditions, requiring materials with high electrocatalytic activity, mixed (i.e. electronic and ionic) conductivity, adequate porosity, thermal and mechanical stability, and TEC compatibility with other cell components (Kopras et al., 2024). Polarization resistances in oxygen electrodes increase further as the operation temperature is decreased to <500°C which necessitates the use of special fabrication methods for assuring the necessary micro- or nanostructures that possess the optimal electrochemical performance. Perovskites with the general formula $ABO_3$ with the A site occupied by a large cation (such as La) and the B site with a smaller transition metal ion (such as Mn or Fe) have been proved ideal substitutes for the expensive Pt used in the past. Moreover, they have allowed great flexibility in terms of crystal structures by substituting the A- site with alkaline earth metal ions (such as Sr) and adopting different cation distributions. At the same time the extent of electronic and ionic conductivity is controlled by the formation of different types and localization of O defects within the crystal structure. Typically, in as cubic perovskite structure, the A cations are distributed randomly on A-sites, rendering a random distribution of O defects on the O sublattice, and a three-dimensional vacancy network $O^{2-}$ diffusion. At >750°C, the most traditional oxygen electrode material in rSOC cells is Sr-doped $LaMnO_3$ (LSM). It shows high electronic conductivity and excellent Thermal Expansion Coefficient (TEC) compatibility in contact with the most commonly used electrolyte material, Yttria Stabilized Zirconia (YSZ). It also offers good chemical stability and catalytic activity.

For lower temperature applications (i.e. <700°C), perovskites with Co and Fe at the B-site have been proved a better choice, particularly in contact with ceria-10% gadolinia or 20% gadolinia (CGO10 or CGO20) electrolyte allowing for mixed electronic and ionic conductivity and extension of the electrochemical reaction zone from the Triple Phase Boundary to a two-phase boundary (also known as gas electrode). Thus, compositions of $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) have been tried and shown excellent promise for lower temperature applications (Jiang, 2019). In fact, this material showed promised even with a YSZ electrolyte when a protective thin barrier layer of CGO was inserted between the LSCF cathode and the YSZ electrolyte. In another application, LSCF formed as nanoparticles deposited on a Scandia Stabilized Zirconia (ScSZ) also showed excellent performance between 600 and 750°C demonstrating that, in this design, common problems such as Sr segregation, electrode degradation, and long-term stability are significantly improved (Zhang, 2016). Generally, nanostructured components seem to yield significant improvements in performance and this demonstrate the need for adopting and studying specialized electrode fabrication processes. Thus, nanostructured LSCF–CGO20 electrodes fabricated conventionally and decorated with CGO20 nanoparticles by an infiltrating aqueous solution, have exhibited excellent performance and stability in SOEC mode of operation as both anodic and cathodic electrodes (Guan, 2018). Substituting La with Ba in the A-site (BSCF) results in a higher oxygen vacancy concentrations and thus an enhanced activity for the

Oxygen Reduction Reaction (ORR) of the electrode. This, however, comes with a compromising crystal structure stability which is quite detrimental below 900°C, resulting in the formation of different crystal phases. Clematis et al., (2019), however, has shown that mixing BSCF and LSCF improves electrocatalytic activity while maintaining stability even at several different mixing volume rations. Their results indicate that cation inter-diffusion occurs after sintering and causes the observed enhancement in both activity and stability.

Generally, LSCF electrodes are superior to LSM under electrolysis conditions in terms of electrocatalytic activity and structural stability. As shown, Sr surface segregation is less intense under electrolysis operation mode than in a SOFC mode. Removing the environmentally toxic Co from the structure towards LSF compounds ameliorates the high TEC coefficients encountered with Co as well as the Sr surface segregation issues which are more intense in LSCF electrodes. This comes, however, with a conductivity penalty as well as somehow higher polarization resistances in LSF electrodes due to differing crystal structures and conduction mechanisms between the two materials (Jiang, 2019, Huang et al., 2004).

The prospect of the spray pyrolysis technique to produce nanostructured cathodic films has been shown recently by dos Santos-G´omez et al. (2016,2021) on a porous electrolyte scaffold. Catalytic nanoparticles have also been applied on LSCF scaffolds leading to superior performances with a CGO20 electrolyte at 700°C (Hong et al., 2017).

In the present study, we continue our previous effort (Ziazias et al., 2023) and investigate Co-free LSF ($La_{0.5}Sr_{0.5}FeO_3$) thin films on dense CGO10 pellets using the technique of Solution Spray Pyrolysis (SSP) and aqueous solutions. Variables such as deposition temperature, time, precursor concentration (0.1 M and 0.025 M), and spray mode (continuous vs. interrupted) were examined for their effects on film morphology, structure, and adhesion, and compared to films made in other studies using organic solvents.

## 2. MATERIALS AND METHODS

Aqueous solutions of La, Sr and Fe with a total ion concentrations of 0.1M and 0.025M where prepared by mixing the appropriate amount of their soluble nitrate salts in deionized water. The cation ratio in the resulting precursor solutions was La:Sr:Fe = 1:1:2. Dense ceramic pellets of CGO were prepared by uniaxially by pressing a certain amount of CGO powder in a hydraulic press at 187 MPa that was subsequently sintered at 1500°C for 8 hours. Actual density of the weighted pellets was estimated geometrically and compared with the theoretical density from XRD. It was found that pellets had attained 92-99% of their theoretical density.

The Solution Spray Pyrolysis (SSP) method (Figure 1) was then applied to spray the precursor solution on the CGO substrate at temperatures in the range 103 to 114°C (± 4) °C. Solution and air were mixed at 2.5bar (air flowrate 18.36 L/min) in a spray nozzle, which produced a spray with 10-100 μm diameter droplets. After continuous spraying at various time intervals (15min, 30min, 45min, 60min) at a solution flowrate of 50 ml/h and at a nozzle-substrate distance of 36 cm, the films were sintered in situ for 1h and then were placed in a high temperature tubular furnace at 700 °C for 4hr with heating – cooling rates of 3 °C /min, to be further sintered. The procedure was repeated under interrupting mode of spraying (i.e. 1min spray ON/1min spray OFF) for a total spraying time of 45min and 60min, under the same pressure and temperature conditions. All samples were characterized by X-Ray diffraction and SEM-EDS.

## 3. RESULTS AND DISCUSSION

Table 1 shows a list of the prepared films that were fabricated along with the respective deposition temperatures and times, spraying and sintering modes and total ion precursor concentrations. Figure 2 shows XRD results taken for the film LSF4. In the Figure the standard PDF file for the composition $La_{0.6}Sr_{0.4}FeO_3$ is designated which indicates an hexagonal perovskite structure (i.e. rhombohedral) dominates with space group R-3cH and unit cell parameters of a= 5.52780 Å, c=13.43680 Å. The peak is somehow broadened indicating a small crystallite size but also the existence of multiple lines at lower angles that are consistent with the existence of small amounts of orthorhombic phase (Dann et al., 1994). Nevertheless, the pattern differences between atomic La/Sr ratios of 6/4 and 5/5 would be negligible particularly under air but according Dann et al. (1994) the 5/5 composition tends to always exist in mixtures

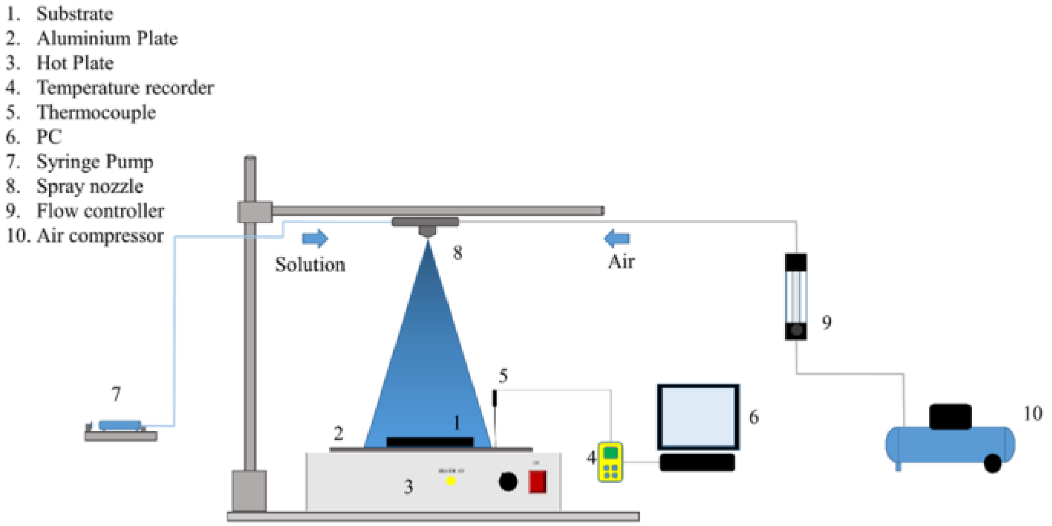

***Figure 1.*** *Spray Pyrolysis set up.*

***Table 1.*** *Experimental conditions*

| **Sample** | **Film (Total precursor ion concentrations, M)** | **Substrate** | **Spraying mode** | **Sintering scheme*** | **$T_{dep}$ (°C)** |
|---|---|---|---|---|---|
| **LSF1** | 0.1 | CGO10 | 15min | A | 103±4 |
| **LSF2** | 0.1 | CGO10 | 30min | A | 107±4 |
| **LSF3** | 0.1 | CGO10 | 45min | A | 114±2 |
| **LSF4** | 0.1 | CGO10 | 60min | A | 114±3 |
| **LSF3 - on/off** | 0.1 | CGO10 | 1 min spray on -1 min spray off (total spray on: 45min) | B | 124±10 |
| **LSF4-on/off** | 0.1 | CGO10 | 1 min spray on -1 min spray off (total spray on: 60min) | B | 130±13 |
| **LSF5** | 0.025 | CGO10 | 15min | A | 103±2 |
| **LSF6** | 0.025 | CGO10 | 30min | A | 103±2 |
| **LSF7** | 0.025 | CGO10 | 45min | A | 106±2 |
| **LSF8** | 0.025 | CGO10 | 60min | A | 104±2 |
| **LSF7 - on/off** | 0.025 | CGO10 | 1 min spray on -1 min spray off (total spray on: 45min) | B | 125±12 |
| **LSF8-on/off** | 0.025 | CGO10 | 1 min spray on -1 min spray off (total spray on: 60min) | B | 128±13 |

*A: Intermediate sintering of first deposit layer in situ for 1h followed by additional sintering at 700°C for 4h.
*B: In situ intermittent sintering step performed between two spray intervals (on/off) followed by scheme A.

of rhombohedral and orthorhombic phases and this is supported by the existence of multiplets in our peak for 2θ between 32-33°. This indicates that the final film composition is quite close to the nominal solution atomic ratios. These peaks were evident at lesser intensities at diffractograms taken on films after 45 min of deposition which actually points to the minimum deposition time required to obtain a detectable crystallized film under these conditions.

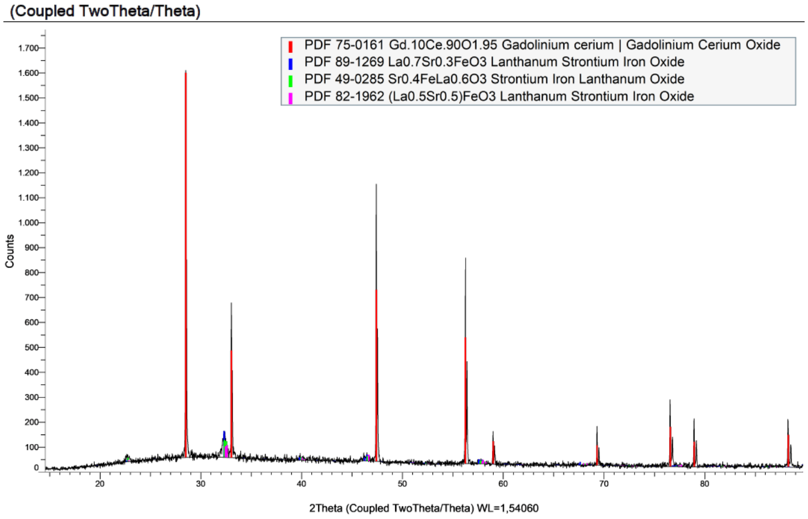

***Figure 2.*** *Diffraction pattern of film LSF4 (see Table 1)*

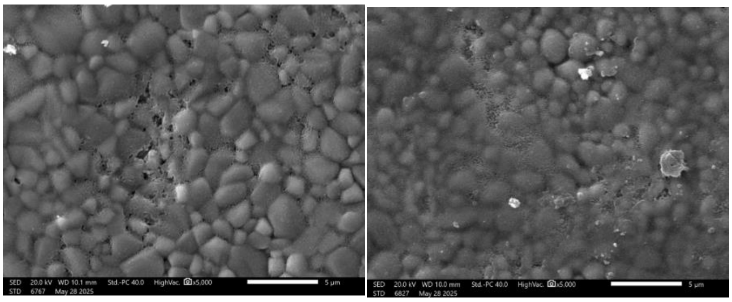

**Figure 3.** SEM surface features of films LSF2 (left) and LSF3(on/off) (see Table 1)

The existence of nanocrystallites was indicated by the surface SEM pictures taken at relatively high magnification where blurred coherent film is shown above the CGO10 substrate. Generally, a somehow more coherent film was obtained under the on/off rather than the continuous spraying mode. These nano-coatings were evident at deposition times ≥ 30 min while at 15 min no discernible films were observed. These features are shown in Figure 3 for deposition times of 30 and 45 min at both spraying modes. Map EDS (not shown) also verified a full coverage of LSF films onto the CGO10 surface. In fact, other authors (Paiva et al., 2020) have also verified that LSF films crystallize even above 450°C reporting a grain size of about 200 nm (crystallite size from XRD 17 nm) and actual density of 5.946 g/cm$^3$ (theoretical 6.234 g/cm$^3$) which is consistent with our XRD estimated range of theoretical densities of 5.870- 6.129 g/cm$^3$ (for Sr content stoichiometries of 0.3 to 0.5). Notice also, that according to the above authors, partial solubilization of crystalline phases starts taking place above 600°C which is consistent with our data here as no traces of the orthorhombic $Sr_2Fe_2O_5$ phase are evident. These nanocrystallized films were of the order of less than 0.5 µm as verified by cross-section EDS at the longest deposition times (i.e. 45 and 60 min) (Figure 4).

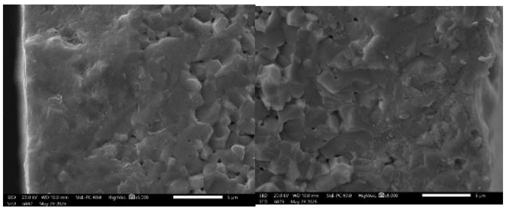

**Figure 4.** SEM cross sections of films LSF3 (left) and LSF4(on/off) (see Table 1)

## 4. CONCLUSIONS

Films of $La_{0.5}Sr_{0.5}FeO_3$ were fabricated on Ceria Gadolinia (CGO10) dense pellet substrates by means of conventional Solution Spray Pyrolysis. These films could be applied as efficient oxygen electrodes in Reversible Solid Oxide Cells. The resulting coatings were found to be most probably nanocrystalline after post-deposition sintering at 700°C for 4 hours as shown by SEM surface features with accompanied EDS mapping. Crystal structure was found to consist most probably of a mixture of rhombohedral and orthorhombic phases. These features conduce to an efficient oxygen electrode in which nanocrystalline features and low sintering temperatures are highly desirable for reduced polarization resistances and low fabrication cost. Future work will focus on technique optimization and electrochemical testing.

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## REFERENCES

Clematis, D., Barbucci, A., Presto, S., Viviani, M., Carpanese, M.P., 2019. Electrocatalytic activity of perovskite-based cathodes for solid oxide fuel cells. *International Journal of Hydrogen Energy*, 44,6212-6222.

Dann, S.E., Currie, D.B., Weller, M.T., Thomas, M.F., and Al-Rawwas, A.D., 1994. The Effect of Oxygen Stoichiometry on Phase Relations and Structure in the System $La_{1-x}Sr_xFeO_{3-\delta}$ ($0 \le x \le 1$, $0 \le \delta \le 0.5$). *Journal of Solid State Chemistry*, 109, 134-144.

dos Santos-Gomez, L., Porras-Vazquez, J.M., Martín, F., Ramos-Barrado, J.R., Losilla, E.R., Marrero-Lopez, D., 2016. *Journal of Power Sources* 319, 48-55.

dos Santos-Gomez, L., Zamudio-García, J., Porras-Vazquez, J.M., Losilla, E.R., Marrero-Lopez, D., 2021. Recent progress in nanostructured electrodes for solid oxide fuel cells deposited by spray pyrolysis. *Journal of Power Sources* 507, 230277.

Euzébio Paiva, J.A., Cajas Daza, P.C., Amaral Rodrigues, F., Ortiz-Mosquera, J.F., Moreira da Silva, C.R., Montero Muñoz, M., Muñoz Meneses, R.A., 2020. Synthesis and electrical properties of strontium-doped lanthanum ferrite with perovskite-type structure. *Ceramics International,* 46, 18419–18427.

Guan, F., Zhang, X., Song, Y., Zhou, Y., Wang, G., Bao, X., 2018. Effect of $Gd_{0.2}Ce_{0.8}O_{1.9}$ nanoparticles on the oxygen evolution reaction of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ anode in solid oxide electrolysis cell. *Chinese Journal of Catalysis* 39,1484–1492.

Hong, T., Lee, S., Ohodnicki, P., Brinkman, K., 2017. A highly scalable spray coating technique for electrode infiltration: Barium carbonate infiltrated $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite structured electrocatalyst with demonstrated long term durability. *International Journal of Hydrogen Energy*, 42, 24978-24988.

Huang, Y., Vohs, J.M. and Gorte, 2004. Fabrication of Sr-Doped $LaFeO_3$ YSZ Composite Cathodes. *Journal of The Electrochemical Society*, 151(4), A646-A651.

Jiang, S.P., 2019. Development of lanthanum strontium cobalt ferrite perovskite electrodes of solid oxide fuel cells-A review. *International Journal of Hydrogen Energy*, 44,7448-7493.

Kopras, P., Tsanaktsidis, C., Kiratzis, N., 2024. Advanced ceramic materials for electrolytes and electrodes in reversible solid oxide cells. *Academia Green Energy,* 1, 1-34.

Krestou, A., Barmpatsis, A., Tsanaktsidis, C., Matsouka, Ch., Nalbandian L., and Kiratzis, N., 2021. Fabrication and Characterization of Functional Ceramic Films By Solution Spray Pyrolysis: Correlations with the Thermal Decomposition Characteristics of the Constituent Salts. *ECS Transactions*, 103 (1) 123-138.

Zhang, S.-L., Yu, H.-X., Li, C.-X., Lai, S.Y., Li, C.-J., Yang, G-J., Sun, H.-B., Wei T. and Liu M., 2016. Thermally sprayed high-performance porous metal-supported solid oxide fuel cells with nanostructured $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ cathodes. *J. Mater. Chem. A*, 4,7461-7468.

Ziazias, C., Matsouka, Ch., Tsanaktsidis, C., and Kiratzis, N., 2023. Fabrication of Ceramic Composite Films for Solid Oxide Electrochemical Cells (SOEC) by Solution Spray Pyrolysis(SSP). *2nd International Conference on Sustainable Chemical and Environmental Engineering* 14– 18 June, Limassol, Cyprus.

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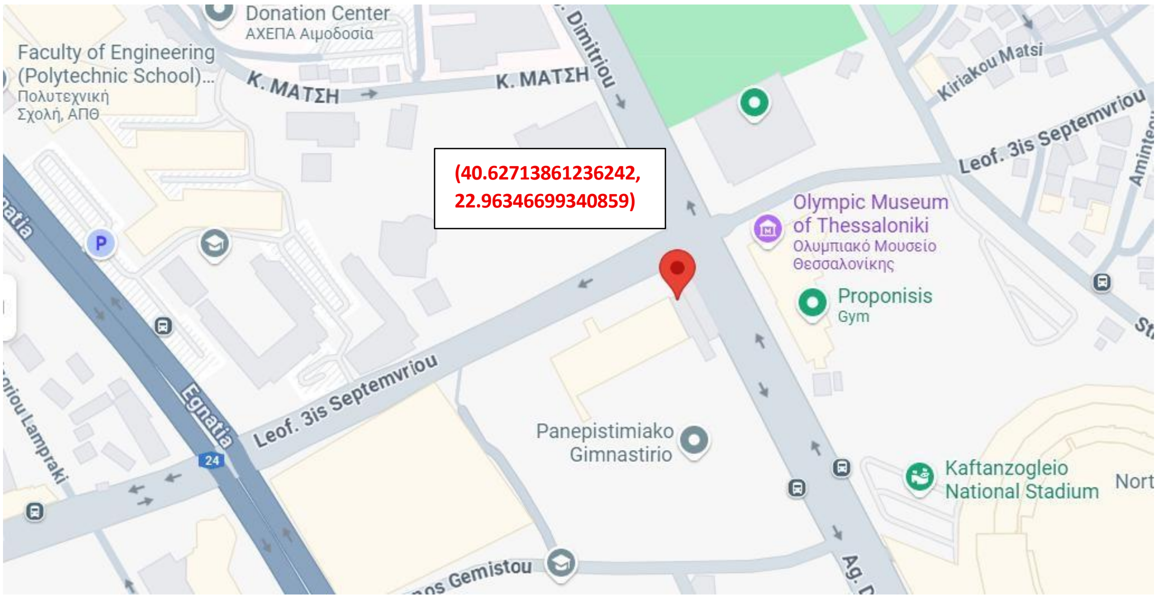

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