detritus | Multidisciplinary Journal for Waste Resources & Residues

Research to Industry and Industry to Research

PYROLYSIS OF ORGANIC INDUSTRIAL SEWAGE SLUDGES: OPPORTUNITIES AND CHALLENGES

Alberto Pivato [1]*, Maria Cristina Lavagnolo [1], Claudia Mensi [2], Giovanni Beggio [1], Sergio Basso Ricci [3], Huanghu Peng [4] , Maja Arsic [5], Cathryn A. O'Sullivan [5], Diogenes L. Antille [5], Anton P. Wasson [5], Rebecca E. Haling [5], Giorgia Lombardelli [6], Daniele Di Bona [6], Federico Viganò [7], Stefano Consonni [7] and Andrea Schievano [8]

[1] Department of Civil, Environmental and Architectural Engineering, University of Padova, Via Marzolo 9, 35131 Padova, Italy
[2] Laboratory Manager, A2A Life Company (IT)
[3] Agrimeccanica Srl (IT)
[4] Huzhou University and Zhejiang ECO Environmental Solution Co. Ltd., China
[5] CSIRO Agriculture and Food, St. Lucia, Queensland, Australia
[6] LEAP Scarl - Laboratorio Energia e Ambiente Piacenza, Piacenza, Italy
[7] Department of Energy, Politecnico di Milano, Milan, Italy
[8] Department of Environmental Science and Policy (ESP), University of Milan, Italy

The industrial sector is responsible for an annual production of approximately 400 million Mg (wet basis) of pulp and paper mill sludge, and up to 125 million Mg of biosolids (Mohajerani et al. 2017; Berendes et al. 2018; Turner et al. 2022). In 2020, the European Union (EU) produced approximately 11 million Mg of industrial effluent sludge, of which about 20% was classified as hazardous waste (Eurostat, 2022).

Industrial sludges can be divided into two sub-categories; namely: (i) organic sludge with high carbon (C) content, such as sludges from the food industry, paper manufacturing industry, plants, petrochemical industry and municipal wastewater treatment plants (e.g., where wastewater treatment plants receive sludge from domestic and industrial origin); and (ii) inorganic sludge, mainly from steelworks, metallurgy, and galvanic processes.

The focus of the present column is on industrial organic sludges, which are mainly disposed of through landfill without prior recovery of energy, carbon or nutrients. Options available for the treatment of organic sludge include: (i) physical-thermal treatment (drying); (ii) biological treatments (anaerobic digestion and composting); (iii) low-temperature thermal treatments (hydrothermal carbonisation and liquefaction), and (iv) high-temperature thermal treatments (pyrolysis, gasification, and combustion). Following appropriate treatment, and where regulations allow to do so, industrial organic sludges can also be applied to land as soil amendments (Paz-Ferreiro, et al. 2018). Other than incineration, a range of technical solutions have been explored to recover energy and nutrients from these organic waste streams, but they tend to be limited to specific conditions or are at the pilot or laboratory scale (Wang et al. 2008). Land application of organic sludges is less expensive compared to other disposal options and it allows closing the carbon and nutrient cycles, but it does not eliminate risks such as soil contamination (e.g., heavy metals, microplastics, pathogens) and transfer of potentially toxic elements to the food chain, and soil emissions of greenhouse gasses following application. Whilst recycling to agricultural land brings about opportunities to improve soil carbon and fertility, it misses opportunities for energy recovery and higher-value product applications.

Research and industry sectors need to work together to devise strategies that enable implementation of management practices for improved recovery of carbon, nutrients and energy from organic sludges. Successful implementation of such practices will improve both socio-economic and environmental outcomes needed to meet the Sustainable Development Goals (SDGs) by 2030 (e.g., SDG 2 Zero Hunger, SDG 7 Affordable and Clean Energy, SDG 12 Responsible Consumption and Production, SDG 13 Climate Action, SDG 15 Life on Land). This is, therefore, necessary to increase current levels of resource recovery. This may be achieved by speeding up the transition from linear to circular economy and bioeconomy while being able to observe, and where needed modify, existing legislation and policy (e.g., the EU Green Deal, 2020).

Among the emerging technologies, pyrolysis is regarded as a promising option that could play a relevant role in future management strategies. Pyrolysis is increasingly considered for the treatment of sludges as it offers opportunities for: (i) the recovery of energy, (ii) the treatment of emerging contaminants (e.g., PFAS), and (iii) the production of biochar, which can be used as a soil amendment to improve soil fertility and carbon sequestration through Pyrogenic Carbon Capture and Storage (PyCCS) (Paz-Fer-

Managing editor:
Alberto Pivato
email: alberto.pivato@unipd.it

Detritus / Volume 22 - 2023 / pages IV-VII
https://doi.org/10.31025/2611-4135/2023.17249

reiro et al. 2018; Werner et al. 2022) or as biochar-functionalized materials in other sectors. The risk of heavy metal contamination in soils and their potential transfer to the food chain may also be reduced following conversion to biochar, which makes it safer for land application (Marchuk et al., 2021).

Experts from the academic and industrial sectors convened to discuss the state-of-the-art knowledge and application of pyrolysis to industrial sewage sludge in a Special Workshop during the 9th International Symposium on Energy from Biomass and Waste, held in Venice (Italy) between the 21st and 23rd November 2022.

TABLE 1: SWOT analysis of the application of pyrolysis to industrial sewage sludges

Strengths (characteristics of the technologies that give it an advantage over others)	**Weaknesses (characteristics that place technology at a disadvantage relative to others)**
• Pyrolysis is attractive for its relative simplicity and suitability for operation at small and medium scales, which are more aligned with the distributed nature of biomass resources, or with the size of industrial plants that may require decentralized processes. • With proper tuning of operating conditions, pyrolytic processes can be oriented towards production favouring the char or oil yield over gas. • Pyrolysis products may have a higher energy content than the raw material pyrolyzed (endothermic reaction). • By-products such as bio-oil and syngas can be captured and used as bioenergy, and/or the waste heat can be used to dry sludge prior to pyrolysis, increasing process efficiency. • Possible production of high value-added chemicals (when biochar and bio-oil are not used for energy purposes). Other technologies (e.g., gasification or combustion) have only one product (e.g., syngas or heat). • Emerging contaminants such as PFOS and PFOA in biosolids can be drastically reduced in pyrolysis (Kundu et al., 2021). • When a contaminant is more likely to end up in a specific product (gas, oil or char), pyrolysis concentrates that contaminant in that product (e.g., chromium (Cr) in char). When contaminants are concentrated in syngas, the concentration of the species is higher and the syngas volume is lower (than gasification or combustion, where O_2 is added): the removal of such species can be done more easily. • Due to the zero supply of oxygen, pyrolysis is carried out under strongly reducing conditions, producing only reduced chemical species: some reduced species may be less harmful than the corresponding fully oxidized forms (this is the case of Cr, which mostly ends up in the char as Cr III, instead of being oxidized to Cr VI). Typically, neither dioxins nor furans are produced and, if initially present, they decompose thermally into less harmful species. • Working in absence of air, the flow rates of flue gas generated by the pyrolytic process are significantly smaller than those generated by engineered composting of sewage sludge (which operates under aerobic conditions with an excess of air). • The technology is flexible and can be integrated into different energy systems, and potentially used to co-treat a range of organic waste streams. • Pyrolysis can contribute to achieving carbon neutrality through PyCCS. Biochar can represent a carbon sink (e.g., when used in soil, building materials, and asphalt). In fact, the storage of carbon is successful in the long term, i.e., it is not released into the air as CO_2. Therefore, in the case of biogenic feedstock, it is removed from the atmosphere, achieving a "negative emission" (Werner et al., 2022). • In some countries and regions, pyrolysis has better public perception and social license to operate than incineration and landfilling (Hušek et al., 2022).	• Process setup is complex (e.g., compared to biological treatment or combustion). • Little known technology: pyrolysis could be subjected to further technological development. • By-products such as bio-oil, syngas and biochar are strongly dependent on feedstock characteristics and operating conditions (temperature, residence time), affecting their performance. Operating conditions need to be co-designed with end-users in mind and potential trade-offs assessed via a cost-benefit analysis (e.g., if a stable, high C biochar for agricultural users is the main material, the production of a viable amount of syngas or bio-oil may be affected). • When the raw material contains contaminants, all products can be contaminated: Pyro-oil (and to a greater extent char), if contaminated, can become hazardous waste, which requires special care for disposal. Like all solids, char involves management/handling difficulties. • Contaminant species can reach high concentrations in the syngas, making management difficult. • Contaminated feedstocks can produce contaminated products and by-products. For example, heavy metals are concentrated in the char. • The need for specific treatment of gasses/liquids increases the complexity and cost of the plant as well as operating costs. • The oil may have characteristics that make it difficult to manage: e.g., unstable and time-varying chemical and physical properties; very high viscosity or non-Newtonian behaviour, with residue. deposition. • The technology is not well developed for sewage sludge in comparison to other technologies (anaerobic digestion, combustion, etc.). • The energy balance of the process is very dependent on feedstock characteristics. Very often it is not well known and "magic" numbers are sometimes proposed without proper scrutiny. • The operating conditions of high-temperature processes, such as pyrolysis, usually pose safety issues while low-thermal processes, such as hydrothermal carbonisation and liquefaction, do not present these problems. • Pyrolytic processes may involve the presence of streams at high temperatures, posing flammable, explosive, and toxic substances risks (e.g., syngas with oil vapours). • Sealing problems to avoid air/gas leaks, which can lead to explosions; while the need for zero O_2 import (to avoid process instability and to obtain the desired product) could be difficult to guarantee. • Pyrolysis is an endothermic process that typically needs an external supply of heat. The use of by-product energy is often not enough to sustain the process. • The required heat transfer (to heat up the feedstock) can be problematic and poses relevant challenges in the upscaling of the process.
Opportunities (elements in the environment that the technology could exploit to its advantage)	**Threats (elements in the environment that could cause trouble for the technology)**
• The application of industrial sludge in agriculture is limited by transport costs, on-farm logistics and increasing regulation concerning chemical concentration limits; while direct landfill disposal is increasingly becoming unsustainable. • The biochar market has been developing in recent years and is likely to continue growing as interest in the application of biochar for carbon sequestration through PyCCS increases. • Disposing of sludges represents a cost for the company. Pyrolysing sludges can produce residues that have high value (e.g., biochar); technologies which can both treat sludges and obtain value-added products should be preferred. • The potential of new materials or residues as a catalyst in the pyrolysis process could enhance energy recovery. • Organic Rankine Cycle (ORC) is a state-of-the-art technology that allows for the efficient conversion of waste heat from pyrolysis into electricity.	• The stringent regulations on gas emissions could limit technology adoption. • Depending on feedstock characteristics and operating conditions, products and by-products can contain hazardous properties, possibly leading to their classification as hazardous wastes. • There is a move towards regulating untreated or minimally treated sludges, especially in terms of agricultural or land-based applications, particularly due to emerging contaminants of concern (e.g., PFAS, microplastics, pharmaceutical products). The regulation of biochar-based products appears to be less developed, and it is likely that guidelines will be developed to anticipate and address these risks both during pyrolysis and in the subsequent by-products. • Policies regulating the implementation of thermal treatment processes (including pyrolysis) vary between and within countries. A lack of harmonization between waste, energy and emerging circular (bio)economy policies can limit the adoption of pyrolysis. • The capital costs of pyrolysis facilities with associated sludge dewatering and flue gas treatment can present barriers in some countries.

The most relevant considerations from this expert meeting were synthesized in the form of a qualitative Strengths, Weaknesses, Opportunities, and Threats (SWOT) analysis (Table 1) where the process of pyrolysis was analyzed and compared to the cited alternatives. The expert group agreed that pyrolysis represents a promising solution for the treatment of sludges.

Examples of commercial, successful implementation of pyrolysis at full industrial scale are the following projects conducted in China:

- A 7200 Mg (wet basis) per year pyrolysis project undertaken in 2014 in Jilin Province to treat industrial sewage sludge from the petrochemical industry. The sludge had an oil content of approximately 5% (w/w), which reduced to less than 0.3% after thermal treatment allowing the remaining residue to be used in the construction industry (Figure 1).
- A sludge pyrolysis disposal project in Shengli Oilfield, Shandong Province undertaken in 2019. The sludge used in this project had oil contents between 12% and 15% (w/w), and it was treated by chemical hot washing, thermal pyrolysis and desorption technologies at a rate of 80000 Mg (wet basis) per year (Figure 2).
- A 15000 Mg (wet basis) per year chemical sludge pyrolysis project together with another 10000 Mg year industrial waste salt pyrolysis project conducted at the Shaoxing Hazardous Waste Center (2022) in Zhejiang Province. The rotary indirect heating pyrolysis technology used in these projects can reduce the organic content of the residue to less than 5% (w/w) allowing the entry criteria for non-hazardous landfills to be met (Figure 3).

The expert group also anticipated that future expansion and adoption of pyrolysis may face the following challenges:

- There is currently limited knowledge of the energy efficiency of pyrolysis technology in terms of specific technical configurations associated with feedstock chemical composition, physical characteristics (moisture content, particle size, ash content) and heating value of the treated industrial sewage sludge.
- The increasing market demand and market value of pyrolysis by-products, particularly for biochar. There is an increasing body of scientific literature supporting the efficacy of biochar as a soil amendment and potentially to achieve soil carbon sequestration through PyCCS (Joseph et al. 2021). The potential for biochar and other organic industrial by-product materials to support soil carbon and soil fertility has also been acknowledged by the updated regulations on fertilizers under the EU Circular Economy Action Plan (EU Regulation 2019/1009). However, the effectiveness of biochar-based fertilizers or amendments depends on a range of factors ranging from feedstock characterisation, pyrolysis conditions and the receiving soil-crop system. Therefore, a combination of engineering, agronomic and soil science research is needed to co-design the product from feedstock characterisation through to the pyrolytic process and to potentially blend the biochar with other materials or recycled products to create a viable agricultural product. For biochars that are unable to be used in agricultural systems, the pyrolytic process should be designed to exploit feedstock characteristics to produce "biochar-functionalized materials", which may be used as substitutes for concrete materials, alternative adsorbents, catalysts and electrodes constituents for energy storage tools.

In conclusion, pyrolysis technologies present major opportunities to meet Sustainable Development Goals across the energy-waste-carbon content nexus. While the identified techno-economic weaknesses (e.g., safety, cost-effectiveness and process efficiencies) and emerging socio-political threats (e.g., regulation, capital costs) present challenges for technology adoption, these can be addressed by developing strong partnerships between the research and industry sectors to develop co-designed, targeted solutions with multiple value-added product streams.

FIGURE 1: Jilin Petrochemical, Jilin Province, China (2014). Capacity: 7200 Mg per year (wet basis) industrial sewage sludge.

FIGURE 2: Shengli Oil-field, Shandong Province, China (2019). Capacity: 80000 Mg per year (wet basis) of oil sludge.

FIGURE 3: Shaoxing Hazardous Waste Center, Zhejiang Province, China (2022). Capacity: 15000 Mg per year (wet basis) of chemical sludge.

REFERENCES

Berendes, D. M., Yang, P. J., Lai, A., Hu, D., Brown, J., 2018. Estimation of global recoverable human and animal faecal biomass. Nature Sustainability, 1, 679-685. https://doi.org/10.1038/s41893-018-0167-0.

Eurostat, 2022. Generation of waste by waste category, hazardousness and NACE Rev. 2 activity. Industrial effluent sludges. https://ec.europa.eu/eurostat/databrowser/view/ENV_WASGEN__custom_4304319/default/table?lang=en. Accessed 2022-12-23.

Hušek, M., Moško, J., Pohořelý, M., 2022. Sewage sludge treatment methods and P-recovery possibilities: Current state-of-the-art. Journal of Environmental Management, 315, Article number: 115090. https://doi.org/10.1016/j.jenvman.2022.115090.

Joseph, S., Cowie, A.L., Van Zwieten, L., Bolan, N., Budai, A., Buss, W., Cayuela, M.L., Graber, E.R., Ippolito, J.A., Kuzyakov, Y., Luo, Y., 2021. How biochar works, and when it doesn't: A review of mechanisms controlling soil and plant responses to biochar. GCB Bioenergy, 13(11): 1731-1764. https://doi.org/10.1111/gcbb.12885.

Kundu, S., Patel, S., Halder, P., Patel, T., Hedayati Marzbali, M., Pramanik, B.K., Paz-Ferreiro, J., De Figueiredo, C.C., Bergmann, D., Surapaneni, A., Megharaj, M., Shah, K., 2021. Removal of PFASs from biosolids using a semi-pilot scale pyrolysis reactor and the application of biosolids derived biochar for the removal of PFASs from contaminated water. Environmental Science: Water Research & Technology, 7(3): 638–649. https://doi.org/10.1039/D0EW00763C.

Marchuk, S., Antille, D.L., Sinha, P., Tuomi, S., Harris, P.W., McCabe, B.K., 2021. An investigation into the mobility of heavy metals in soils amended with biosolids-derived biochar. ASABE Paper No.: 2100103. St. Joseph, MI.: 2021 ASABE Annual International Meeting, American Society of Agricultural and Biological Engineers. https://doi.org/10.13031/aim.202100103.

Mohajerani, A., Lound, S., Liassos, G., Kurmus, H., Ukwatta, A., Nazari, M., 2017. Physical, mechanical and chemical properties of biosolids and raw brown coal fly ash, and their combination for road structural fill applications. Journal of Cleaner Production, 166: 1-11. https://doi.org/10.1016/j.jclepro.2017.07.250.

Paz-Ferreiro, J., Nieto, A., Mendez, A., Askeland, M.P.J., Gasco, G., 2018. Biochar from biosolids pyrolysis: A review. International Journal of Environmental Research and Public Health, 15(5): 956. https://doi.org/10.3390/ijerph15050956.

Turner, T., Wheeler, R., Oliver, I.W., 2022. Evaluating land application of pulp and paper mill sludge: A review. Journal of Environmental Management, 317, Article number: 115439. https://doi.org/10.1016/j.jenvman.2022.115439.

Wang, H. L., Browin, S. L., Magesan, G. N., Slade, A. H., Quintern, M., Clinton, P. W., Payn, T. W., 2008. Technological options for the management of biosolids. Environmental Science and Pollution Research, 15(4): 308-317. https://doi.org/10.1007/s11356-008-0012-5.

Werner, C., Lucht, W., Gerten, D. and Kammann, C., 2022. Potential of land-neutral negative emissions through biochar sequestration. Earth's Future, 10(7), p.e2021EF002583.