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Ph.D. Thesis

"BIOLOGICAL LEACHING: A SUSTAINABLE SOLUTION FOR CONSTRUCTION AND DEMOLITION WASTE"

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to Chiara and my family

Abstract

The construction sector is notoriously associated with serious environmental impacts, mainly due to the generation of construction waste. This construction and demolition waste (CDW) includes a wide range of materials, including inert and hazardous waste, often resulting from construction, renovation and demolition activities. This category also includes debris produced by natural disasters such as earthquakes and floods. Despite the relevance of such wastes, ambiguity currently exists in their definition, revealing differences in waste management philosophies between regions. The composition and volume of CDWs are subject to variations based on numerous factors, both internal, such as the age of buildings and the technologies used, and external, such as population growth and regional regulations. This thesis mainly focused on cement waste, particularly those potentially contaminated with asbestos, due to their dangerous effects on human health. The research has highlighted biological bioleaching treatments through the action of volatile fatty acids (VFAs) produced in dark fermentation (DF) processes capable of effectively degrading this class of waste. These treatments have also been further applied to the treatment of cement waste not contaminated by asbestos, showing a promising ecological way for the management of CDW.

Introduction

The construction industry is widely acknowledged as a significant contributor to environmental degradation and is associated with the generation of construction waste. Generally, CDW encompass a mixture of various materials, including inert waste, non-hazardous non-inert waste, and hazardous waste as asbestos, resulting from construction, renovation, demolition activities, and even natural disasters like earthquakes, floods, hurricanes, and tsunamis (*Silva et al., 2017; Villoria Sáez et al., 2018; Wang et al., 2019; Zhang et al., 2020*). Currently, there exists a lack of consensus concerning the definition of CDW, reflecting differing waste management philosophies and priorities. The quantity and composition of CDW exhibit regional variations influenced by factors such as population growth, legislative measures, regional planning, and the construction industry's practices within a given country. These variations are shaped by internal factors like the age, type, construction materials, and construction technologies used, as well as external factors such as demolition techniques, the capabilities of construction firms in managing CDW, and population growth trends.

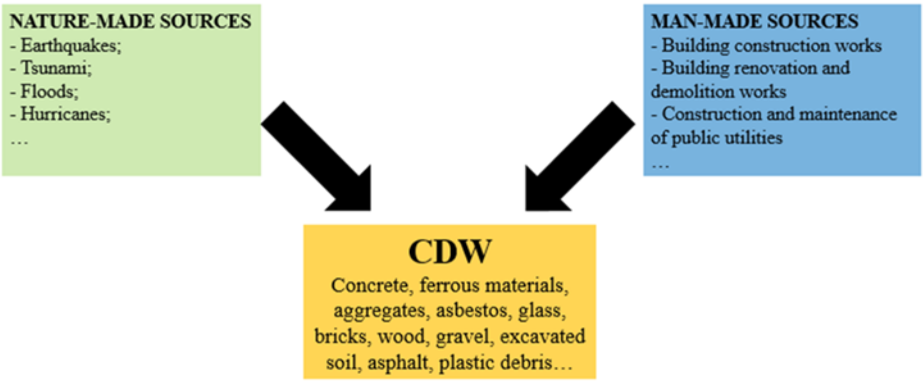

Figure 1. *Classification of CDW according to the source of origin*

In addition to legal frameworks, effectively managing CDW necessitates an initial step: estimating CDW generation. The most recent available data indicates that approximately 275 million tons of CDW (excluding soils) were generated in the European Union (EU) in 2020.

This total comprises 247 million tons of inert waste, 24 million tons of non-inert waste, and 3 million tons of hazardous waste (*Eurostat., 2020*). This estimation encompasses various waste streams, including W061 (ferrous metals), W062 (non-ferrous metals), W063 (mixed ferrous and non-ferrous metals), W071 (glass), W074 (plastic), W075 (wood), W077 (waste containing PCBs), and W12B (other mineral waste containing asbestos) from NACE F, as well as W121 (mineral waste from construction and demolition) across all NACE activities. Detailed data on CDW, categorized by waste type, for several European countries is presented in Table 1.

	W061	**W062**	**W063**	**W071**	**W074**	**W075**	**W077**	**W12B**	**W121**
	ferrous metals	non-ferrous metals	mixed ferrous and non-ferrous metals	glass	plastic	wood	waste containing PCBs	Mineral wastes containing asbestos	Mineral wastes
Austria	83	9	0	3	5	110	0	41	9160
Belgium	132	6	33	77	37	616	3	173	16560
Czech R.	78	1	1	2	4	13	0	27	2888
Denmark	249	24	71	15	7	123	11	159	3177
Finland	42	7	65	0	13	380	1	35	1041
France	1043	138	1725	237	586	1615	0	1	59962
Germany	6566	453	187	269	100	3056	3	482	74870
Hungary	40	2	1	1	4	2	0	13	2685
Italy	3621	397	152	72	28	184	0	336	34018
Netherlands	841	193	126	52	27	1377	0	387	19225
Norway	0	0	127	9	12	273	3	0	1911
Poland	183	3	7	1	17	43	0	554	4358
Romania	5	0	1	0	0	4	0	220	1050
Spain	19	16	19	0	6	59	0	331	7041
Sweden	50	10	270	1	1	250	0	26	1737
EU27	13253	1276	2702	773	871	7961	20	2833	244761

Table 1. *CDW by selected waste categories in EU countries, in 2020 ('000 tons).*

Globally, policies and regulations concerning CDW align with the widely recognized waste minimization hierarchy of 3Rs or 4Rs, which stands for reduce, reuse, recycle, and recover (*Monier et al., 2017; Huang et al., 2018*). In the European Union (EU), CDW management is guided by the EU Waste Framework Directive (2008/98/EC), which establishes a target of achieving a minimum recycling rate of 70% for non-hazardous CDW by 2020. Some EU member states have enacted specific legislation to further these goals. In line with various European countries, Italy's legal framework, as set out in D.Lgs. 278/2022, has adopted the European directive emphasizing waste management priorities. The directive prioritizes waste prevention, followed by recovery, and ultimately disposal. This legislation defines specific criteria under which inert waste from construction and demolition (and other mineral-based inert waste) can be reclassified. Once these wastes meet the set criteria, they are no longer considered waste and can be reintroduced into new civil engineering projects, fostering a cycle of reuse. In Germany, national laws governing CDW management mandate waste generators and owners to categorize, recycle, and reuse CDW. In Spain, national legislation outlines the responsibilities of all stakeholders involved in construction activities. In the United Kingdom, on-site waste reduction through sorting and recycling is mandatory. In Taiwan, construction sites have been subject to monitoring since 2005, and CDW waste must be transported to designated treatment facilities. Australia has implemented several CDW policies across different state governments, promoting on-site CDW reuse and sustainable building practices. In the United States, both federal and state highway contracts often specify the use of recycled materials in highway construction. Japan mandates the recycling of specific demolition materials, while Brazil requires the use of recycled aggregates in paving projects (*Menegaki et al., 2018*). In China, governmental policies are under development at the state level, and provincial regulations encourage the utilization of recycled building materials in foundational works, road bases, subgrades, and more. Similar laws and regulations are also in effect in Hong Kong (*Chen et al., 2017; Jin et al., 2017; Lai et al., 2016; Ogunmakinde et al., 2022; Park et al., 2017; Peduzzi et al., 2023; Rodrìguez et al., 2016*).

Among the different categories of CDW, one of the most worrying is that of ACW. The intersection between CDW in general and asbestos highlights the need for comprehensive waste management strategies that prioritize safety and environmental sustainability.

Asbestos represents a significant fraction of CDW (*Gherman et al., 2023*). The extensive historical utilization of asbestos has resulted in numerous structures and materials that still contain this hazardous substance. Asbestos denotes naturally occurring fibrous silicate minerals found in various forms. There are six primary asbestos minerals, categorized into two main mineral configurations: serpentine asbestos (chrysotile) and amphibole (actinolite, amosite, anthophyllite, crocidolite, and tremolite) *Fig. 2*. Serpentines, also known as white asbestos, possess the chemical formula $Mg_3(OH)_4(Si_2O_5)$ (*Mazzeo et al., 2018*). Comprising sheets of silicates (with both tetrahedral and octahedral sheets), this mineral constitutes the predominant commercially utilized form of asbestos, accounting for over 90% of global asbestos production (*Gualtieri et al., 2023*).

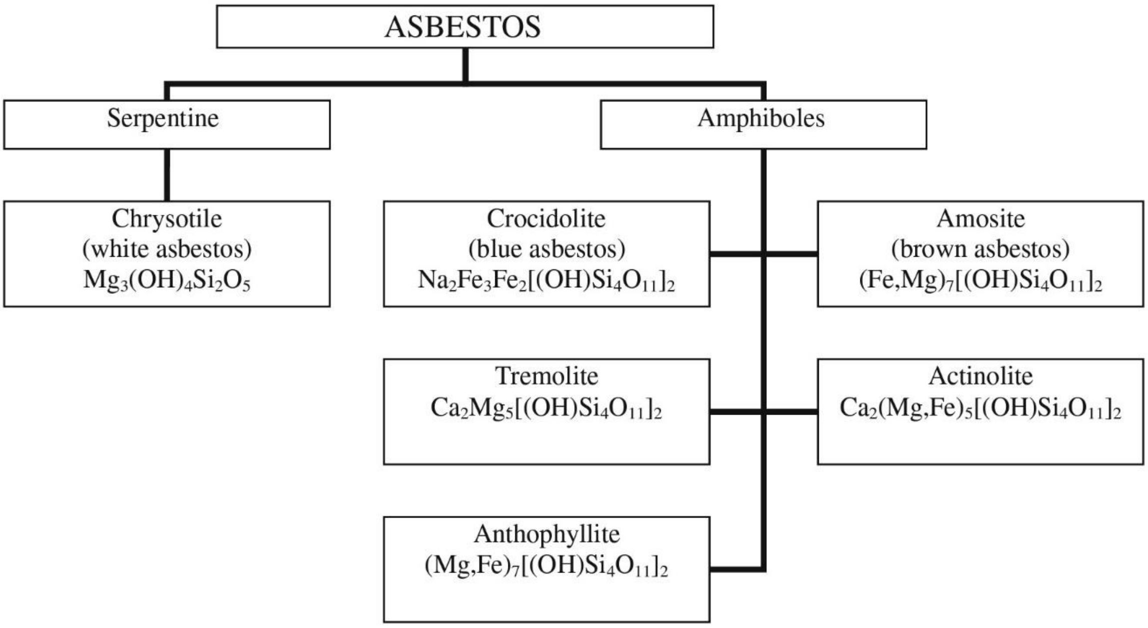

Figure 2. *Different types of asbestos (Kusiorowski et al., 2012)*

Each type of asbestos exhibits distinct physical characteristics. Chrysotile fibers, for instance, are exceedingly thin, flexible, and soft, making them suitable for weaving, while amphibole asbestos fibers are coarser and more brittle compared to chrysotile.

Asbestos has found widespread use, especially in construction and insulation materials, acoustic and thermal sprays, plasters, paints, flooring products, flat sheets, tiles, corrugated roofing sheets, rainwater and pressure pipes, and various other building materials. The asbestos content in these materials ranges from 5% by weight to over 10%, providing a cost-effective and easily workable substance for roof repairs, sealing around chimneys, dormer windows, skylights, scuppers, shingles, and nail holes (*Paolini et al., 2019*).

Figure 3. *Elements used for buildings containing asbestos: insulation, roofing and water tanks*

The International Agency for Research on Cancer has classified asbestos as a human carcinogen (*Paris et al., 2023*). Each year, more than 107,000 individuals succumb to asbestos-related diseases, including lung cancer, mesothelioma, and asbestosis, stemming from occupational exposure (*Furuya et al., 2018*).

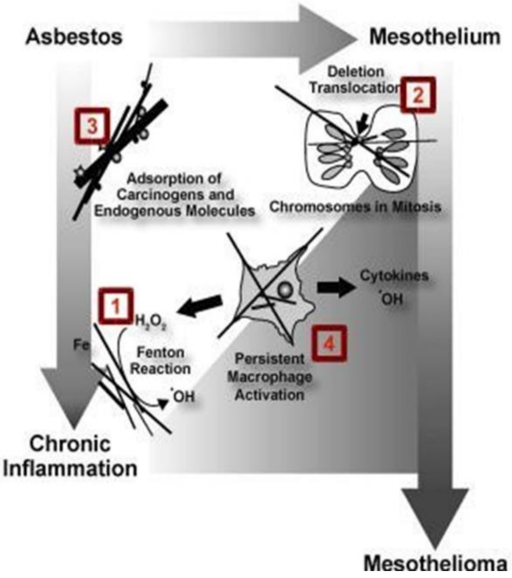

Figure 4. *Pathogenic mechanism caused by inhalation of asbestos fibers (Nagai et al., 2010)*

A significant hazard arises from the release of fibers from asbestos-containing products, as these fibers can enter the respiratory system, leading to asbestosis and carcinogenesis. The size of asbestos fibers is a critical factor, with the most hazardous fibers falling within the length range of 5–10 μm and diameters between 0 and 1 μm. Health issues attributed to asbestos have resurfaced as a societal concern, affecting not only industrial workers but also nearby residents of such industries (*Dodson et al., 2003*). To date, the focus on asbestos exposure prevention primarily targets the friable type of asbestos found in CDW, as over time, asbestos products can release asbestos fibers. Recognizing its detrimental health effects, efforts to safely dispose of asbestos-containing materials have become paramount. Research studies aimed at sustainable disposal methods are of utmost importance in mitigating the environmental and health risks associated with asbestos.

Developing safe and eco-friendly techniques for the removal, containment, and disposal of asbestos waste is not only a pressing concern for public health but also a crucial step toward creating a more sustainable future in the construction and demolition industry.

Cement waste containing asbestos presents significant challenges, prompting the need for effective and safe treatment methodologies. Among the main approaches are thermal, chemical, and mechanical processes. *Thermal treatments*, often referred to as high-temperature treatments, involve heating the asbestos-containing materials (ACMs) to temperatures where the asbestos fibers are altered structurally or fully destroyed, rendering them non-hazardous. This method is advantageous as it neutralizes the carcinogenic properties of asbestos. *Chemical treatments*, on the other hand, utilize various chemical solutions to break down the asbestos fibers. By changing the chemical composition of the asbestos, these processes ensure that the harmful effects of the mineral are mitigated. M*echanical treatments* involve physical methods to encapsulate or crush asbestos-containing materials. Techniques like grinding or encapsulation physically lock or alter the asbestos, preventing the release of hazardous fibers into the environment. While each method has its benefits, the choice of treatment often depends on the specific context, economic considerations, and the nature of the asbestos waste at hand (*Spasiano et al., 2017*).

Biological processes

Anaerobic biological processes play a pivotal role in waste treatment and energy production, primarily functioning in environments devoid of oxygen. These processes can be broadly categorized based on operational conditions and microbial communities involved (*Timofeeva et al., 2023*). The efficiency and effectiveness of anaerobic processes are influenced by several factors. *Temperature* plays a critical role; for instance, mesophilic bacteria operate best around 30-40°C, while thermophilic bacteria thrive at higher temperatures of 50-60°C. The *pH level* of the system is another determinant, with a near-neutral pH often being optimal for hydrogen (H_2) and methane (CH_4)-producing microorganisms. *Substrate concentration* and *hydraulic retention time* can affect the rate and extent of digestion. Additionally, toxic compounds, if present, can inhibit microbial activity. Properly managing these factors ensures the stability of anaerobic processes and maximizes their utility in various environmental applications (*Corsino et al., 2023; Odejobi et al., 2023*).

One of the primary types is the Anaerobic Digestion (AD), a multi-stage process involving hydrolysis, acidogenesis, acetogenesis, and methanogenesis, leading to the production of biogas CH_4-rich. Dark Fermentation (DF) is another significant process, primarily focusing on the conversion of organic substrates into bio-H_2 and volatile fatty acids (VFAs). Unlike AD, which produces CH_4, DF yields H_2 gas as the principal energy carrier (*Villanueva-Galindo et al., 2023*). In this thesis work, DF processes were applied by adopting different reactor configurations:

- The Anaerobic Sequential Batch Reactors (ASBR) function in batches, merging both ydigestion and settlement phases, which grants operational adaptability (*Nirmala et al., 2023*);
- The Anaerobic Moving Bed Biofilm Reactors (AnMBBR) deploy floating carriers to promote biofilm formation, ensuring an efficient microbial-substrate interaction (*He et al., 2023*).

The choice among these varied processes depends on multiple factors, including the nature of the waste, desired end-products, space constraints, and financial aspects. Collectively, these anaerobic processes play an integral role in organic waste degradation and sustainable energy production.

AD is a biological process conducted by anaerobic microorganisms, i.e. by a structured and balanced set of bacterial families that do not use oxygen as the final electron acceptor during the performance of their specific metabolic activities. Like all biological processes, it occurs spontaneously in specific natural ecosystems, and consists of the conversion of carbon present in organic substance into CH_4 and CO_2.

The anaerobic microorganisms operating this process carry out their metabolic activities by simultaneously carrying out two fundamental phases:

- substrate degradation: microorganisms feed on the substrate, degrading it over time;
- biomass growth: the microorganisms, feeding on the substrate, increase their number by duplicating their DNA and dividing by binary fission.

In a biological process it is possible to simultaneously observe a reduction in the substrate and an increase in cellular biomass over time. In the AD process, in particular, different metabolic reactions, operated by different microbial families, occur simultaneously in the same reaction environment, giving rise to a sequential structure due to the fact that some of the metabolism products of a generic microbial species constitute the substrates for the microbial species that carry out the next degradation step. The classic schematization, therefore, refers to the subsequent five stages of degradation of the organic substance, which is gradually converted into simpler organic compounds, by the different microbial families, until it forms a gaseous current consisting mainly of CH_4 and CO_2.

The disintegration phase of the complex organic substance takes place if the substrate is introduced in a suspended form inside the biological reactor. It consists in the transformation of suspended organic substance into dissolved organic substance through solubilization. Subsequently, the hydrolysis of the organic substance occurs, which is further simplified by means of enzymatic reactions depending on the quantity of microorganisms present in the reaction environment. At this point, the fermentative bacteria can assimilate the organic matter directly (assimilation through the cell membrane) or using a vast range of enzymes that are capable of secreting in an anaerobic environment. In this phase carbohydrates are degraded into simple sugars, proteins into amino acids and fats into fatty acids. The organic substrate is subsequently degraded by acidogenic bacteria, in a phase called acidogenesis phase, which allows the formation and accumulation of VFAs in solution. In the next phase, carried out by acetogenic bacteria, the same VFAs (e.g. butyric acid, $CH_3CH_2CH_2COOH$) are used and further converted into acetic acid (CH_3COOH) and H_2 following the following reaction:

$$CH_3CH_2CH_2COOH + 2\ H_2O \rightarrow 2\ CH_3COOH + 2\ H_2$$

The last phase of AD is called methanogenesis, as it is carried out by methanogenic bacteria, and consists of the final production of CH_4 by means of two different metabolic pathways:

- consumption of acetic acid, with consequent production of CH_4 and CO_2:

$$CH_3COOH \rightarrow CO_2 + CH_4$$

- consumption of H_2 and CO_2, resulting in the production of CH_4:

$$CO_2 + 4\ H_2 \rightarrow 2\ H_2O + CH_4$$

The AD process, despite being widely studied and widespread on a real scale, is very delicate as it is carried out through chemical-biological reactions that depend on each other; if one of them is not carried out adequately, the process does not reach completion.

The factors that influence these reactions are mainly:

- temperature conditions;
- pH;
- concentrations of substrates and products of metabolism.

Anaerobic microbial activity is possible over a wide temperature range. It is, in fact, possible to select different microbial families depending on the temperature range at which the process is carried out: psychrophilic (if temperatures are below 20°C), mesophilic (if temperatures are between 20°C and 40° C), thermophilic (if temperatures are above 40 °C). Some studies have shown that the most appropriate conditions in which to conduct the AD process, in terms of maximizing efficiency (substrate degraded compared to the biogas produced), are mesophilic conditions (*Sriram et al., 2017; Leca et al., 2023; Sambusiti et al., 2015*).

Implementing the process at higher temperatures allows the process to be operated with higher kinetics and, consequently, the process to be operated in shorter times and in reduced volumes. These advantages, however, are counterbalanced by a greater energy requirement, in terms of thermal energy, to heat the bioreactors and, for this reason, the process is less advantageous than that carried out in a mesophilic regime. Furthermore, in thermophilic conditions, microorganisms are more sensitive to environmental variations (*Nath et al., 2004; Lima et al., 2020; Kim et al., 2003*) determining the need for more demanding management of the installed anaerobic reactors. A further control parameter of the AD process is the pH of the environment in which the reactions take place. The optimal pH values are typically between 6 and 8. During the evolution of the process, the pH must be constantly monitored as a variation of the latter outside the range of optimal values can compromise the process itself, influencing both the growth of the microbial families operating the process and the reaction environment itself generating chemical-physical reactions (for example precipitation) which can alter and compromise the environmental conditions in which the process takes place.

The growth of methanogenic bacteria, for example, is not only the slowest compared to all the other microbial families involved in the process, but also the most sensitive to acidic pH values, which partially or completely inhibit the process, determining a poor yield in methane terms and the accumulation of organic acids in the reaction environment and effluents. To control the pH and obtain a complete AD process it is advisable, among other things, to work with a specific ratio between substrate and bacterial biomass (F/M) typically depending on the characteristics of the organic substrate to be degraded. The F/M ratio, i.e. the ratio between food and microorganisms, defines the mass of substrate fed to the system per unit of biomass which provides for its degradation. Usually this ratio is expressed in grams of COD (Chemical Oxygen Demand) fed per grams of volatile suspended solids (SSV) of inoculum (*Panesar, 2020*). When a high quantity of substrate is supplied compared to the quantity of biomass, the increased hydrolytic and acidifying capacities of the system determine an unbalance of the bacterial population in favor of the acidogenic component, and therefore to the detriment of the methanogenic component. Therefore, a transitional phase takes place in which it is possible to observe an increase in the concentration of VFAs due to a consequent unbalance of the trophic chain to the detriment of methanigens and a change in the system towards acidic pH conditions. The result to be avoided in all ways is the total inhibition of the last stage of the process (*Pu et al., 2019; Ali et al., 2023*).

Compared to an aerobic process, in a AD process no oxygen is insufflated in any case; this leads to significant savings on the total management cost of the system.

Furthermore, in the case of an anaerobic process, it is possible to produce biogas, with a high energy value, starting from a notable variety of waste products, such as:

- sewage from cattle farms;
- poultry manure (manure);
- crop residues;
- waste and wastewater from agro-industry;
- organic waste from slaughter;
- sludge from purification plants;
- organic fraction of urban waste.

The CH_4 produced at the end of the AD is usually collected and sent for combustion and can, therefore, be considered the final product of the entire process (*Capodaglio et al., 2019; Corigliano et al., 2023*).

Producing energy from renewable sources has advantages from both an economic and environmental point of view. In fact, the controlled production of biogas in AD plants determines a reduction (indirectly) of CH_4 emissions into the atmosphere caused by the inadequate management of the treated biomass, a reduction (indirectly) of emissions of further greenhouse gases and the possibility to produce alternatives to fossil fuels by producing clean energy from renewable sources.

Biogas is nothing more than a mixture of gases which, in the case of an anaerobic process conducted in optimal conditions, is mainly made up of CO_2 and CH_4, with percentages of CH_4 ranging from 40% to 70%. From biogas it is subsequently possible to obtain biomethane through an upgrading process, which consists in the removal of CO_2 by means of a purification treatment. The gas that can be obtained is characterized by approximately 95-98% methane content, is chemically very similar to natural gas and, as such, can be introduced into the distribution network via gas pipelines. Furthermore, it is no longer classified as biogas but as bio- CH_4. Biogas, in fact, contains other substances such as water, N_2 (nitrogen), H_2S (hydrogen sulphide) and halogenated organic compounds. The carbon dioxide, nitrogen and water it contains lower its lower calorific value (PCI), resulting in a poorer yield in terms of energy conversion. For this reason, biogas can typically be subjected to a wide range of purification treatments such as: dehumidification by means of refrigeration units, desulphurization by means of scrubbers, treatments on activated carbon or adsorbent materials, removal of CO_2 by membrane adsorption (*Lòrànt et al., 2022; Chinea., 2023*).

DF is a particular process operated by anaerobic bacteria which can be schematized by referring to the first three stages of the AD process (*Fig.5)*. The latter, as previously introduced, is stopped before the methanogenesis stage can take place, interrupting the process of degradation of the complex organic substance to the production of a gaseous mixture, consisting of H_2 and CO_2, and that of VFAs in the liquid effluent. Over the last ten years, numerous studies have been conducted in order to provide for the treatment of organic waste of different origins, agricultural residues such as lignocellulosic biomass (for example rice straw, wheat and corn straw, stalks), agro-industrial waste such as that of the food products (for example waste water from the processing of whey cheeses), effluents from livestock farms, in DF processes developed for specific application cases (*Race et al., 2019*). This interest is due to the fact that these residues are by their nature abundant, economical, renewable and biodegradable, and consequently an ad hoc DF process for them presents advantages from both an economic and environmental point of view (*Aziz et al., 2021; Kovalev et al., 2020*). In order to avoid the traditional auto-inhibition of AD due to reaching acidic pH, reference was made to the ratio between organic substrate and bacterial biomass brought into contact in an anaerobic reactor. In the case of DF, unlike AD, it is necessary to guarantee a higher supply of organic substrate than AD, so as to guide the process towards optimizing the production of hydrogen and organic acids and avoid the persistence, in continuous reactors, of bacterial species operating the conversion of H_2 to CH_4. *Yuan et al., 2019,* studied the effect of different F/M ratios on H_2 production in terms of potential yield and production rate. The F/M ratios investigated (0.5, 0.9, 1.4, 1.9 and 2.8 g COD/g SSV) allowed us to assume that H_2 production increases up to a certain threshold value of F/M, after which the H_2 produced tends to decrease. The optimal F/M ratio, which leads to the maximization of H_2 production, seems to be at a value of 1.4 g COD/g SSV. The VFAs predominantly produced by DF are lactic acid, butyric acid and acetic acid. If the DF process is conducted with the aim of maximizing the biological production of H_2, the acids most present in terms of concentration in the liquid effluent are acetic and butyric acid (*Slezak et al., 2017*). In general, the most frequently used substrates are rich in carbohydrates, particularly glucose, sucrose and starch mixtures (*Ghimire et al., 2015*).

In the case of glucose, often taken as a reference due to its simple structure, the reactions of facultative anaerobic bacteria that lead to the production of organic acids can be defined as follows:

- Acetic acid: $C_6H_{12}O_6 + 2\ H_2O \rightarrow 2\ CH_3COOH + 2\ CO_2 + 4\ H_2$
- Butyric acid: $C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2\ CO_2 + 2\ H$

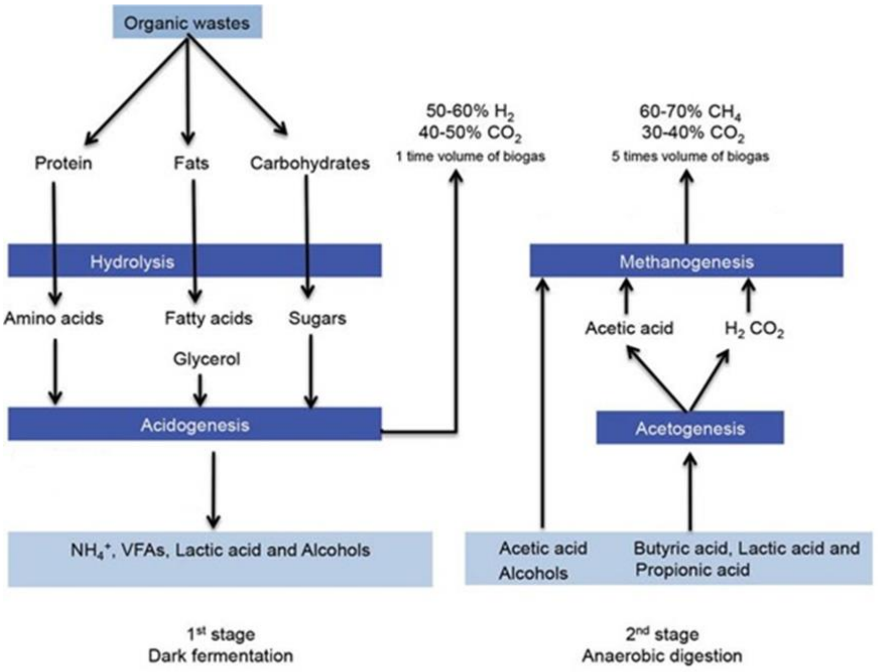

Fig. 5 *- Schematization of the anaerobic digestion and dark fermentation process*

DF processes are essential for producing VFAs mixtures, which serve as valuable resources for bioleaching treatments. These VFAs can then be used as raw material for bioleaching treatments. Bioleaching, in turn, is a biotechnological approach used to extract precious metals and minerals from various waste streams. In this thesis these treatments will be used for the denaturation, weight and volume reduction of some categories of CDW. The advantages of bioleaching treatments lie in their sustainability and applicability, particularly in countries with limited economic resources. Bioleaching reduces the environmental burden of waste disposal by contributing to a circular economy. This makes bioleaching an attractive solution to manage the challenging W121 and W12B fractions of CDW in an economical and environmentally friendly manner, thus promoting sustainable waste management practices even in regions with limited resources.

Objectives

Research aims to use a bioleaching method with VFAs from a DF process to treat some types of CDW. This approach offers several exciting opportunities for sustainable waste management. First of all, the primary objective is to optimize the DF process in such a way as to generate an efficient and high yield of VFAs, since these organic acids have harmful effects towards the cement matrices and chrysotile fibers of category waste W121 and W12B of CDW. Secondly, the research aims to identify and cultivate the most effective microbial consortia, in terms of yield, for the production of VFAs mixtures, capable of thriving in DF processes aimed at CDW bioleaching. Furthermore, the study seeks to establish optimal operating conditions, such as temperature, pH and reactor design, to maximize bioleaching efficiency while minimizing environmental impact. Ultimately, assessing the economic feasibility and environmental sustainability of this integrated approach will be a key research objective, to ensure that the bioleaching process is a viable and environmentally friendly solution for CDW.

This thesis is structured in two main parts, the first consists of a literature on the problems related to the asbestos exposure:

- Chapter 1. *Environmental exposure to asbestos: sustainable and innovative treatment solutions*

  This chapter presents the characteristics of asbestos, its traditional types of disposal and innovative and sustainable treatment solutions, respecting the circular economy. While most of the literature on asbestos-related diseases (ARDs) has focused on those resulting from occupational exposures, environmental exposures are also garnering increasing attention. In particular, studies that examine the impact of exposure to asbestos, including not only para-occupational exposure, but also that linked to the presence of asbestos in homes, schools and other environments.

The second part, consisting of three chapters, reports the experimental studies carried out during the PhD activities. Each chapter of this part is presented in form of a journal publication or submission and is initiated by a general introduction of the main topic and scientific issue addressed:

- Chapter 2. *A combined system for asbestos-cement waste degradation by dark fermentation and resulting supernatant valorization in anaerobic digestion*

  This chapter shows the results of some preliminary studies conducted in fed-batch mode on ACW samples; the objective was to denature the chrysotile asbestos contained in the cement matrix of the ACW samples through a bioleaching process using VFAs produced through DF. Several operational parameters such as solid content and temperatures were modified to maximize asbestos leaching. In addition, adjustments to the composition and concentration of the medium used in DF process were also explored, as well as a thermal pre-treatment on the inoculum used.

- Chapter 3. *Bioleaching Treatment of Concrete Waste from Construction and Demolition Waste (CDW): Advantages and Implications*

  This chapter shows a reactor system set to different pH conditions was used, with the aim of increasing the quantity of VFAs produced and the selectivity of the biomass with continuous enrichment, cyclically replacing part of the volume with medium and in the leaching reactor. Solid samples of concrete created in the laboratory were used. In the context of CDW concrete, bioleaching involving the action of VFAs produced in dark fermentation processes can weaken the material, leading to a decrease in its weight and volume.

- Chapter 4. *Synergizing Construction and Demolition Waste Management with Dark Fermentation: Sustainable Resource Recovery and Waste Reduction*

  This chapter explores using effluents in leaching processes to reduce CDW volume by dissolving cement components. It examines through tests with synthetic acid mixtures at different concentrations the efficiency of various organic acids produced during DF, identifying lactic and acetic acids as the most effective. Using cheese whey as a substrate, the study applies optimal conditions for acid production and assesses the process with real effluent. The method proves environmentally and economically superior to traditional landfilling, validated by Life Cycle Assessment (LCA) and economic analysis.

Finally, the conclusions summarize the most important results obtained, the challenges encountered during the experimental period and the eventual future evolution of the techniques investigated.

This thesis offers a comprehensive view of the present state and challenges related to potential treatments of CDW. It also delves into the policy framework supporting effective CDW management. However, the main emphasis is placed on understanding the generation of category W121 (mineral wastes) and W12B (mineral wastes containing asbestos) CDW, the factors influencing it, and the barriers and rationales for implementing sustainable bioleaching treatments for the management of these CDW categories. Using the results of the literature review, the existing knowledge regarding the components of the CDW system and the positive or negative relationships between them were illustrated. This thesis summarizes the main results of this study.

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Chapter 1

Environmental exposure to asbestos: sustainable and innovative treatment solutions

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Environmental exposure to asbestos: sustainable and innovative treatment solutions

Abstract

Asbestos, a dangerous mineral widely used in construction and industry, remains a persistent threat to both human health and the environment. The safe disposal of asbestos-containing waste (ACW) is paramount to prevent the release of asbestos fibers into the environment. This review provides an overview of the treatment solutions used and a statistical study regarding exposure and the relative incidence of related pathologies and on sustainable and innovative treatments aimed at mitigating environmental exposure to asbestos. Cutting-edge techniques, such as bioremediation and bioleaching, are discussed, as well as sustainable practices and policies aimed at safeguarding ecosystems and public well-being. Through a multidisciplinary approach, these solutions offer hope for a cleaner and safer future, addressing the legacy of asbestos contamination and promoting environmental sustainability.

1.1. Introduction

Asbestos refers to a collection of six naturally occurring minerals with fibrous silicate components: chrysotile, amosite, crocidolite, tremolite, anthophyllite, and actinolite. These minerals have been extensively utilized due to their remarkable attributes such as low thermal conductivity, robust mechanical strength, resilience to chemical and biological degradation, and affordability (*Baur et al., 2015; Spasiano et al., 2017*).

This mineral has been a prevalent choice in construction materials for large period. Chrysotile asbestos, in particular, has become the predominantly used form in the construction sector, owing to its adaptability and economic viability.

Asbestos mineral	***Molecular formula***	***Geographic area***
Chrysotile	$Mg_3Si_2O_5(OH)_4$	*Canada (QC), Russia, China, India*
Crocidolite	$Na_2Fe^{2+}{}_3Fe_3{}^{+2}Si_8O_{22}(OH)_2$	*South Africa (NW Cape Province,Transvaal), Western Australia*
Amosite	$Fe^{2+}{}_2Fe^{2+}{}_5Si_8O_{22}(OH)_2$	*South Africa*
Anthophyllite	$Mg_2Mg_5Si_8O_{22}(OH)_2$	*Turkey, Cyprus, Greece*
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	*Finland, USA*
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$	*South Africa (Cape Province)*

Table 1.1. *Geographical diffusion of asbestos minerals (Dana et al., 2002)*

Throughout history, global asbestos consumption reached a peak of approximately 4 million tonnes until mounting concerns regarding its severe health hazards led to a series of bans and restrictions in numerous countries. Despite these efforts, chrysotile asbestos continues to find limited usage, contributing to approximately 1.3 million tonnes of global consumption, as reported by the *United States Geological Survey* (*USGS, 2021*). This enduring presence is most pronounced in countries with less stringent regulatory frameworks.

Throughout the early 21st century, there was a discernible decline in asbestos utilization, with many developed nations committing to phase it out entirely by 2020 (*Singh et al., 2019*). However, a worrisome trend has emerged, primarily in China, India, and Russia, as well as in various developing nations including Kazakhstan and Brazil, where there has been a resurgence in asbestos usage through 2022 (*United Nations Statistics Division, 2021*) *Tab.1.2*.

Country or locality	*2018*	*2019*	*2020*	*2021*	*2022*
Brazil	101.000	12.205	77.057	153.600 [e]	197.100
China [e]	120.000	140.000	130.000	130.000	130.000
India	202.900	210.700	227.400	250.100 [r]	250.100
Russia	752.917	790.000	708.000	750.000 [r]	750.000
Kazakhstan	--	2.500 [e]	8.000 [e]	-- [r,e]	--
Total	1.180.000	1.160.000	1.150.000	1.280.000 [r]	1.330.000

[e] Estimated. [r] Revised. -- Zero.

Table 1.2. *Asbestos: World production and consumption, by country or locality*

This resurgence is occurring despite the mounting body of evidence highlighting the grave health risks associated with asbestos exposure. The persistence of asbestos in construction and demolition waste (CDW) and manufacturing has raised serious concerns, not only regarding public health but also the potential environmental consequences of this revival (*Bonifazi et al., 2022*).

While numerous countries have made substantial strides in banning or restricting asbestos usage due to its well-documented health hazards, there are still instances where asbestos-containing products endure, putting people at risk of exposure. Notable examples include Germany, Italy, and United States, where asbestos can still be found in certain products or existing structures (*Barbieri et al., 2022*). Despite regulatory efforts aimed at minimizing exposure, the continued presence of asbestos in older buildings, infrastructure, and imported goods poses ongoing health concerns for workers and the general population. To address these concerns, stricter enforcement and ongoing initiatives aimed at identifying and safely removing asbestos from various applications are imperative to mitigate the enduring risks associated with its use (*Stevulova et al., 2022*).

This alarming statistic underscores the persistent challenges associated with managing asbestos-related materials and highlights the urgent need for comprehensive waste management strategies. Even today, ACW continues to be generated, posing environmental and health risks during disposal and demolition processes. The management of asbestos waste remains an ongoing priority,demanding robust regulatory frameworks and responsible practices to ensure the safe containment and disposal of these hazardous materials while safeguarding both the environment and human health (*Thives et al., 2022*).

The incidence of asbestos-related diseases among individuals born after the asbestos ban has raised concerns about the long-term effects of past exposure. Although regulatory measures have significantly reduced asbestos use, the latency period for asbestos-related diseases, such as mesothelioma, lung cancer, and asbestosis, can extend for several decades. Consequently, individuals born after the ban can still be at risk due to environmental exposure, occupational hazards, or the presence of asbestos in older structures and materials. This underscores the critical importance of continued monitoring, raising public awareness, and maintaining healthcare vigilance to address the potential health consequences and provide timely diagnosis and treatment for those affected by asbestos exposure, even in the post-ban era (*Canepa et al., 2023 ; Varkey B., 2023*).

The generation of ACW remains a pressing issue, necessitating robust waste management strategies. Moreover, the long-term health effects of asbestos exposure continue to affect individuals born after the ban, emphasizing the importance of continued vigilance and healthcare support (*Paglietti et al., 2021*). The global community must remain committed to addressing these challenges comprehensively to protect human health and the environment from the enduring legacy of asbestos use.

1.2. Non-occupational environmental exposure to asbestos

Asbestos exposure is estimated to have caused approximately 107,000-112,000 deaths over time, but current estimates suggest that the actual number of deaths is much higher. (*Furuya et al., 2018*). At present, approximately 125 million people worldwide are exposed to asbestos in their workplace. It is estimated that around half of all occupational cancer deaths are linked to asbestos exposure. Moreover, non-occupational exposure to asbestos is probably responsible for several thousand deaths each year (*Magnani et al., 2023*). The pattern of asbestos-related diseases (ARDs, *tab 1.3.*) in a particular community is influenced by several factors, including the amount and type of exposure, age at exposure, and genetic predisposition.

Non-malignant Asbestos-Related Diseases	Malignant Asbestos-Related Diseases
❖ Asbestosis ❖ Pleural effusion ❖ Atelectasis ❖ Hyaline pleural plaques ❖ Peritoneal effusion ❖ Pericardial effusion ❖ Pleural thickening	❖ Mesothelioma, pleural and peritoneal ❖ Lung cancer ❖ Laryngeal cancer ❖ Pharyngeal cancer ❖ Stomach cancer ❖ Colon cancer ❖ Ovarian cancer

Table 1.3. *Asbestos-related diseases according to their specificity in relation to asbestos exposure* (*Magnani et al., 2023*)

Predominantly occupational exposures are associated with excess lung cancer, asbestosis, and a higher proportion of peritoneal mesothelioma than pleural mesothelioma. At lower non-occupational exposures, pleural mesothelioma is more common (*Bourdès et al., 2000; Emmett, 2021*). In recent years, more attention has been paid to non-occupational exposure to asbestos, both in countries that have already banned its use and in those where it is still allowed. For countries that have already prohibited asbestos, the challenge is addressing cases of mesothelioma, particularly among workers who were exposed to asbestos at a time when the risks were more significant. While global data on mesothelioma suggests a rising trend, this disease is primarily a concern for countries that have already implemented an asbestos ban (*Boffetta et al., 2017*). Conversely, the younger subjects, who have not had occupational exposure and are most likely exposed to decreasing industrial/ occupational levels, show lower incidences (*Pira et al., 2018*).

Non-occupational asbestos exposures can be divided into three sources according to the exposure pathway: neighborhood, household, and domestic. Neighborhood exposure generally refers to exposure that results from living near asbestos factories or sites of naturally occurring asbestos (NOA). Household exposure results from exposure to asbestos-containing materials used in home structures (e.g., roofs, insulation), home-based hobbies (e.g., gardening), or home improvement projects. Domestic exposure refers to exposure to fibers brought home by asbestos workers on their clothing or in their hair or through living in the same house with occupationally exposed individuals. Distinct types of exposure have different relative risk estimates but for all there is an elevated risk of mesothelioma (*Xu et al., 2018*).

This data has been confirmed by a recent study that was conducted to analyze international case-control and cohort studies focusing on the link between mesothelioma and non-occupational asbestos exposure, encompassing exposures in residential, domestic, and household settings. A meta-analysis was carried out to calculate a summary relative risk estimate (SRRE) along with a 95% confidence interval, utilizing random-effects models. Primary meta-analyses suggested an SRRE of mesothelioma of 5.33 (95%CI: 2.53, 11.23) from neighborhood exposure, 4.31 (95%CI, 2.58, 7.20) from domestic exposure, and 2.41 (95%CI, 1.30, 4.48) from household exposure with large I2 statistics ranging from 83–99%. This suggests a significant association between non-occupational asbestos exposure and an increased risk of mesothelioma. However, it is important to approach certain SRREs with caution due to the substantial heterogeneity observed across studies. Funnel plots also indicated a potential for publication bias (*Xu et al., 2018*).

Differences have been described regarding occupational and non-occupational exposure also in terms of ARDs: in a study that evaluated the exposure to asbestos during the activity of Fibronit plant (Broni, Italy), the authors found out among workers in contact with asbestos, although the majority (about 67%) died from mesothelioma, several subjects did not develop mesothelioma , but instead died for asbestosis (17.4% of cases) or pulmonary carcinoma (11%), or, in a percentage lower than 3%, (2.8+1.8=4.6) for other cancers or cardiopulmonary diseases. However, all 73 cases without occupational exposure, and therefore exposed to low doses of asbestos, died from mesothelioma. This finding is consistent with other similar reports in literature about other plants like Fibronit (*Visonà et al., 2018*). Mesothelioma cases that result from non-occupational exposure in the community tend to occur more often among females and younger individuals compared to occupational exposure. This age distribution can be attributed to the earlier age at which exposure begins, which increases the likelihood of developing the disease over time due to its long latency period. The effect is particularly significant when exposure begins in early childhood (*Reid et al., 2014*).

There are numerous cases in which a correlation between non-occupational exposure to asbestos and mesothelioma has been described in different countries (*Arul et al., 1977; Cazzadori et al., 1992*). For example, *Ascoli et al., 2013* reported five cases of malignant mesothelioma within one family with exposure to asbestos experienced during childhood, as 'next door' residents of a workshop recycling asbestos-contaminated jute sacks in Naples, Italy. Their low mean patient age (45 years) points to exposures during childhood.

Cases of ARDs are also described in India, such as a 42-year-old Indian man who died of pleural mesothelioma. He had been exposed to asbestos both in his household and from the environment since birth. Additionally, two of his close family members worked in a factory where asbestos was used, and their living quarters were situated within the factory premises. The country possesses all the conventional sources of asbestos exposure, including mining waste and industries involved in asbestos manufacturing and consumption, putting thousands of workers and their families at risk. Families with para-occupational exposure face a higher risk of developing asbestosis compared to those with only environmental exposure. Moreover, there are strong associations between mesothelioma and the contamination of clothes, as well as laundering workers' clothing. While mesothelioma cases may be stabilizing in countries that banned asbestos in the early 1980s, it is expected to rise in nations that either delayed the ban or have yet to implement such restrictions on asbestos usage (*Muralidhar et al., 2019*).

However, the ban on asbestos does not allow us to reduce attention to ARDs. For example, *Krówczyńska et al., 2019*, anticipate a high number of asbestos-related cases in Poland in the coming decades. All current asbestos-containing products are slated for removal by the end of 2032 but the demolition process may pose a potential risk for an increase in malignant mesothelioma (MM) incidence. Asbestos-cement building materials are predominant in Poland, forming the basis for estimating the potential risk of environmental asbestos exposure. Since Poland implemented an asbestos ban in 1997 and conducted air measurements for asbestos fibres over 20 years later, it suggests that exposure is primarily due to the use of asbestos-cement roofs. While many countries have taken steps to limit or prohibit asbestos mining and production, asbestos-containing products are still in use, warranting further investigation into their impact on environmental exposure. Studying environmental asbestos exposure is challenging due to the long latency period, and it should be assessed in conjunction with environmental contamination levels. Indeed, the risk of MM incidence rises with higher levels of air pollution. Interestingly, when compared to Italy and Germany, which have similar per capita consumption of asbestos products, the reported MM cases in other European countries are significantly higher than in Poland (*Abdel-Rahman, 2018*).

It's crucial to emphasize that there is no safe level of asbestos exposure. Any amount of contact carries a potential risk, as underscored by *Lee et al., 2021* in their review of Korean studies assessing the carcinogenic risk to residents exposed to asbestos cement slate-roofed houses. They determined that while the risk was low, the absence of a carcinogenicity threshold for asbestos means it should not be disregarded, even if the risk seems minimal. Therefore, it would be prudent to calculate the carcinogenic risk based on the cumulative lifetime exposure.

1.3. Childrenhood environmental exposure to asbestos

Laborde et al. 2015 studied the influence of environmental exposures on children's health in Latin America: environmental changes have swept Latin America, including urbanization, industrialization, changes in patterns of land use, deforestation, and the effects of regional climate change. Toxic chemicals in the environment have become an important problem and are recognized as major causes of disease and disability among children in Latin America; in particular, the authors comment how, while the use of asbestos has been virtually eliminated in most industrially developed countries, in Latin America, progress is being made in reducing asbestos use. Argentina, Chile, Uruguay, and Honduras have all banned asbestos, consumption is declining in other countries, even where it is not illegal. But progress is slow and not necessarily irreversible (*Laborde et al., 2015*). Indeed, some sources report rising asbestos consumption in a handful of countries such as Mexico and El Salvador. Annual production in Colombia in 2003 and 2004 was an estimated 60,000 tons (*Roselli, 2014*). In 2012, Brazil produced 306,500 tons of asbestos and was the world's third largest producer (*Virta et al., 2014*). About 80% of the asbestos used in Brazil is consumed in the form of asbestos cement: for roof tiles and roofing panels, wallboard, and domestic and industrial water tanks (*Berman, 1986*). Therefore, the risk of environmental exposure is highly possible, even in children. In a recent Italian report, Sixth SENTIERI Report (*Zona et al., 2023*), the authors evaluated the epidemiological evidence on causal links between sources of environmental exposure and health effects to identify pathologies of a priori interest. Mortality from total mesotheliomas is three times higher at sites with asbestos present and pleural mesotheliomas are more than two times higher at the group of sites with asbestos and port areas.

Certain regions around the world continue to pose risks of exposure to NOA due to the geological characteristics of the area. Challenges persist in the form of indoor exposure in specific locales, outdoor exposure to NOA, environmental contact with asbestos from industrial or mining activities, as well as exposure to NOA resulting from agricultural practices and urban development in rural regions (*Bayram et al., 2014*).

It must also be considered that asbestos has also often been used as a construction material, especially in schools, therefore environments widely frequented by children: in a 1982 study, Baldwin CA et al. estimate that as many as 1,124 (89 per cent) of the 1,263 public schools in Colorado may have asbestos in friable form, and 380 (38 per cent) may have asbestos sprayed on ceilings. The authors further comment that if the potential exposure values for the small number of schools we surveyed are typical of the values that might be found in other schools in the State, a severe problem exists that could result in adverse health effects in the future and that the cost of dealing with asbestos containing materials (ACM) may be high, but this should not be an excuse for ignoring the problem (*Baldwin et al., 1982*).

Campopiano A. et al. 2021 in a recent study about ACM in schools in Rome and the surrounding area found out that about 16% of the surveyed schools had ACM. Most of the ACM were not accessible to students (water tanks, boiler thermal insulations). ACM and vinyl floor tiles were the most common non-friable materials found in schools. The authors underline how it is necessary, given the asbestos health hazard for the students, to manage these hazards appropriately and propose a larger study leading to ACM national mapping in schools (*Campopiano et al., 2021*).

In recent years, numerous authors have pondered the implications of childhood exposure to asbestos. However, there are several uncertainties and gaps in the available data that make it difficult to draw definitive conclusions. According to the UK's Committee on Carcinogenicity, due to the increased life expectancy of children compared to adults, there is an increased lifetime risk of mesothelioma because of the long latency period of the disease. Because of differences in life expectancy, for a given dose of asbestos the lifetime risk of developing mesothelioma is predicted to be about 3.5 times greater for a child first exposed at age 5 compared to an adult first exposed at age 25 and about 5 times greater when compared to an adult first exposed at age 30, so the exposure of children to asbestos is likely to make them more vulnerable to developing mesothelioma than exposure of adults to an equivalent asbestos dose (*Blain et al., 2003*). This conclusion appears to agree with the evidence that the risk of mesothelioma does not decrease after cessation of asbestos exposure, while lung cancer risk does (*Boffetta et al, 2019*). However, a study by *Reid et al., 2018* finds that those first exposed to asbestos as children appear to have no greater intrinsic susceptibility to injury from asbestos exposure than those first exposed as adults but given the long latency of mesothelioma and the differences in life expectancy, their lifetime risk of developing mesothelioma is likely to be greater.

In a recent study conducted by *Dalsgaard et al., 2021* a cohort of 12,111 former school children, born between 1940 and 1970, was examined. This cohort was identified using 7th-grade school records from four schools situated at distances ranging from 100 to 750 meters in the prevailing wind direction from a large asbestos-cement plant in operation from 1928 to 1984 in Aalborg, Denmark. The researchers utilized the Danish Cancer Registry to assess standardized incidence rates (SIRs) for asbestos-related cancers, as well as all cancers and multiple cancers. These rates were compared to those of a reference cohort, matched by gender and five-year frequency. The study revealed a slight increase in the overall incidence of cancer for the school cohort (SIR 1.07, 95% CI 1.02–1.12) when compared to the reference cohort. This rise was predominantly attributed to a significantly elevated SIR for malignant mesothelioma (SIR 8.77, 95% CI 6.38–12.05). Furthermore, the authors examined the risk associated with various combinations of asbestos exposure. Individuals with additional household exposure due to a relative showed a notably increased SIR for pharyngeal cancer (SIR 4.24, 95% CI 1.59–11.29) (*Fig. 1*). This study highlights how complicated it is to establish the extent and association between one or more types of asbestos exposure and the onset of ARDs.

Other authors evaluated the mortality for MM by age group, in particular among ≤50 years (ys) old people in Italy, in 2003-2016 (*Fazzo et al., 2020*). Mortality from MM in ≤50 years old people, considering the long latency, is likely related to asbestos exposure in childhood. In Italy, 487 people ≤50 ys old died from MM, in 2003-2016 (2.5% of all MM deaths), corresponding to 35/year. Considering the lengthy period of latency (about 40 years and over) (*Marinaccio et al., 2015*) of the disease and the high attributable fraction to asbestos exposure, these deaths could be probably due to asbestos exposure occurring in childhood. For this reason, localized excesses of MM mortality in ≤50 ys old people, could also be used as a sentinel event of past, or current, contexts of environmental asbestos exposure.

Furthermore, *Kang D et al., 2013* performed a review evaluating studies highlighting the difference in MM risk, based on the age at first asbestos exposure. Six studies reporting the risk of MM mortality by age class, childhood included, among occupational and environmental asbestos exposed subjects (*Chen et al., 2012; Rake et al., 2007*) were considered. Four studies found the highest risk in subjects aged 15 years (ys) or less at first exposure (*Pira et al., 2007*), meanwhile the other one reported a lower risk in subjects exposed at young age (less than 20 ys) than in adulthood (*Reid et al., 2007*). The subjects exposed at birth showed the highest risk in the only study that included birth as age at first exposure (*Luce et al., 2000*).

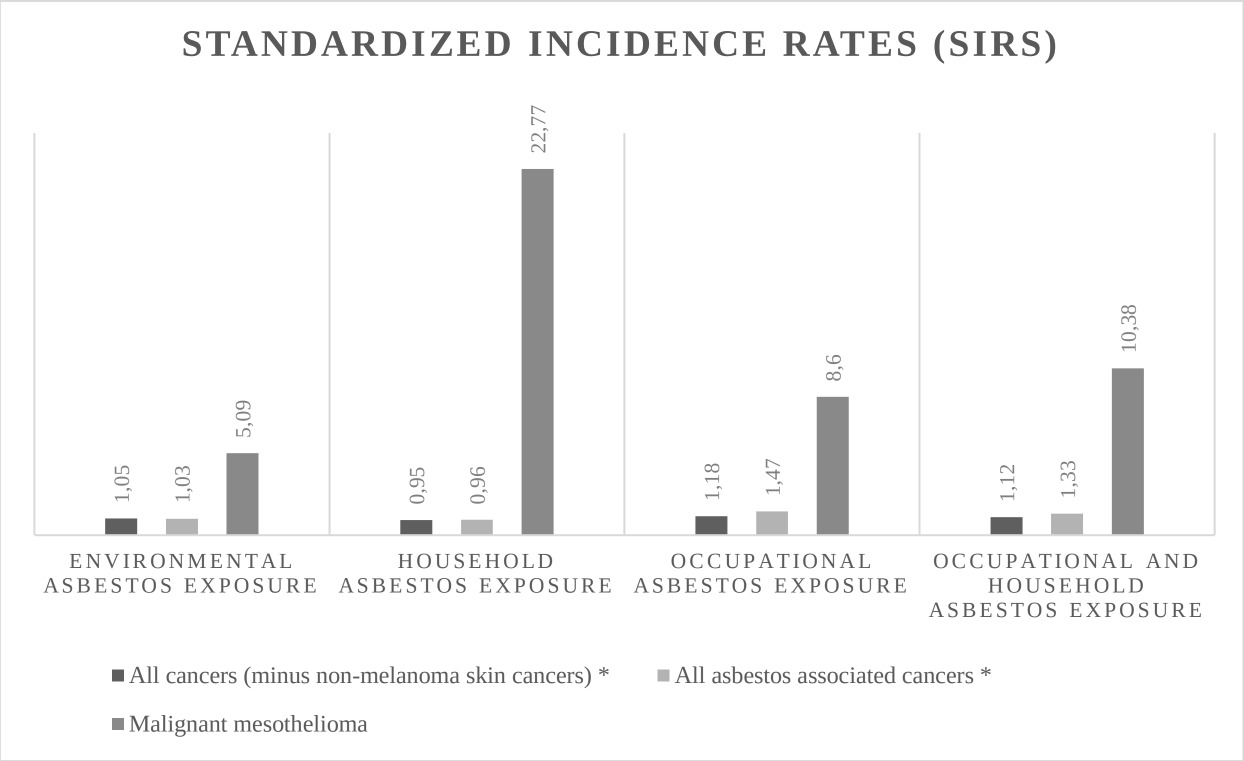

Figure 1.1. *Standardized incidence ratios (SIR) for selected cancers among those in the school cohort exposed only to environmental asbestos and the subgroups also exposed to household or/and occupational asbestos exposure (*Data from Dalsgasrd et al., 2021)*

1.4. Asbestos disposal methods and strategies for fiber release mitigation

Proper asbestos disposal is vital in mitigating environmental and health risks. Various methods, including landifill disposal, encapsulation, enclosure, controlled demolition and recycling, have been developed to limit the release of asbestos fibers into the environment. However, strict regulatory compliance, continuous monitoring, and community engagement are equally important in ensuring the efficacy of these disposal methods and maintaining public safety (*Paglietti et al., 2016*).

The most common method of asbestos disposal is transferring the waste to controlled landfill sites. ACM are securely enclosed in leak-tight containers or double-bagged using 6-mil polyethylene bags to prevent the release of fibers during transportation. Clearly labeled with appropriate warning signs, these containers are then transported via authorized vehicles adhering to safety and environmental protection regulations. Once at the landfill, the asbestos waste is disposed of in designated areas, segregated from other types of waste to avoid cross-contamination (*Promentilla et al., 2003; Marian et al. 2021*). The landfills employed for this purpose are specifically engineered with liners and covers to impede the escape of asbestos fibers into the surrounding environment, protecting both groundwater and atmospheric quality. After the disposal, the asbestos-containing areas are covered daily with layers of soil or other EPA-approved cover materials to further secure the waste and mitigate the release of fibers (*EPA, 2021*).

The encapsulation method is a strategic approach to dispose of ACM by sealing the asbestos fibers and preventing their release into the environment. In this methodology, ACMs are treated with a liquid encapsulant, a penetrating or bridging sealant that forms a membrane over the surface or penetrates the material and binds its components (*Malinconico et al., 2022*). The encapsulant, usually composed of polymers, is carefully applied to the ACM, ensuring thorough coverage. It is crucial to apply the encapsulant under controlled conditions, avoiding disturbance of the asbestos fibers. Once the encapsulant has cured, it immobilizes the asbestos fibers, reducing the risk of their release.

This method is widely regarded as a short-term and valid solution, especially when the removal of asbestos is impractical. This technique requires ongoing monitoring and maintenance to check the integrity of the encapsulation and to ensure the continued containment of fibers. In the event of deterioration or damage to the encapsulated materials, remedial actions, including repair or removal, must be promptly undertaken to avoid asbestos exposure. The encapsulation method is primarily focused on mitigating the risk of asbestos exposure rather than full disposal and involves high costs (*Arfò et al., 2019; Vergani et al., 2022*).

Enclosure is a meticulous approach for managing ACM, serving to isolate asbestos materials and prevent the release of hazardous fibers into the environment. This methodology involves constructing an airtight, impermeable barrier or containment structure around the ACM. Initially, a detailed assessment is undertaken to determine the extent and condition of the ACM, and based on this, a custom-designed enclosure is planned. The enclosure, often constructed of rigid, durable materials, is built to entirely encapsulate the ACM, ensuring no gaps or points of egress for fibers (*Flòrez Gutierrez., 2023*). The construction of the enclosure is performed under stringent safety protocols to avoid any disturbance of the asbestos material, with personnel employing protective equipment to mitigate exposure risks (*Kim et al., 2013*). Once completed, the enclosure serves to contain the asbestos fibers effectively, necessitating regular inspections and maintenance to ascertain the structural integrity and effectiveness of the containment. The enclosure method is particularly advantageous for large, immovable ACMs where other methods of disposal, like removal or encapsulation, are not feasible (*Senavirathna et al., 2022*). Regular monitoring and prompt repairs are vital to maintain the efficacy of the enclosure in the long term, ensuring continued environmental and human safety. However, several negative and disadvantageous aspects are associated with this methodology. Firstly, the enclosure method does not eliminate the asbestos; it merely contains it, leading to a persistent risk of exposure if the structure is compromised or deteriorates over time (*Cherrie et al., 2005*). The long-term management and monitoring of enclosure structures can be resource-intensive and costly, potentially posing logistical challenges.

Additionally, in the case of structural failure or accidental breaches, immediate remedial actions and repairs are crucial, which can incur additional unforeseen costs and resources (*Marshall et al., 2023*). This method, while effective as a temporary solution, does not address the permanent resolution of asbestos hazards and requires unwavering vigilance to maintain public and environmental safety.

Controlled demolition is a meticulous and regulated methodology deployed for disposing of asbestos contained within CDW (*Mckenzie et al., 2019*). The method requires a prior comprehensive survey to locate and quantify ACMs. Post-identification, ACMs are, where possible, removed under controlled conditions before demolition. Pre-demolition asbestos abatement processes, such as removal or stabilization, are usually performed to reduce the potential release of fibers during demolition. If removal is not feasible, stringent measures are employed to minimize the release of asbestos fibers during demolition (*Bolan et al., 2023*)

	Removal	***Encapsulation***	***Enclosure***
Advantages	Eliminate asbestos An inspection and maintenance program is no longer necessary	Reduces fiber release No replacement material is needed Lower cost than removal	Reduces the release of fibers outside the containment barrier No replacement material is needed Fair impact resistance No toxic waste is produced Lower cost than removal
Disadvantages	High risk of contamination due to incorrect interventions High risk for workers involved A replacement material is needed Production of toxic waste	The asbestos remains in place and may need to be removed at a later time Removing encapsulated asbestos can be difficult Risk of detachment due to the increase in weight of the covering An inspection and maintenance program must be activated Poor impact resistance It may be necessary to repeat the operation after some time	The asbestos remains in place and may need to be removed at a later time Release of dry fibers during surgery The release of fibers continues within the enclosure if an encapsulation treatment is not associated An inspection and maintenance program must be implemented The enclosure barrier must be maintained in good condition
Indications	It can be implemented in almost any situation It is indicated in conditions of serious and extensive degradation of the material	Slightly deteriorated materials Slightly friable materials Materials that are difficult to access	Easily accessible materials Asbestos localized in limited areas If it is not necessary to enter the confined space
Contraindications	--	Poor adhesion to the support Very deteriorated materials Water infiltrations Easily accessible materials High coating thickness	Need to access the confined space Water infiltrations Fair impact resistance Insufficient space (e.g. low ceilings) Possible damage to the enclosure barrier

Table 1.4. *Overview of asbestos interventions for fiber release mitigation*

The execution of controlled demolition involves the utilization of specialized equipment and skilled personnel to dismantle structures systematically, prioritizing the minimization of asbestos disturbance and release (*Bonifazi et al., 2019*). Wetting down the site is a common practice to suppress dust and fiber dispersal.

Additionally, air monitoring is continuously conducted to detect any release of asbestos fibers, and debris is promptly and appropriately managed to avoid contamination (*Gregson et al., 2010*).

However, this method harbors intrinsic disadvantages. Firstly, even with meticulous controls, the potential for inadvertent release of asbestos fibers during demolition remains, posing risks to both the environment and public health. The stringent regulations and procedures necessitate significant investments in time, equipment, and specialized skills, escalating the overall cost of demolition projects (*Bhuvaneswari et al., 2017*). Moreover, managing and disposing of contaminated debris post-demolition is challenging and necessitates secure, approved facilities, further elevating the operational complexities and costs (*Tangtong et al., 2010*). Lastly, the subsequent health monitoring for the demolition workforce underscores the inherent risks and potential long-term implications associated with controlled demolition in asbestos-laden environments.

1.5. Advancements in thermal, chemical and mechanical asbestos treatments

Emerging technologies in thermal, chemical, and mechanical treatments are evolving as promising alternatives for disposing of asbestos in CDW, offering innovative approaches to decontaminate and recycle ACM (*Paolini et al., 2019*).

1.5.1. Thermal treatments

Thermal Treatments involves the application of high temperatures to alter the asbestos fibers' structure, rendering them non-asbestos and non-hazardous (*Iwaszko, 2020*). The majority of identified applications and analyzed research anticipate employing temperatures reaching or exceeding 1200 °C. Nonetheless, it's critical to note that recent applicationsy suggest a thermal treatment at merely 700 °C is adequate to neutralize the risks associated with asbestos-cement (*Carneiro et al., 2021*).

The thermal breakdown of asbestos minerals unfolds in three distinctive phases: initial stages are marked by the elimination of absorbed water; following this, structural OH groups are extricated from the asbestos minerals' configuration; and, finally, the third phase encompasses the crystallization of non-crystalline substances, with new phases emerging post-dehydroxylation (*Kusiorowski et al., 2015*). Vitrification stands as the most straightforward form of thermal treatment. In this procedure, ACW materials undergo heating, typically surpassing 1000 °C, to transform into an inert, fiber-free silica substance. Beyond 700 °C, the release of (structural) crystallization water induces the breakdown of the fibrous crystalline framework, culminating in the creation of a non-reactive glass-like substance. Leveraging this transformation, certain vitrification techniques expose ACW materials to temperatures around 900 °C, whereas, in some instances, the materials are melted at elevated temperatures, reaching up to 1300 °C (*Ruiz et al., 2018*). This results in a liquefied silicate mass which, upon cooling, solidifies into a predominantly amorphous, asbestos-devoid glass mass that exhibits minimal leachability (*Iwaszko et al., 2021*). A highly effective yet notably costly alternative heating technique is epitomized by the INERTAM process, originating in Morcenx, France, which employs a plasma torch (of arc discharge variety) to melt ACW (*Guillot et al., 2012*). The INERTAM method utilizes what is known as "thermal plasma," a semi-ionized gas, which attains temperatures between 1000–1200 °C via an electric arc, despite asbestos having a considerably lower melting point (*Witek et al., 2017*). The alteration of asbestos fibers is complete, and gas emissions are consistently regulated, complying with the standards set by European legislation.

Microwave air plasma treatment employs an electrical discharge and leverages microwaves for energy. These electromagnetic waves have a wavelength situated between infrared light and radio waves, operating at high frequencies (*Leonelli et al., 2006*). This method boasts several benefits: it operates without an electrode discharge, attains high gas temperatures around 3000 °C, features a compact size, and necessitates minimal energy. Indeed, the energy consumption of microwave air plasma can be up to 100 times less compared to thermal inertization, with the melting time being 200 times shorter (*Averroes et al., 2011*).

Moreover, the availability of oxygen isn't restrictive in this process due to the absence of electrode discharge. This atmospheric microwave air plasma treatment technique is capable of handling airborne building materials laden with asbestos. Therefore, materials like cement and concrete can undergo treatment, courtesy of the plasma's elevated temperatures. The end product of microwave treatment primarily consists of magnesium oxide, forming solid blocks laden with forsterite (Mg_2SiO_4) as the predominant crystalline component (*Yoshikawa et al., 2015*).

Various studies have validated that asbestos fibers can be swiftly and effortlessly broken down through microwave irradiation. For example, ACW treated with microwaves resulted in the formation of forsterite, a benign magnesium silicate. Specifically, examinations revealed amorphous structures rich in cordierite that have the potential for recycling, serving as a substitute for Mg-rich talc in raw material applications (*Zheng et al., 2019*). Researchers have also delved into the fluctuations in the microstructure and attributes of the finalized products with varying ratios of inertized ACW in ceramic items.

1.5.2. Chemical treatments

Chemical Treatments deploys various chemicals to break down the asbestos fibers, neutralizing the hazardous effects. The hydrothermal treatment is a chemical approach that eradicates the issues related to the management of corrosive/dangerous agents. It employs supercritical water at 250 MPa and 650 °C. In such states, water exists as a supercritical fluid, allowing operations at a neutral pH (*Anastasiadou et al., 2010*). The principal critical issues associated with this process include the extremely high pressures involved; the filtration of the resultant water, and, in certain applications, the necessity to incorporate 6% hydrogen peroxide (*Nzogo Metoule et al., 2019*).

Regarding the necessity for an additional hydrolytic agent, the Chemical Center holds a European patent that exploits the potential acidity of whey. Initially, an acidic liquid phase and a solid phase containing asbestos are segregated by dissolving the cement component. Subsequently, the asbestos fibers undergo a hydrothermal process in whey under elevated temperature and pressure—ranging from 120 to 250 °C and 5 to 20 bar—resulting in the decomposition of the fibers (*Spasiano et al., 2017*). The TRESENERIE method is a distinctive alkaline chemical treatment intended for various kinds of cement-asbestos. This methodology, spanning 20–30 minutes, hinges on the dissolution of asbestos fibers in a dense, aqueous basic solution (> 25 M) of either sodium hydroxide (NaOH) or potassium hydroxide (KOH), situated within a reactor. The operation unfolds at a relatively mild, fluctuating temperature, ideally 170 °C, ranging between 160 and 175 °C, coupled with a minimal pressure of 8 to 10 kg/cm^2. Subsequent to this, the derived material undergoes centrifugation (*Debailleul, 1997*).

This centrifugation stage facilitates a separation of solid and liquid, yielding liquids capable of regeneration to initiate a new basal attack phase and a concentrated solid (precipitated) phase, which sees a 70% volume reduction from the initial stage. This reduced solid phase can be reclaimed and transferred to an additional reactor for a secondary basic attachment at elevated temperatures, preferably around 200 °C, varying from 190 to 210 °C, and pressure preferably between 2.5 and 5 kg/cm^2, ranging from 2 to 10 kg/cm^2 (*Tabata et al., 2016*).

This subsequent treatment results in the absolute dissolution of the fibers. The processed materials, both compact and crumbly, are subjected directly to the reactor without prior shredding. The end products of this chemical transformation vary depending on the asbestos type treated, possibly resulting in silica, diverse silicates of various oxides, or iron hydroxides. The main challenges associated with this form of treatment include the substantial energy consumption required by the high temperatures necessary for the proper conduct of the process, in addition to the high costs of the essential reagents.

1.5.3. Mechanical treatments

Mechanical Treatments, on the other hand, involves processes like crushing and grinding combined with other treatments to decontaminate the waste. These methods aim to transform the hazardous characteristics of ACMs, allowing for safer disposal or even recycling of the treated materials. The transition of chrysotile to an amorphous form is likely due to the intense fragmentation induced by milling: the direct OH bonds interconnecting the silica and brucite sheets are disrupted or severed. As a result, the structured crystalline framework breaks down, leading to the attainment of chrysotile amorphization (*Colangelo et al., 2011*).

The final outcomes of these mechanisms are powders devoid of asbestos, which have the potential to be repurposed for creating mortars with mechanical attributes surpassing those derived from lime-pozzolana conglomerates (*Alam et al., 2011*).

The emissions of gas and dust from mechano-chemical reactors are minimal since the procedures are confined to a sealed and restricted space. The methodology could be intricate and necessitates specialized proficiency and expertise, rendering it a challenging option for smaller entities or nations with constrained resources. Additionally, the technique might generate by-products that mandate appropriate management and processing, presenting further environmental and operational hurdles (*Mezhov et al., 2018*).

	Thermal	***Chemical***	***Mechanical***
Process temperature range (°C)	600 to 1600	50 to 650	80 to 100
Energy consumption (kWh/kg)	0.5 to 1.5	0.1 to 0.3	*12 to 15*
Consumptions of reagents	Require the use of various reagents and additives to stabilize, facilitate, or enhance the treatments processes.	The utilization of chemical reagents is high, given the resilient nature of asbestos, and this can lead to substantial environmental concerns.	Need for lubricants, coolants, and other auxiliary substances to ensure the smooth operation of mechanical systems. These substances must be managed properly to prevent environmental contamination.
Enviromental impact	These methods potentially emits air pollutants, including particulate matter and potentially hazardous gases, necessitating stringent emission control measures to mitigate atmospheric contamination. The production of residual waste necessitates meticulous management to prevent environmental degradation.	The synthesis and disposal of these chemicals can lead to the contamination of soil and water bodies if not managed properly. Some chemicals used may be hazardous and pose a risk of spillage or leakage, which can have severe ecological repercussions, impacting aquatic life and potentially entering human food chains.	Generation of airborne asbestos fibers during the treatment, posing significant risks to air quality and, consequently, human health, necessitating stringent containment and air filtration mechanisms. The waste products and residues generated during the mechanical treatment may still retain hazardous properties and necessitate secure disposal or further treatment to mitigate any environmental repercussions.

Table 1.5. *Analysis of asbestos treatment technologies reviewed*

However, these emerging technologies also present several challenges and disadvantages. The energy consumption in thermal treatment is significantly high, making it less environmentally friendly and more costly (*Zaremba et al., 2010*). The efficacy of chemical treatments is highly dependent on the correct chemical mixtures and reaction conditions, necessitating precise control and extensive knowledge, and any mishandling can lead to incomplete treatment and lingering hazards (*Talbi et al., 2019*). Mechanical treatments often entail the risk of releasing fibers during the process, necessitating stringent containment measures which can be difficult to maintain.

Moreover, the development and implementation of these advanced treatments require substantial investments in research, development, equipment, and training. Additionally, the lack of comprehensive guidelines and regulations surrounding these novel methods can lead to variability in treatment efficacy and safety, creating uncertainties and potential risks (*Bloise et al., 2019*).

Strict regulatory guidelines and standards have been established to ensure the safe disposal of asbestos. Compliance with these regulations is essential to mitigate risks to human health and the environment. Moreover, continuous monitoring of asbestos disposal sites is crucial for early detection of potential contaminations and ensuring long-term environmental safety (*Tomassetti et al., 2020*).

Community awareness and engagement play a pivotal role in asbestos disposal management. Informing communities about the hazards of asbestos and the importance of proper disposal can enhance public safety and encourage responsible handling and disposal practices.

1.6. Sustainable and innovative asbestos management solutions

The exploration of biological methods for breaking down asbestos fibers has not been the focal point of extensive research. This is predominantly attributed to the asbestos structure being chiefly inorganic and the indefinite and presumably extensive durations required for degradation. Nevertheless, due to their cost-effectiveness and ecological sustainability, such treatment options are becoming viable solutions for nations with restricted financial capabilities (*Frangioudakis et al., 2023*).

There is potential for asbestos to undergo partial decomposition through the activity of certain biological entities, predominantly soil-based microorganisms, inclusive of select fungi and lichens. While organic materials are essential for the growth of all organisms, inorganic substances can act as energy sources for microbial metabolic processes and can provide crucial trace elements, like iron. Extracting iron from asbestos through biological entities could potentially diminish its carcinogenic properties (*Ito et al., 2021*).

The bioremediation of areas contaminated with asbestos may leverage a range of processes. The selection of these processes is contingent upon various factors such as the nature and levels of asbestos minerals present, the extent of contamination, and the coexistence of other pollutants, like harmful heavy metals (*Wallis et al., 2020*). Several viable approaches encompass phytostabilization, employing plants to encase and solidify the substrate without interacting with the asbestos. Establishing new flora can be especially beneficial when the contaminated locations are so expansive that artificial coverings, layered with untainted soil and plant life, are impracticable for containment. Most sites designated for asbestos disposal exhibit scant or no vegetation, predominantly due to profound infertility. Selected flora must be resilient to the prevailing substrate conditions (*Gopishankar et al., 2022*). Deciding on suitable plant species and/or amendments to the soil necessitates an assessment of the soil's acidity or alkalinity, existence of heavy metals, nutrient availability, and local pedoclimatic scenarios (*Muscetta et al., 2023*).

Quick establishment of plant cover substantially mitigates soil erosion and curtails the release of asbestos fibers. Nonetheless, safeguards against intermittent exposures to the fibers, possibly through landslides or animal excavations, are imperative. Certain plants and lichens naturally thrive on asbestos-abundant substrates, allowing mature plant ecosystems to progressively envelop the debris entirely, thus fabricating a natural shield and conceivably diminishing the aerial spread of fibers. Phytoextraction is another approach, where plants that can accumulate specific elements are used to decrease soil metal pollutants by harvesting. Additionally, rhizodegradation or bioweathering involves using plants and/or soil microorganisms to induce chemical modifications in asbestos fibres. Microbial actions within the rhizosphere, primarily fueled by bacteria and fungi, have the potential to modify the chemical and physical attributes of the neighboring soil. Frequently, this zone is a habitat for mycorrhizal fungi, establishing symbiotic relationships with the roots of a multitude of plant species (*Jeevanantham et al., 2019; Thulasisingh et al., 2023*).

There are also non-mycorrhizal fungi in the rhizosphere, like saprotrophic fungi, which can serve as biofertilizers, enabling the mobilization of crucial plant nutrients directly from minerals through processes like rock degradation (*Daghino et al., 2010*).

The activities occurring beneath the soil surface can bolster microbial functionalities to transform the constitution of asbestos fibers.

Bioleaching emerges as a pioneering approach for addressing ACW treatment, originating from the conventional sulfuric acid leaching solutions renowned for metal extraction from various minerals (*Aarabi-Karasgani et al., 2010*). This technique harnesses volatile fatty acids (VFAs) generated through a specialized dark fermentation (DF) process, a distinctive anaerobic fermentation method designed to convert organic substrates into VFAs and a blend of H_2 and CO_2 gases (*Race et al., 2019*). Recent advancements in this field are reflected in numerous research initiatives focusing on the treatment of diverse organic wastes, including agricultural byproducts like lignocellulosic biomass and effluents from animal husbandry, using specially developed DF processes. These endeavors not only present economical solutions but also offer environmentally sustainable alternatives (*Trancone et al., 2022*).

To avoid self-inhibition arising from acidic pH levels, maintaining an optimal organic substrate supply is crucial to enhance hydrogen and organic acid production. A DF process utilizing glucose yields H_2 and VFAs, essential for dissolving the cement matrix and brucitic layers of chrysotile fibers in ACW. This is especially pertinent as chrysotile $Mg_3Si_2O_5(OH)_4$ undergoes a significant denaturation process in an acidic solution, leading to the dissolution of its brucitic $Mg(OH)_2$ layer and releasing Mg^{2+} ions and related calcium compounds found in ACW's cement matrix. Additionally, the residual VFAs and wastewater from the DF process can be further optimized by converting them into biomethane through an AD process (*Fig. 1.2.*).

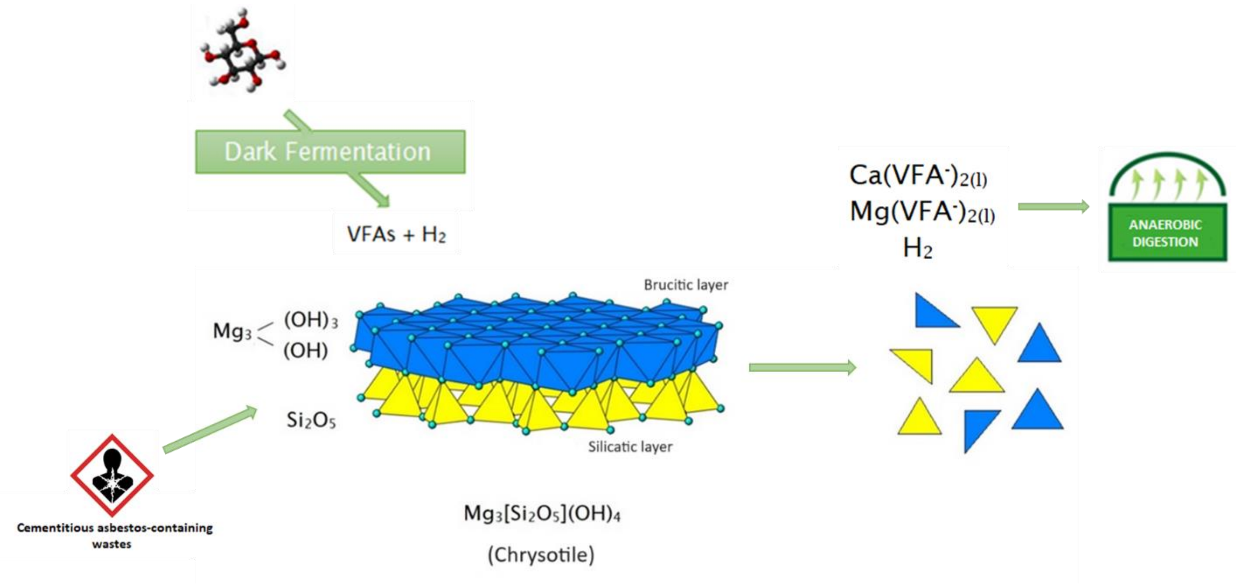

Figure 1.2. *Diagram of ACW treatment via bioleaching. The VFAs produced in the DF process leached the Ca and Mg contained in the ACW, denaturing the chrysotile fibers. Biomethane was obtained from the process wastewater through an AD process.*

Comparatively, bioleaching surpasses sulfuric acid leaching due to its eco-friendly nature, minimizing ecological risks through the utilization of organic compounds and microorganisms. Employing sustainable resources such as glucose, this approach is less corrosive and toxic, easing handling, storage, and disposal challenges, and yielding valuable byproducts like H_2 and VFAs, beneficial in energy and chemical industries. In contrast, sulfuric acid leaching, while proficient, is fraught with multiple downsides. Its corrosive attribute requires elaborate handling and stringent disposal strategies, intensifying operational intricacies and financial burdens (*Saha et al., 2023*). It's also notable for its high energy consumption and stringent regulatory requirements, posing substantial operational hurdles, with significant investments in safety infrastructure and potential limitations in recovery rates further emphasizing its constraints.

Bioleaching offers an advanced, eco-conscious, and versatile solution for managing and recovering resources from ACW, standing as a preferable alternative to the environmentally detrimental and operationally intricate sulfuric acid leaching technique.

1.7. Conclusions

The presence of a significant number of cases of asbestosis and mesothelioma both in non-working adults and in children is a wake-up call that underlines the urgency of targeted interventions and a concrete commitment in the management and treatment of asbestos. These data emphasize the dangers of asbestos not only for professionally exposed workers, but also for the general population, including children, highlighting the need for innovative and effective solutions for the decontamination and treatment of ACW. The current practice of encapsulating ACWs in glove bags and sealing them underground is not a suitable solution, as it leaves a toxic legacy for the future. Nature offers the possibility of transforming highly dangerous substances into less harmful compounds, and microbial alteration, phytoremediation and bioleaching represent promising strategies that could contribute to the detoxification and denaturation of asbestos fibres. Furthermore, the possibility of applying these technologies in areas with limited resources makes bioremediation and bioleaching optimal strategies to address the ACW problem in an ecologically sustainable and accessible way, overcoming current barriers and limitations. Bioleaching techniques are particularly interesting as they use resources and energy in an effective and sustainable way, making them valid options even for countries with limited technological and economic resources. These techniques have numerous advantages, such as low energy consumption, ecosystem conservation and their applicability in areas without advanced waste management infrastructure.

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Chapter 2

A combined system for asbestos-cement waste degradation by dark fermentation and resulting supernatant valorization in anaerobic digestion

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A combined system for asbestos-cement waste degradation by dark fermentation and resulting supernatant valorization in anaerobic digestion

Abstract

The use of biological processes for the treatment of asbestos cement waste (ACW) has gained interest in recent years. Nevertheless, this methodology is not yet consolidated because of the incomplete ACW conversion during the biological treatment and the consequent need for further treatments that generally require a high amount of energy and chemicals. In this study, the efficiency of both mesophilic and thermophilic dark fermentation (DF) fed with glucose in fed-batch conditions was assessed for ACW biological treatment. Both thermophilic and mesophilic DF of glucose resulted in a partial conversion of glucose into organic acids that successfully degraded all the asbestos fibers contained in an ACW sample. A hydrogen-rich biogas was produced as well: at the end of the mesophilic DF treatment 0.14 L_{H2} $g_{glucose}^{-1}$ were obtained. In addition, the anaerobic digestion (AD) of the DF supernatants led to the production of 0.38 L_{CH4} $gCOD^{-1}$.

2.1. Introduction

The term “asbestos” indicates six different minerals belonging to the class of silicates: actinolite, amosite, anthophyllite, chrysotile (white asbestos), crocidolite and tremolite. In particular, the World Health Organization (WHO) classified as asbestos the above-mentioned minerals in a respirable size with length >5 µm, width <3 µm, and length/ width ratio ≥3 (*Gaudino et al., 2020*). The reasons why asbestos, especially white asbestos, was widely used as a construction material are as follows: (i) low cost, (ii) high resistance to chemical agents and tensile stress; (iii) strong thermal, electrical, and acoustic insulation. Such properties have promoted its commercial success (*Paolini et al., 2019*). On the other hand, asbestos has been proved to be very dangerous: chrysotile fibers can cause lung cancer and mesothelioma. When inhaled, chrysotile fibers enter the lungs, which are gradually damaged over time because these fibers are resistant to degradation (*Xu et al., 2018*). As a result, a state of persistent inflammation is generated and DNA-damaging molecules are produced, thus favoring cancer (pleura mesothelioma) occurrence. The disease development is extremely slow since it generally takes more than 25 years (often 40–50 years) from exposure before cancer appears (*Vimercati et al., 2018*). Therefore, the presence of materials containing asbestos in buildings or industrial plants represents a risk for human health caused by the release and following inhalation of fibers. The risk increases proportionally with the friability level of the structures that contain asbestos, such as panels, beams, and pipes, and after demolition of wall partitions, roofs, sheets, etc. (*Neitzel et al., 2020*). For these reasons, the EU Regulation No.(1907)/2006 of December 18, 2006 prohibits the manufacture, placing on the market and use of asbestos fibers and of articles and mixtures containing these fibers added intentionally. In addition, EU Resolution P7_TA, (2013) 0093 encouraged the EU members to develop and share action plans for the removal of asbestos-containing materials from buildings and the sustainable management of the resulting ACW. As an alternative to landfilling, the treatment of ACW is an increasingly prominent issue in the sustainable management of these carcinogenic materials. Consequently over the last two decades numerous processes, such as mechanical, chemical, thermal, and hydrothermal, have been proposed for the denaturation of asbestos, thus producing harmless by-products (*Colangelo et al., 2011; Kusiorowski et al., 2015; Nam et al., 2014; Valouma et al., 2016*). Apart from some patented processes tested on real or pilot scale, such treatments are currently little-used due to the high consumption of energy and reagents (*Spasiano and Pirozzi, 2017*). As an example, a hydrothermal process based on the use of sulfuric acid at 100 ◦C for 24 h was successfully tested on laboratory scale for the denaturation of chrysotile ($Mg_3Si_2O_5(OH)_4$) contained in an asbestos-cement waste (*Nam et al., 2014*). However, this process required a large amount of sulfuric acid to dissolve the other constituents of the hardened cement paste, such as calcium-based compounds. Specifically, 0.49 g sulfuric acid were required for the hydrothermal treatment, carried out at 100 ◦C and lasting 24 h, of 1 g ACW. For this reason, innovative and low-cost biological processes could be used to treat asbestos fibers to overcome these limitations. Dark fermentation (DF) is a biological anaerobic process that can convert a biodegradable substrate into bio-hydrogen, carbon dioxide, and organic acids (OAs), mainly composed of lactic, butyric, and acetic acid (*Ghimire et al., 2015; Spasiano et al., 2017*). The most suitable substrates for DF processes are typically rich in carbohydrates, such as glucose, sucrose and starch blends (*Wang and Wan, 2009*). However other, more complex, substrates can be used, such as the organic fraction of municipal solid waste (*Shin et al., 2004; Gomez et al., 2006*), wastewater sludge (*Wang et al., 2019*), agricultural lignocellulosic waste (*Kumar et al., 2015; Motte et al., 2015; Hu et al., 2018*), and by-products from agro-food industry (*Buitròn et al., 2014; Mamimin et al., 2016; Ghimire et al., 2017*). DF of biodegradable compounds can be used as an efficient pre-treatment of the hydrothermal phase to denature the chrysotile fibers and, at the same time, reduce costs for energy and reagents supply (*Spasiano, 2018; Spasiano et al., 2019*). Basically, OAs produced by DF can dissolve not only the cement fraction, but also the brucitic layers of chrysotile fibers contained in ACW (eq (1)), thus minimizing the amount of acid required for the hydrothermal treatment.

$$Mg_3Si_2O_5(OH)_{4(s)} + 6OA_{(L)} \leftrightarrow 3Mg(OA^-)_{2(L)} + 2SiO_2 + 5H_2O \qquad \text{(eq1)}$$

This process represents a promising environmentally sustainable ACW treatment since different types of organic waste could be simultaneously used as biodegradable compounds. Moreover, the resulting bio-H_y can be used as a green energy source for the hydrothermal process. Furthermore, a large amount of OAs, such as acetic, butyric, lactic, formic, and propionic, are produced, and they can strongly reduce the requirement of reagents during the hydrothermal phase. Finally, the whole treatment chain can be completed with a mesophilic anaerobic digestion (AD) stage of the hydrothermally treated effluents. This stage promotes the conversion of the residual OAs into a biogas rich in methane that, in addition to bio-H_2, could be used to conduct the hydrothermal stage (*Race et al., 2019*) thus further reducing the global cost of the integrated treatment system. However, even if the consumption of acids to be added during the hydrothermal step was halved, the cost of the treatment is still high. Indeed, 0.25 kg sulfuric acid per kg ACW should be added to the DF effluent before the beginning of a hydrothermal treatment carried out at 100 ◦C and lasting 24 h (*Spasiano, 2018*).

To further reduce the cost of ACW treatment, this study was aimed at the elimination of the expensive hydrothermal phase by using only biological processes. To this purpose:

- the DF treatment was conducted in a fill-and-draw activated sludge system, named sequencing batch reactor (SBR), aimed at obtaining a complete degradation of the asbestos fibers by the biologically produced OAs;
- the DF phase was carried-out both under mesophilic (35 ◦C) and thermophilic (55 ◦C) conditions, to evaluate the effect of the operating temperature on the process efficiency;
- the treatment chain was completed by a mesophilic AD process, to convert the residual OAs contained in the DF supernatant into a methane rich biogas.

2.2. Material and methods

2.2.1. Materials

The digestate used as inoculum to perform both DF and AD processes was collected on two different days from a full-scale AD plant fed with dairy and livestock waste, managed by Powerinasce s. r.l. and located in Santa Maria La Fossa, Caserta, Italy. The ACW sample used for the experimental activities was the same characterized and utilized in previous studies conducted by the same authors of this manuscript (*Spasiano, 2018; Race et al., 2019*). It derives from an Eternit slate which was cleaned, milled and sieved to get a particle size below 2.0 mm. Specifically, it is characterized by a chrysotile content approximatively equal to 10% w/w, and Mg and Ca contents equal to 3.1% w/w and 30.0% w/w, respectively. D-(+)-Glucose (≥99.5%), used as biodegradable substrate, was purchased from Sigma Aldrich. Ammonium bicarbonate

(>99.0%) and potassium phosphate monobasic (>99%) were purchased from Sigma Aldrich, and used to provide N and P in the mixed liquor of DF bioreactors, as further described in section 2.2.2.

2.2.2 DF experimental apparatus and procedures

The digestate used for DF experiments was thermally treated to inhibit methanogens. In particular, 1 L of digestate was poured into a glass bottle and was subsequently placed for 1 h in a laboratory oven maintained at a constant temperature of 100 ◦C. The digestate used for AD experiments was used with no further treatment. The characterization of the two digestates is reported in Table 2.1.

	TS (g/L)	**VS (g/L)**	**Total Ca (mg/L)**	**Dissolved Ca (mg/L)**	**Total Mg (mg/L)**	**Dissolved Mg (mg/L)**
Digestate used for DF	79	52	1961	263	916	123
Digestate used for AD	48	31	1025	233	463	87

Table 2.1. *Inoculum characterization*

Afterwards, the thermally treated digestate was diluted with different volumes of demineralized water with the aim of evaluating the best conditions for carrying out the DF experiments in fed-batch. With a dilution ratio of 1:10 mL mL^{-1}, the amounts of sediments accumulated at the bottom of an Imhoff cone, after 1 h and 2 h of settling were 120 mL L^{-1} and 110 mL L^{-1}, respectively. By adopting this dilution ratio, the loss of microbial biomass due to the removal of the supernatant was avoided. Mesophilic and thermophilic DF experiments were carried out in 2.0 L borosilicate glass bottles closed with airtight screw caps, equipped with two sampling tubes for liquid and gaseous samples collection. Bottles were filled with approximately 1.0 L solution obtained by mixing 100 mL inoculum, 5 g ACW sample, 900 mL demineralized water, and 13 g glucose, thus setting a food to microorganism ratio of 2.65 (COD substrate (g)/VS inoculum (g)). Prior to running DF experiments, bioreactors were sparged with pure N_2 for 30 min to ensure anaerobic conditions. Successively, the bioreactors were magnetically stirred at 370 rpm and maintained at 35 ± 1 ◦C or 55 ± 1 ◦C to ensure mesophilic or thermophilic conditions, respectively. At the beginning, the DF experiments were carried out under batch-wise conditions until the H_2 production rate slowed down. Afterwards, the stirring system was tuned off for 2 h, to allow the sedimentation of the microbial biomass and ACW fragments, and 500 mL of supernatant was removed and replaced with 500 mL of a water solution containing 13 g glucose, 1.46 g $(NH_4)HCO_3$, and 0.23 g KH_2PO_4. In this way, the C:N:P ratio of DF experiments was continuously brought back to 100:5:1. This procedure was repeated until the conversion of the asbestos fibers in harmless by-products was completed.

2.2.3. AD experimental apparatus and procedures

The supernatant collected at the end of each DF feeding cycle was firstly characterized physically as well as chemically, and then stored at 4 ◦C until the end of the DF experiments. Later, the supernatant was anaerobically digested to produce bio-CH_4 through the conversion of the OAs and other residual biodegradable compounds present in the mixed liquor. The AD tests were carried out in duplicate at 35 ± 1 ◦C in 250 mL borosilicate glass bottles closed with airtight screw caps equipped with a sampling tube for the collection of gaseous samples.

2.2.4. Analytical methods

Total and volatile solids of digestate were measured by thermal processes at 105 ◦C and 600 ◦C, respectively, carried out on 100 mL samples. The total concentrations of Ca^{2+} and Mg^{2+} ions in the digestate were obtained by an acidic mineralization process. The concentrations of dissolved Ca^{2+} e Mg^{2+} ions in the digestate and the concentrations of dissolved Ca^{2+} e Mg^{2+} ions in the solutions were evaluated through atomic adsorption spectrometry (AAS) using a Varian Model 55B SpectrAA (Agilent Technologies, USA) F-AAS equipped with a flame (acetylene/air) and a deuterium lamp for background correction. The concentrations of organic acids, glucose, and ethanol were measured with a high-pressure liquid chromatography. Specifically, a Dionex LC 25 Chromatography Oven (P/N 051602 - Dionex, USA) equipped with a polymer-based cation-exchanger column Metrosep Organic Acids - 250/ 7.8 (Metrohm, Switzerland), a Dionex AD25 Absorbance Detector (Dionex, USA), and a Jasco RI-2031 (Jasco, Japan) refractive index detector were combined with a gradient pump Dionex GP 50 (Dionex, USA), eluting the samples with sulfuric acid 0.5 mM at the flow rate of 0.7 mL min^{-1}. The elution time was 21.5 min. COD concentration was measured by the close reflux colorimetric method based on the adoption of a H_2SO_4 digestion solution containing 20.432 g L^{-1} $K_2Cr_2O_7$. Specifically, 2.5 mL diluted sample was mixed in a 16 × 100 mm culture tube with 1.5 mL digestion solution and 3.5 mL H_2SO_4. The sampling tubes were closed with a screw cap, placed in a block digester at 150 ◦C for 2 h. Finally, the solution absorbance at 600 nm was measured with a WTW Photolab spectrophotometer 6600 UV-VIS (Wheilheim, Germany). The pH of the solution was monitored with a HI 98190 pH/ORP pH-meter (Hanna Instruments, USA). Biogas composition was characterized by a Varian Star 3400 gas chromatograph (Agilent Technologies, USA) equipped with a ShinCarbon ST 80/100 column (Restek, Germany) and a thermal conductivity detector. Argon was used as carrier gas with 1.4 bar front and rear end pressure. All the analysis were carried out in triplicate.

2.3. Results and discussion

2.3.1. DF treatment

The DF process in both mesophilic and thermophilic conditions was conducted for 167 h and consisted of three cycles with two nutrient and substrate additions, as summarized in *Table 2.2*. According to *Sekoai et al. (2021) and Zhou et al. (2018)*, DF comprises of (i) acetate fermentation, (ii) butyrate fermentation, (iii) propionate fermentation, (iv) lactate fermentation, and (v) ethanol fermentation. Amongst these pathways, acetate and butyrate pathways are regarded as the most common intermediates during the acidogenic conversion of organic feedstocks along with H_2 in both thermophilic and mesophilic conditions.

	Duration (h)	Cumulative duration (h)
Cycle I	64	64
1st feeding procedure	2	66
Cycle II	31	97
2nd feeding procedure	2	99
Cycle III	68	167

Table 2.2. *Timeline of the operations of the DF reactors*

However, the production of these by-products is also governed by other operational parameters such as pH, temperature, substrate type, organic loading rate, partial pressure, and hydraulic retention time. In general, it can be stated that high load experiments (in terms of F/M ratios) are characterized by relevant OAs accumulation in bioreactors, which can lead to inhibiting phenomena due to low pH values. On the other hand, a high F/M ratio is able to positively affect the butyric acetic ratio (B/A), which is an important managing parameter to ensure relevant hydrogen yields (*Pandei et al., 2022; Policastro et al., 2021, 2022*). As shown in Fig. 2.1., in this study the biological conversion of glucose resulted in the production of high amounts of OAs, mainly acetic, butyric, and lactic acid, under mesophilic as well as thermophilic conditions. More in detail, even if acetic acid showed the same concentration trends in both thermal conditions, different concentrations of other OAs were observed when the operating temperatures were different. Indeed, at the end of the DF process carried out at 35 ◦C, butyric and lactic acid concentrations accounted for 6300 and 1900 mg L^{-1}, respectively (Fig. 2a), whereas, at the end of the DF process carried out at 55 ◦C, the concentration of lactic acid, 4600 mg L^{-1}, was twice the concentration of butyric acid (Fig. 2.1.b). Apart from the lactic acid accumulation due to the initial stress conditions of the inoculum (*Luongo et al., 2019*), thermophilic DF showed higher hydrogen yields with lower butyric acid accumulation in bioreactors according to the recent literature (*Dessì et al., 2018a; Słupek et al., 2020; Pradhan et al., 2021*). In addition, analysis of liquid samples withdrawn during the biological processes showed the presence of other organic compounds, such as ethanol and formic acid, with concentrations mainly ranging between 500 mg L^{-1} and 1500 mg L^{-1}.

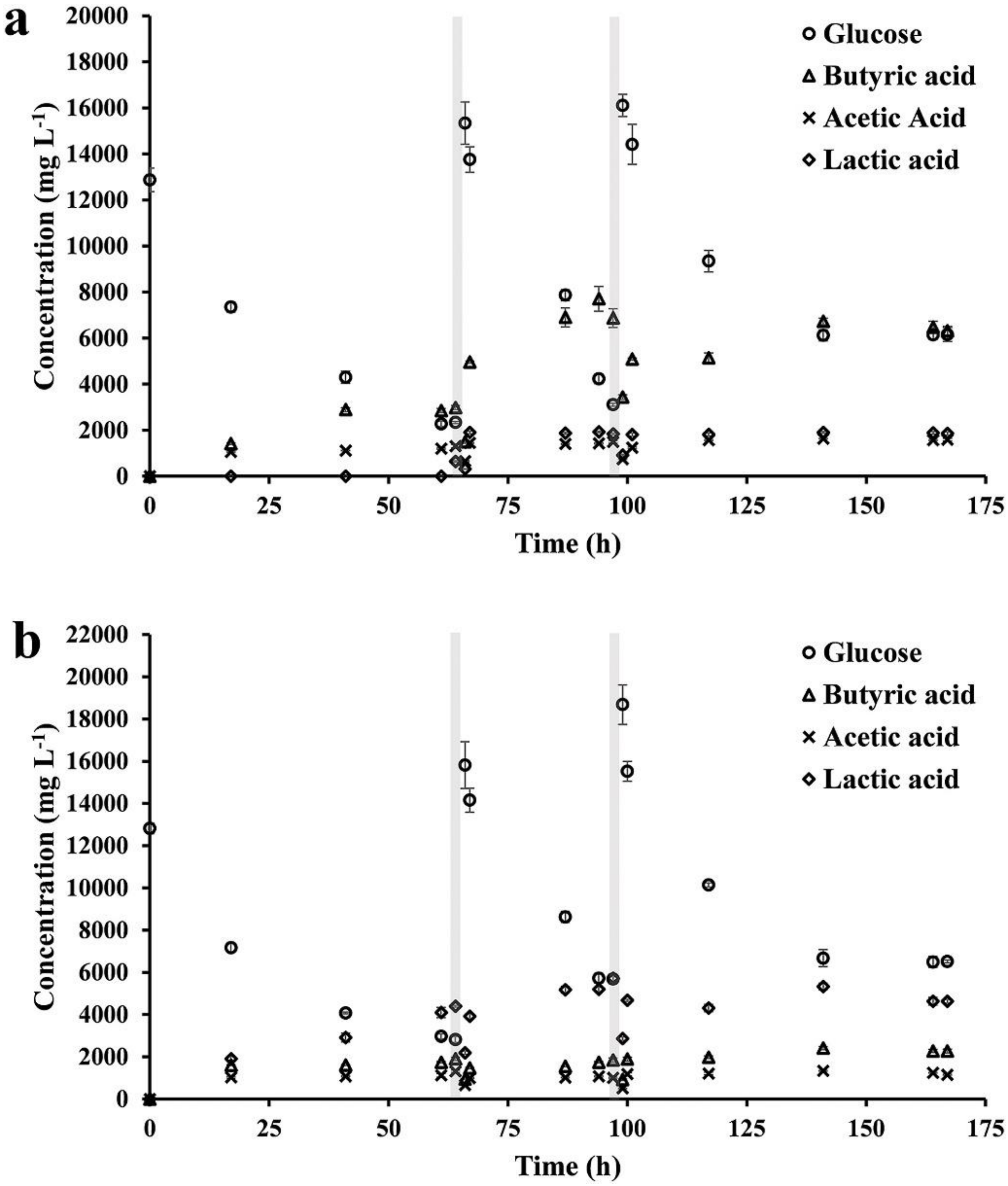

Fig. 2.1. *OAs production under mesophilic (a), and thermophilic (b) conditions: thick grey lines mark the two feeding procedures*

Besides OAs and dissolved compounds, another valuable by-product from the glucose fermentation is bio-H_2. More in detail, during the first step of the DF process (i.e. between 0 and 64 h), a higher bio-H_2 production was observed under mesophilic rather than under thermophilic conditions. However, during the second DF process step (i.e. between 66 and 99 h) the cumulative production of bio-H_2 under thermophilic conditions was higher than that obtained under mesophilic conditions, thus reaching a value of 5.2 L. At the end of the DF process (i.e 167 h), the cumulative bio-H2 production was 6.4 L and 4.9 L from experiments conducted under thermophilic and mesophilic conditions, respectively. Regarding the CO2 production, the trend follows the bio-H_2 cumulative production under mesophilic and thermophilic conditions, as reported in Fig. 3. According to *Dessì et al., 2018b,* the low bio-H_2 production at the beginning of the thermophilic experiments is probably due to a slow adaptation of fermentative microorganisms. Indeed, the sludge used as inoculum was collected from a mesophilic anaerobic digester, and therefore already adapted to mesophilic conditions. According to the literature (*Cakır et al., 2010; Kargi et al., 2012*), when microorganisms adapted to thermophilic conditions, a higher bio-H_2 production (*Fig. 2.2.*) was observed from a DF process conducted at 55 ◦C rather than at 35 ◦C.

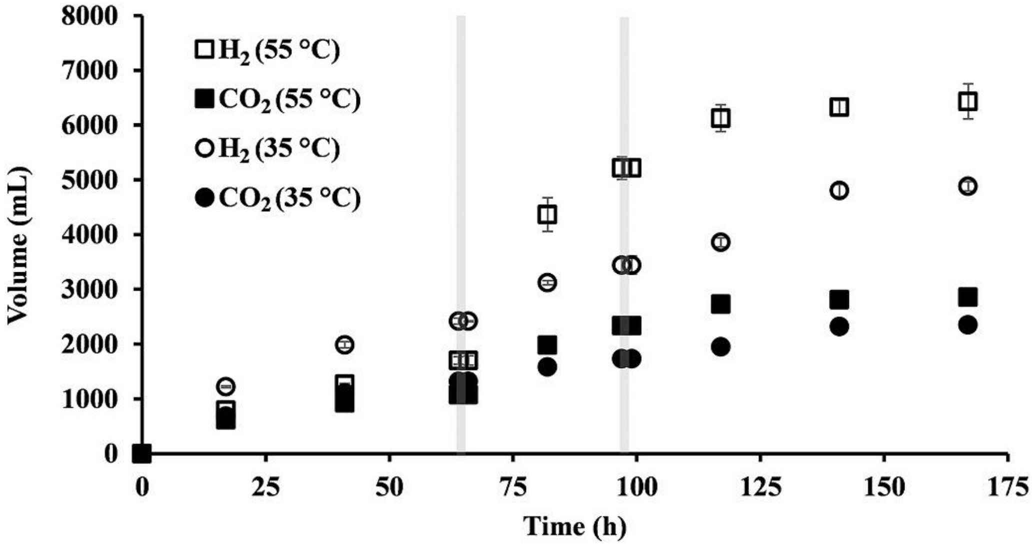

Fig. 2.2. *Bio-H2 (empty symbols) and CO2 (full symbols) production under mesophilic (○,●) and thermophilic (□,■) conditions: thick grey lines mark the two feeding procedures*

This result is a consequence of the enhanced conversion efficiency of the biodegradable substrate into biogas induced by the temperature (Fig. 2.2.). Indeed, the total amount of lactic, acetic, and butyric acid at the end of the DF process were 9800 mg/L and 8100 mg L^{-1} under mesophilic and thermophilic conditions, respectively. In addition, by considering the theoretical COD of all the detected catabolites at the end of the DF in mesophilic and thermophilic conditions, the COD conversions were 9.1% and 28.3%, respectively. Despite the low OAs production under thermophilic conditions, the pH from the DF process under both thermal conditions shows the same trend, to the extent that the values almost overlap (*Fig. 2.3.)* in all the experimental points. At the end of each step of the DF process, the pH reached values in the range of 4.1–4.6 regardless of the temperature. Notably, due to the accumulation of the OAs in the mixed liquor, the second and third step of the DF process began with pH values equal to 6.6 and 6.0 under mesophilic and thermophilic conditions, respectively. The lowest pH value at the beginning of the third step of the DF process decreased the bio-H_2 production rate. As reported in Fig. 4, at the beginning of the DF process under mesophilic conditions, the pH decreased faster than under thermophilic conditions.

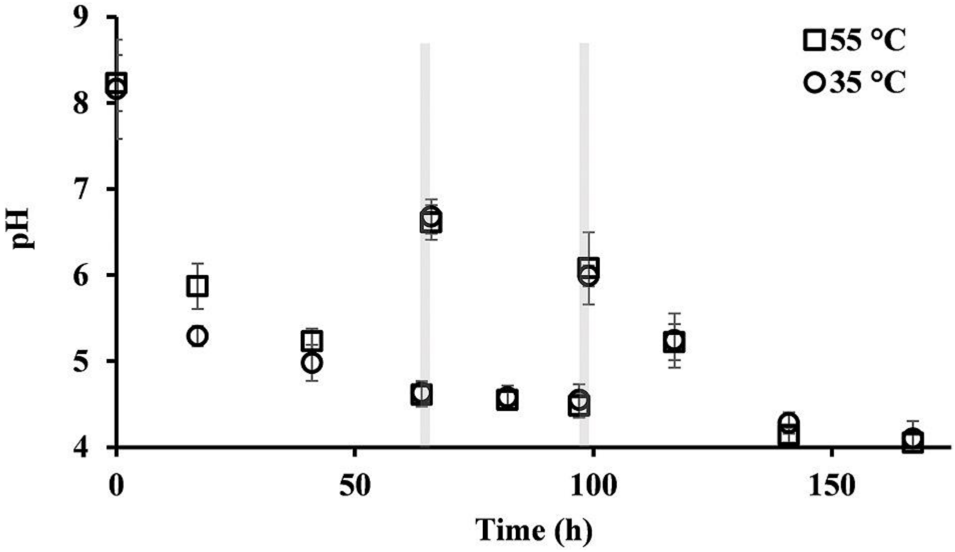

Fig. 2.3. *pH trends in mesophilic (○) and thermophilic (□) conditions: thick grey lines mark the two feeding procedures*

Such occurrence resulted in the quickest dissolution of the suspended Ca (*Fig. 2.4.a*) and Mg (*Fig. 2.4.b*) in the mixed liquor. Such compounds are present in the 5 g L^{-1} of ACW added, as well as in the inoculum, i.e. the sludge collected from the anaerobic digestion of dairy and livestock waste that are commonly rich in Ca and Mg, especially dairy waste. Specifically, the raw inoculum was characterized by Ca and Mg total concentrations of 1961 mg L^{-1} and 916 mg L^{-1} (*Table 2.2.*). Before the experiments, 100 mL inoculum was diluted with 900 mL deionized water achieving a final concentration of Ca and Mg equal to 196 mg L^{-1} and 92 mg L^{-1} in the reactors, respectively. Consequently, the total amounts of Ca (Ca_0) and Mg (Mg_0) contained in the solution at the beginning of the experiments are calculated as follows:

$$Ca_0 = Ca_{inoculum} \cdot DIL \cdot V_{sol} + ACW \cdot \%_{Ca} \cdot V_{sol} = 1696\ mg \qquad \text{(eq.2)}$$

$$Mg_0 = Mg_{inoculum} \cdot DIL \cdot V_{sol} + ACW \cdot \%_{Mg} \cdot V_{sol} = 246.6\ mg \qquad \text{(eq.3)}$$

Where: $Ca_{inoculum}$ and $Mg_{inoculum}$ are the total Ca and Mg concentrations in the digestate (*Table 2*); DIL is the dilution ratio of the digestate; V_{sol} is the working volume equal to 1.0 L; ACW is the initial concentration of the asbestos cement waste (5 g L^{-1}); $\%_{Ca}$ and $\%_{Mg}$ are the calcium and magnesium concentrations contained in the asbestos cement sample. In the presented experimental campaign, they were 30% and 3.1%, respectively. As reported in *Fig. 2.5.*, at the end of the first DF cycle the concentrations of Ca and Mg ions reached approximatively 1300 mg L^{-1} and 175 mg L^{-1}, respectively. Consequently, 77% of Ca and 71% of Mg were dissolved by 64 h of incubation. At the end of the second DF cycle the dissolution of both Ca and Mg was almost complete. Indeed, during the third fermentation step, concentrations of Ca and Mg remained almost constant. It is noteworthy to highlight the positive buffer effect provided by the cementitious matrices. Indeed, the absence of suspended Ca and Mg based compounds during the third step led to a quick pH drop in the mixed liquor to the lowest values (*Fig. 2.4.*), thus reducing the biogas yield (*Fig. 2.3.*) as well as the substrate conversion rate (*Fig. 2.2.*).

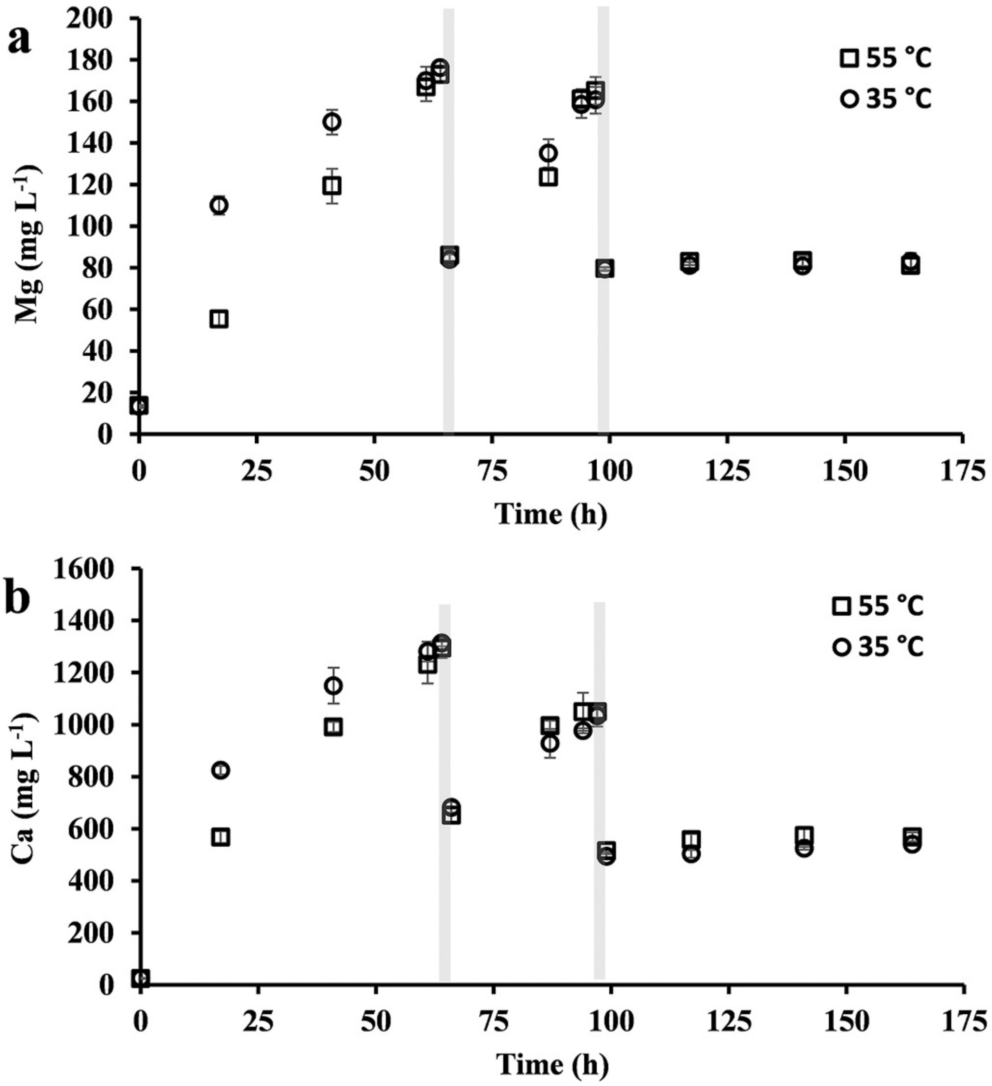

Fig. 2.4. *Concentrations of Ca (a) and Mg (b) ions during the DF process carried out under mesophilic (○), and thermophilic (□) conditions: thick grey lines mark the two feeding procedures*

The occurrence of a plateau for the concentrations of Ca and Mg ions during the third step of DF was not sufficient to assess the efficiency of the ACW treatment. Indeed, with regard to the fate of the Mg ion, which is representative of the white asbestos fibers ($Mg_3Si_2O_5(OH)_4$) conversion, the following phenomena may have occurred:

- some chrysotile fibers or fibrils were still present in the reactor at the end of the third cycles and the OAs produced during the DF processes were unable to dissolve their respective brucitic layers;
- some chrysotile fibers or fibrils did not settle properly and were removed from the reactors suspended in the supernatants.

Consequently, a mass balance on both Ca and Mg was carried out singularly. By considering the amounts of Ca and Mg dissolved in the 500 mL of supernatant collected from the DF bioreactors at the end of each of the three cycles and the amount of Ca and Mg ions in the 500 mL solution left in the bioreactors after the withdrawal of the last supernatant, it can be proved that all the suspended Ca and Mg based compounds contained initially in the bioreactors were dissolved (*Fig. 2.5.*).

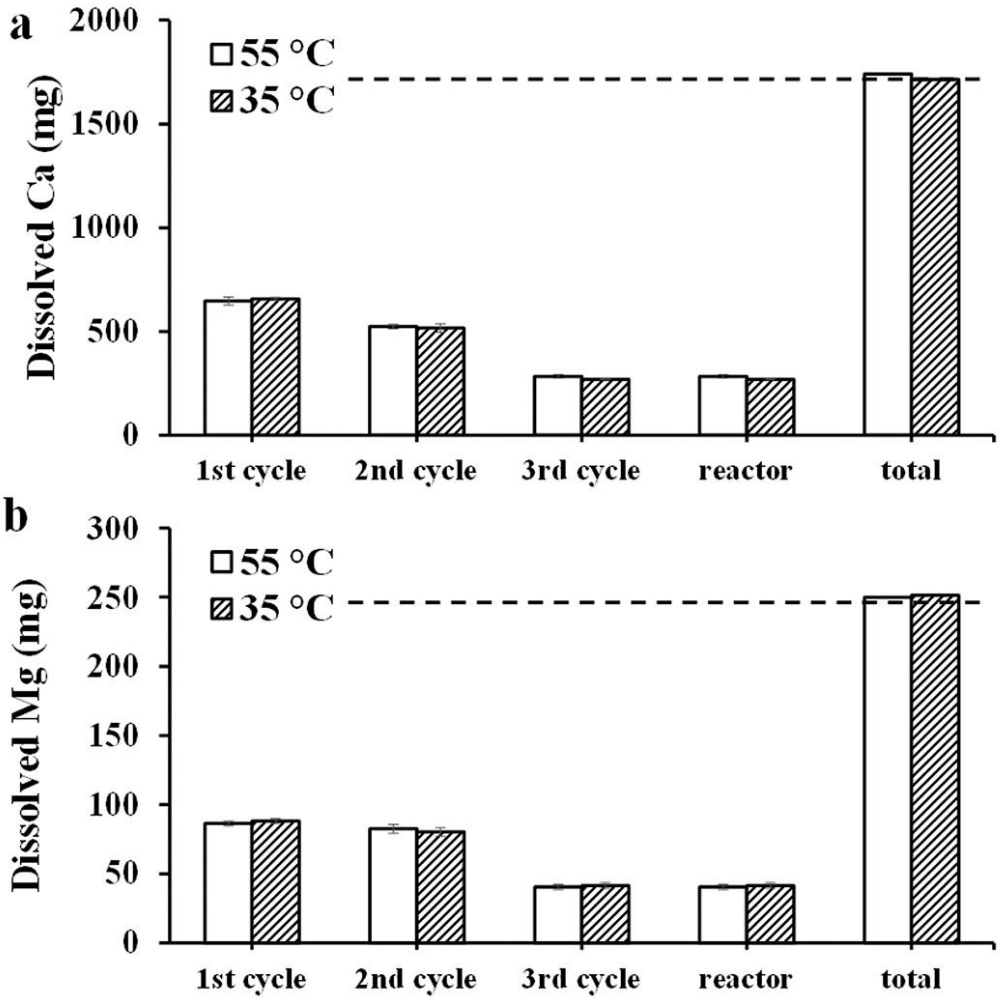

Fig. 2.5. *Mass balance on calcium (a) and magnesium (b). The dashed lines represent the* Ca_0 *and* Mg_0 *amounts evaluated by eq. 2 and 3, respectively*

Indeed, the sum of dissolved Ca and Mg contained in the six supernatants (as a consequence of 2 thermal conditions and 3 steps for each DF process) and in the solution left in the bioreactors equaled the Ca_0 and Mg_0 amounts (*Fig. 2.5.*, dashed lines) evaluated with eq. 2 and 3. On this basis, since all the suspended Mg was dissolved, all the white asbestos fibers contained in the ACW were successfully treated (eq. (1)). The DF process operated in fed-batch conditions is therefore an effective treatment of ACW, regardless of the operative temperature. However, in fermentation processes, temperature has a relevant impact as it can affect the biochemical reaction in five main ways: i) increase in reaction rates with increasing temperature; ii) decrease in reaction rate with increasing temperature above optimum; iii) decrease in yields, and increase in half saturation constants, due to increased turnover and maintenance energy with increased temperature; iv) shifts in yield and reaction pathway due to changes in thermodynamic yields and microbial population; v) increase in death rate due to increased lysis and maintenance. Although in mixed cultures DF processes there are many undetected side reactions, which lead to the production of undetected by-products, the main change from mesophilic to thermophilic conditions is due to homoacetogenesis reaction, which is outcompeted for molecular hydrogen by other metabolic pathways when increasing the working temperature (*Sekoai et al., 2021*). This leads to a higher hydrogen and lower acetate accumulations in bioreactors in thermophilic conditions, with consequences on hydrogen partial pressure and on subsequent metabolic activities taking place during carbohydrates bioconversion. In DF processes, temperature controls the formation of VFAs, microbial communities, enzymatic activities, and conversion of substrates (*Kim et al., 2006*). VFAs are generated under both mesophilic (20–45 ◦C) and thermophilic (>45 ◦C) conditions, but thermophilic processes are mostly adopted in VFAs production as they lead to several benefits such as high digestibility of substrates, inhibition of undesired microbes, and minimizes the risks of contamination (*Sekoai et al., 2021*). It is noteworthy to highlight that, beside the higher bio-H_2 production observed under thermophilic conditions, no other advantages were found compared to the mesophilic conditions in terms of ACW treatment efficiency and degradation rate. This result is likely due to the use of a simple organic substrate, such as glucose, whose biodegradation cannot take advantage of the faster hydrolysis induced by thermophilic conditions. Consequently, the DF process could be conducted under thermophilic conditions for the treatment of ACW when more complex substrates are used.

2.3.2. AD treatment of the DF effluents

Since supernatants deriving from the DF process are rich in OAs, they need a further treatment aimed at lowering the COD concentration in order to dispose of them sustainably. AD is a well-known technology for the stabilization of organic wastes, and it is performed in single stage or double stage configurations. In the second case, methanogenic activities are completely separated from the acidogenic stage, with consequent increase of methane yields and decrease of inhibition risks due to acidic pH level (*Kovalev et al., 2022; Ariunbaatar et al., 2015*). In the present study, such a result has been obtained by applying the second stage of an AD process, which is capable of converting the organic compounds, mainly OAs and residual glucose (*Table 2.3.*) into a biogas rich in bio-CH_4.

	Glucose (mg/L)	**Lactic A. (mg/L)**	**Butyric A. (mg/L)**	**Acetic A. (mg/L)**	**Formic A. (mg/L)**	**Ethanol (mg/L)**	**COD (g/L)**
S1	2340	645	2980	1310	810	510	25.4
S2	3110	1840	6871	1490	1050	550	29.1
S3	6160	1860	6317	1590	1020	800	45.1
Smix	3850	1460	5410	1450	920	640	33.7

Table 2.3. *Characterization of the single supernatants deriving from the mesophilic DF process and their mix (Smix)*

To this purpose, an AD process on the three supernatants obtained from the mesophilic DF treatment, namely S1, S2, and S3 was carried out. In addition, the AD of the solution (Smix) obtained after mixing the three supernatants (S1:S2:S3 = 1:1:1) was performed. More in detail, 20 mL of each solution were mixed with 130 mL fresh digestate, characterized by a VS content equal to 31 g L^{-1} (*Table 2*), thus obtaining F/M ratios in the range of 0.13–0.22 COD substrate (g)/VS inoculum (g). In this way, it was possible to ensure the complete bioconversion of organic compounds into methane as it is a common practice to fix the F/M ratio lower than 0.5 COD substrate (g)/VS inoculum (g) to avoid anabolic reaction increasing the net methane yields (*Franca et al., 2018; Khadka et al., 2022*). As a result, after 30 d of incubation a gross bio-CH_4 production ranging between 266 mL and 421 mL was observed from AD process fed with S1 and S3, respectively (*Fig.2.6.*).

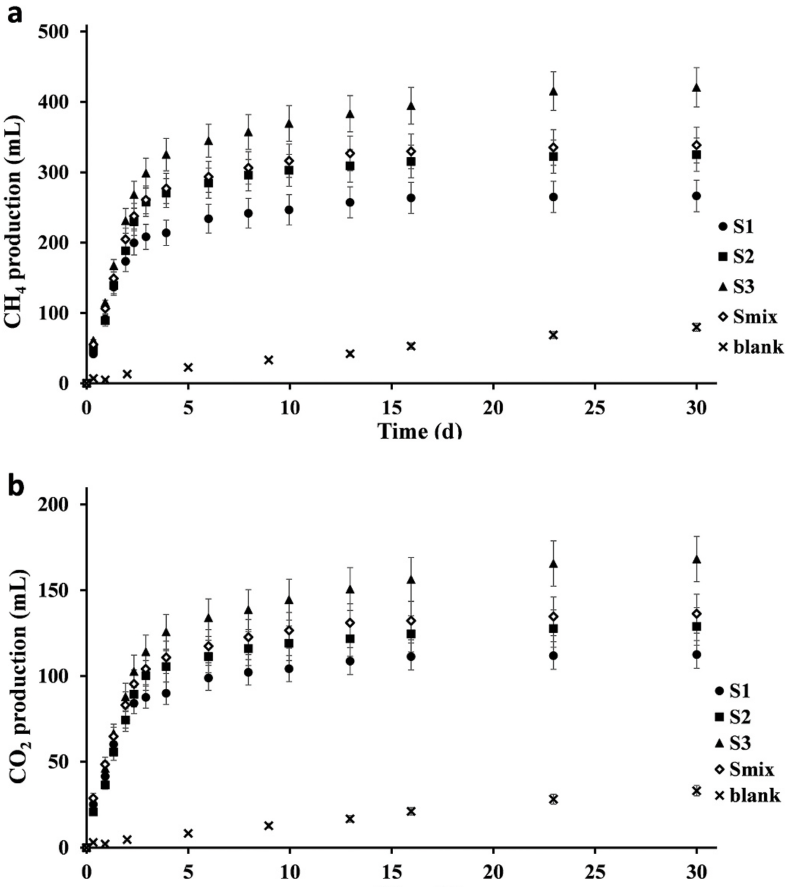

Fig. 2.6. *Bio-CH_4 (a) and CO_2 (b) production from the AD of the supernatants of the DF under mesophilic conditions. The blank test was carried out by mixing 20 mL distilled water with 130 mL digestate*

In particular, by subtracting the amount of bio-CH_4 produced from the blank test (80 mL), it has been possible to evaluate an average net methane yield from the AD of mesophilic DF supernatants. Furthermore, the AD process fed with Smix resulted in the net production of CO_2 and bio-CH_4 equal to 103 mL and 259 mL, respectively, corresponding to a methane yield equal 0.38 LCH4 $gCOD^{-1}$. This net methane yield is close to the theoretical value reported in *Yeshanew et al. (2016)*, and it is comparable with many recent reports (*Achouri et al., 2017; Di Capua et al., 2021*).

Specifically this result was achieved thanks to the low F/M ratio, which led to the complete conversion of substrates in AD bioreactors. Consequently, besides the 4.9 L of bio-H_2 produced from the DF process performed to treat ACW, the AD process fed with the total production of DF supernatant (i.e. 1.5 L of Smix characterized by a COD concentration of 33.7 g L^{-1}) may produce 19.7 L of bio-CH_4. In addition to the valorization of DF supernatants, the sludge left in the reactor at the end of the third DF step could be also reused. As an example, the sludge could be used as an already acclimatized inoculum for further DF treatments of ACW. However, part of the sludge must be periodically removed from the bioreactor to avoid an excessive accumulation of suspended solids. Indeed, beside the biomass that reproduces during the DF treatments, it is necessary to consider the accumulation of silica particles, deriving from the ACW treatment. Specifically, even if 7.9 g/L TS (VS/TS = 65.8%) were added to the DF reactor through the inoculum, the analysis of the 500 mL solution left in the DF mesophilic reactor at the end of the ACW treatment revealed the presence of 10.1 g TSS, 67.3% of which consisted of VSS. Consequently, the sludge deriving from the DF treatment could also be sent to the AD treatment.

2.3.3. Future research perspective

Even if this first attempt at the biological treatment of ACWs by DF and AD gave positive results, the following topics need to be investigated in future studies in order to develop this treatment chain at real scale:

- the DF treatment for the ACW degradation should be tested with other inocula and biodegradable substrates;
- in this study the ACW was milled before the DF and particles with sizes <2.0 mm were used. Consequently, other DF experiments should carry out with larger ACW pieces;
- the efficacy of DF on the degradation of other asbestos fibers, such as amosite and crocidolite, should be investigated;
- pilot scale reactors should be employed to evaluate the energy balance of the whole treatment.

2.4. Conclusions

This study proves that the DF process fed with glucose and operated in fed-batch conditions is effective in treating ACW under both mesophilic and thermophilic conditions. Indeed, during the DF process, glucose was partially converted in OAs, which dissolved all the brucitic layers of the chrysotile contained in 5 g L^{-1} of ACW, as well as in a bio- H_2 rich biogas. More in detail, cumulative bio-H2 productions equal to 6.4 L and 4.9 L were obtained under thermophilic and mesophilic conditions, respectively. The ACW treatment by DF could be followed by the AD of the supernatant collected from the DF bioreactors, since 0.38 L_{CH4} $gCOD^{-1}$ can be produced from the digestion of OAs and residual glucose. Based on these findings, the main advantages of this ACW treatment chain compared to the others reported in the literature are: the productions of H_2 and CH_4; adoption of mild operative temperature (35 ÷ 55 ◦C) and pressure (~1 atm) conditions; no requirement for nonrenewable reagents, such as inorganic acids. Furthermore, the degradation of asbestos fibers through DF may be a very promising process in a context of circular economy if waste biodegradable substrates, less valuable than glucose, are used.

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Chapter 3

Bioleaching Treatment of Concrete Waste from Construction and Demolition Waste (CDW): Advantages and Implications

This chapter has been conceptualized and written. is ready for submission to a scientific journal for publication as: Trancone, G., et al. (2023). Bioleaching Treatment of Concrete Waste from Construction and Demolition Waste (CDW): Advantages and Implications.

Bioleaching Treatment of Concrete Waste from Construction and Demolition Waste (CDW): Advantages and Implications

Abstract

Concrete, as one of the most widely used construction materials, provides exceptional durability, strength, and adaptability to diverse environments, making it essential in modern construction. However, the construction industry generates substantial waste, including concrete debris, posing challenges for waste management and environmental sustainability. With rapid urbanization and infrastructure development, the global production of construction and demolition waste (CDW) has surged, straining waste management systems and natural resources. The treatment and reuse of CDW offer environmental benefits by conserving resources and reducing landfill waste. Nevertheless, implementing effective CDW treatment and reuse processes can be technically complex and expensive. Bioleaching, an innovative approach using microorganisms to degrade and extract valuable components from waste, has shown promise in environmental remediation and resource recovery. In the context of concrete CDW, bioleaching involving the action of volatile fatty acids (VFAs) produced in dark fermentation processes can weaken the material, leading to a decrease in its weight and volume. This innovative approach not only offers a sustainable and cost-effective alternative to conventional methods but also contributes to the circular economy reducing environmental impact.

3.1. Introduction

Concrete is one of the most widely used construction materials due to its exceptional durability, strength, and versatility. Its widespread application can be attributed to its ability to adapt to diverse environments and provide long-lasting structures (*Naik T. R., 2008*). The composition of concrete typically consists of four main components: cement (10% to 15%) is the binding agent in concrete that provides strength and durability; aggregates (60% to 75%) include fine aggregates, such as sand and coarse aggregates, such as gravel or crushed stone. They occupy the largest portion of concrete and provide bulk and stability to the mixture; water is necessary for the hydration of cement, which leads to the hardening of the concrete mixture; additives (Less than 5%) are optional components added to enhance specific properties of the concrete, such as workability, strength, or durability as chemical admixtures, fibers, or mineral admixtures like fly ash or silica fume. The proportions of these components can vary depending on the desired strength, durability, and workability of the concrete (*Dhawan et al., 2021*). However, the construction industry generates a significant amount of waste, including concrete debris, which poses challenges for waste management and environmental sustainability. The world's production of construction and demolition waste (CDW) presents a significant and pressing problem. The overall CDW generation in 40 countries worldwide reached more than 3.2 billion tonnes annually until 2020 and this trend is increasing constantly (*Yuan et al., 2023*). With rapid urbanization and infrastructure development, the volume of CDW generated globally has skyrocketed, placing immense strain on waste management systems and natural resources. CDW accounts for a substantial portion of total waste generated worldwide, contributing to environmental degradation and resource depletion. The treatment and reuse of CDW is an essential aspect of sustainable waste management and resource conservation in the construction industry. CDW typically consists of materials such as concrete, bricks, wood, metals, plastics, and insulation, which are generated during the construction, renovation, or demolition of buildings and infrastructure (*Whittaker et al., 2021*). The traditional approach of disposing of CDW in landfills is not only environmentally damaging but also wasteful, as it squanders valuable resources. However, the implementation of effective treatment and reuse strategies has the potential to significantly mitigate these negative impacts. Treatment of CDW involves several processes aimed at sorting, separating, and recycling different types of materials (*Galàn et al., 2019*). The first step is the segregation of CDW at the source, where different materials are separated to facilitate subsequent recycling.

Advanced sorting technologies, including manual and mechanical techniques, such as magnets, sieves, and optical sensors, are used to segregate materials efficiently. Once sorted, the materials undergo further processing. Materials that cannot be recycled directly can often be repurposed or reused in various ways. Crushed concrete can be used as a base material for roads, parking lots, and foundations (*Xu et al., 2022*). Bricks and tiles can be reclaimed and used for landscaping or as decorative elements (*Almssad et al., 2022*). Wooden beams and planks can be salvaged and reused in construction or repurposed for furniture and other woodwork (*Yadav et al., 2021*). By incorporating reclaimed materials into new projects, the demand for virgin resources is reduced, leading to significant environmental benefits. The treatment and reuse of CDW offer numerous benefits, there are also some disadvantages to consider. Firstly, implementing effective CDW treatment and reuse processes can be technically complex and expensive. The sorting, separation, and recycling of various materials require specialized equipment, skilled labor, and substantial investments in infrastructure (*Luciano et al., 2022*). Moreover, certain types of CDW, such as contaminated or hazardous waste as asbestos, pose additional challenges and require careful handling and disposal, adding to the overall cost and complexity of the treatment process (*Stevulova et al., 2022*). Additionally, the quality and suitability of recycled materials may vary, particularly if there are inconsistencies in the sorting and processing methods. This can result in concerns regarding the structural integrity or performance of recycled materials in new construction applications (*Nedeljković et al., 2021*). Furthermore, the transportation of CDW to treatment facilities can contribute to carbon emissions and traffic congestion, especially if there is a lack of local recycling options (*Fufa et al., 2023*). The market demand for recycled CDW materials can fluctuate, which may limit the economic viability and long-term sustainability of CDW treatment and reuse initiatives. Overcoming these disadvantages requires careful planning, investment in research and development, and continuous improvement in CDW management practices (*Yu et al., 2022*). Bioleaching treatment of concrete construction waste is an innovative approach that harnesses the power of microorganisms to degrade and extract valuable components from the waste. Concrete construction waste typically consists of cementitious materials, aggregates, and residual organic compounds. Bioleaching utilizes the volatile fatty acids (VFAs) produced by microorganisms in anaerobic biological processes of dark fermentation to break down these components and facilitate the recovery of useful resources (*Cetecioglu et al., 2022*). Dark fermentation is an anaerobic biological process in which microorganisms convert organic substrates, such as agricultural waste, food waste, or wastewater, into valuable end-products in the absence of light (*Singh et al., 2022*). Unlike traditional fermentation processes, dark fermentation occurs in the absence of oxygen, utilizing a diverse consortium of microorganisms to break down complex organic compounds through a series of metabolic reactions. The process typically results in the production of hydrogen (H_2), VFAs and alcohols as the primary end-products. Dark fermentation offers significant potential for bioenergy generation, waste management, and resource recovery, making it an attractive avenue for sustainable energy production and circular economy practices (*Policastro et al., 2022*). The microorganisms secrete enzymes that catalyze the breakdown of organic ans inorganic compounds, thereby aiding in the decomposition of the waste (*Bhardwaj et al., 2022*). This process not only reduces the volume of waste but also releases trapped minerals and metals from the concrete matrix. These minerals and metals can then be recovered and reused in new construction applications or for other purposes (*Sormunen et al., 2019*). Bioleaching treatments involving the action of volatile fatty acids (VFAs) produced in dark fermentation processes, such as anaerobic moving bed biofilm reactors (A-MBBR), have emerged as a promising approach in environmental remediation and resource recovery. Dark fermentation processes, specifically A-MBBR, provide a controlled environment for the anaerobic degradation of organic substrates to colonise the K1 media in the reactor with acid-producing microorganisms. The biofilm formed on these media is a function of the organic load associated with the incoming inoculum. Unlike the other biofilm processes, the media in this case are free to move and therefore do not maintain fixed positions either in or relative to the reactor. The growth of a biofilm on a substrate is the result of the interaction between biological processes and substrate transport processes. In particular, biofilm formation is mainly due to the growth of microbial cells and the production of extracellular polymers. The development of the biofilm therefore varies depending on the composition of the inoculum and the transport processes; the availability of substrates for the microorganisms within the biofilm depends on these (*Fang H., 2010*). Bioleaching of calcium into concrete from CDW through the action of VFAs produced in DF A-MBBR processes can lead to weakening of the material, resulting in a decrease in its weight and volume. The weakening of the concrete also causes it to crumble and break down more easily, which further contributes to the decrease in weight and volume, making it less dense and more porous *(Li et al., 2022)*. These changes make concrete more susceptible to further degradation and breaking, ultimately affecting its potential for recycling or reuse in new construction applications. Bioleaching offers a sustainable and environmentally friendly alternative to traditional waste management methods by minimizing the need for energy-intensive processes and reducing the reliance on finite resources.

3.2. Materials and Methods

3.2.1. Materials

The digestate used as inoculum to perform the DF A-MBBR processes was collected from an Anaerobic Digestion Plant fed with dairy and livestock waste, managed by Powerinasce srl and located in Santa Maria La Fossa, Caserta, Italy. More in detail, the digestate used for the DF experiments was heat treated (1 h at 100 °C) to deactivate the methanogens *(Ghimire et al., 2015b)*.

C_{TS} (g/L)	**C_{VS} (g/L)**	**CODs (g/L)**	**CODt (g/L)**	**Dissolved Ca (mg/L)**
60.33	22.75	20.14	61.87	279.70

Table 3.1. *Inoculum characterization*

The supports used for the development of the biofilm are Anox-Kaldnes® carriers of type P02/K1 in HDPE.

Diameter (mm)	Heigh (mm)	Density (kg/m^3)	Protected Surface (m^2/m^3)	Filling ratio (%)	Reactor Surface (m^2/m^3)
9.1	7.2	0.95	500	30	150

Table 3.2. *Characteristics of the K1 carriers, filling ratio and effective surface in the reactor*

The CLS samples used for the experimental activities were made in the laboratory using CaCEM IV/B 32.5 R pozzolanic cement and FINBOND fiber-reinforced siliquarzite sand, with a ratio of 60:40 and demineralized water. The CLS samples are characterized by a Ca^{2+} content of 30% w/w.

D-(+)-Glucose (≥ 99.5 %), used as biodegradable substrate, was purchased from Sigma Aldrich. Micronutrients were supplied by adding to the medium $NaC_5NO_4H_8$, 442 mg/L; $MgSO_4.7H_2O$, 200 mg/L; yeast extract, 300 mg/L; $C_6H_5FeO_7$, 24.5 mg/L; NaCl, 400 mg/L; Na_2HPO_4, 497 mg/L; KH_2PO_4, 3000 mg/L; $NaHCO_3$, 700 mg/L; $CaCl_2H_4O_2$, 75 mg/L and 1mL/L of a trace elements solution, whose composition is following reported: $ZnCl_2$, 70 mg/L; $MnCl_2$ $4H_2O$, 100 mg/L; H_3BO_3, 60 mg/L; $CoCl_2.6H_2O$, 200 mg/L; $CuCl_2.2H_2O$, 20 mg/L; $NiCl_2.6H_2O$, 20 mg/L; $NaMoO_4.2H_2O$, 40 mg/L; HCl (25%), 1 mL/L according to *Policastro (2021).*

3.2.2. *Experimental apparatus*

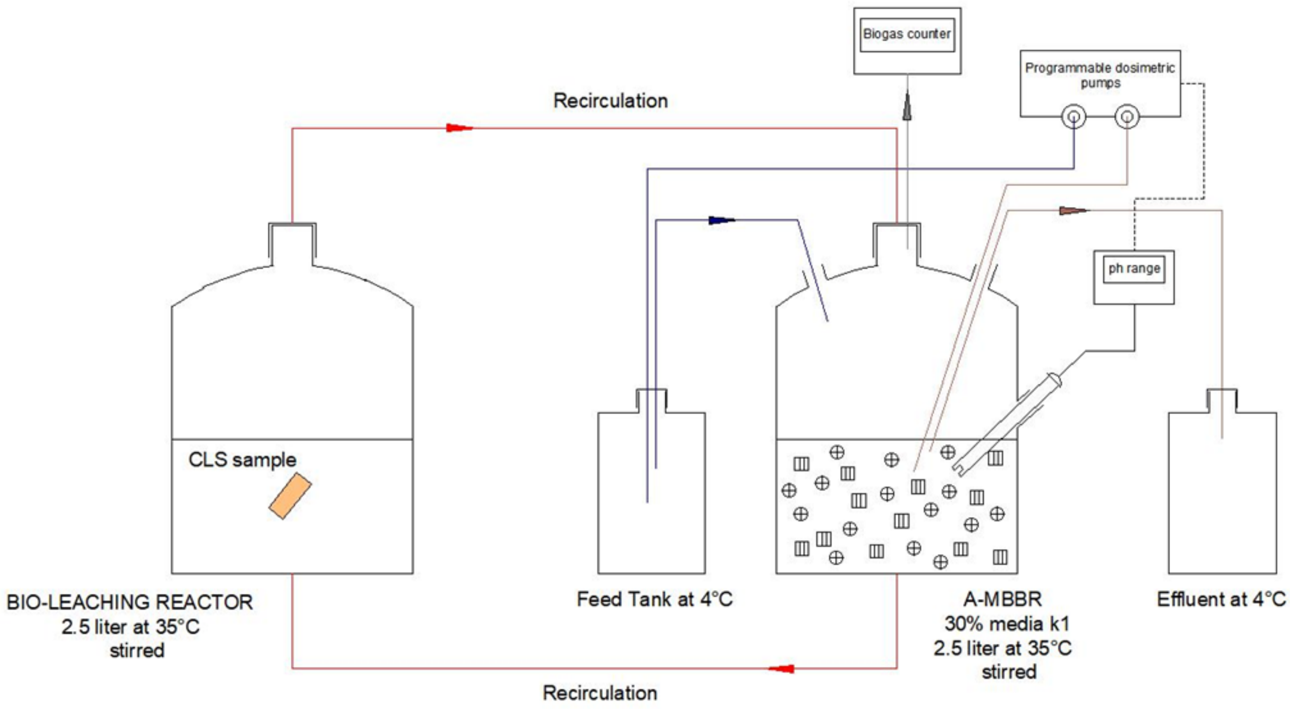

Figure 3.1. *Schematic picture of A-MBBR and bio-leaching reactors*

The DF A-MBBR and bioleaching experiments were carried out in 2 x 5.0 L borosilicate glass reactors closed with hermetic screw caps, equipped with two sampling tubes for taking liquid and gaseous samples and connected to each other via silicone tubing. The first reactor was filled with about 2.5 L of solution obtained by mixing 500 ml of inoculum, 900 carrier K1, 2000 ml of milli-q water, 42.5 g of glucose and 2.5 ml of micronutrients medium, thus establishing an F/M ratio of 2.58 (COD substrate (g)/inoculum VS (g)) in order to optimize the process. The first reactor was connected to a gas meter to evaluate its daily production. Before performing the experiments, the bioreactor was inerted with pure N_2 for 30 minutes to ensure anaerobic conditions.

In the start-up phase, heat-treated digestate was diluted with milli-q water at a dilution ratio of 1:5 mL/mL to prevent the pumps from clogging. The DF experiments maintained at 35 ± 1 °C to ensure mesophilic conditions were carried out in batch-wise conditions with 2 days of steady-state HRT, up to the colonization of the K1 carriers by the acid-forming microorganisms, passing from suspended cultures, to mixed cultures and finally to biofilm *(Ganesan et al., 2022)*. This condition was verified by comparing the volatile solids (VS) present in the influent and effluent *(APHA, 1998)* and by monitoring the production of VFAs and biogas. The passage of the system to biofilm was confirmed by the absence of VS in the effluent combined with constant production of VFAs and biogas, after about 6 weeks. Subsequently, the system was connected to the second 5.0 L borosilicate glass reactor filled with the effluent produced from the first reactor and with the addition of a sample of CLS of about 25g maintaining a liquid/solid ratio (R) of 100:1. The R ratio is a fundamental parameter as a neutral-alkaline pH responds to a higher solid load. This generates a negative effect as the bioleaching is interrupted and in the biological phase it could bring back salt concentrations higher than the inhibition thresholds of the biological process.

DF A-MBBR experiments were conducted at 35 ± 1 °C to ensure mesophilic conditions, at controlled pH, at different ranges (6.0; 5.5; 5.0; 4.5; 4.0) in order to evaluate the different production and composition of VFAs and biogas related to the conversion of substrate used. The selected ranges are all related to the correct conduct of the process. Each of the different pH ranges of the experimental campaign was maintained until the process reached stationary conditions (21 days), thanks to the aid of an automated Reef Factory dosing pump X3 system for influent/effluent loading/unloading equipped with a Ph probe.

The recirculation of the solution produced, rich in VFAs, between the two reactors is ensured by two 12V Comet Elegant 0.2-10 L/m pumps with adjustable flow rate, contained in 0.5 L borosilicate bottles connected via silicone tubes to the bioreactors. The recirculation is automated and was carried out every three hours.

The production and composition of biogas and VFAs, the effluent produced, the concentration of Ca^{2+} were monitored daily. The influent used is an aqueous solution containing 17 g/L of glucose and the micronutrients necessary to ensure correct metabolic activity of the microorganisms. In this way, the C:N:P ratio of the DF A-MBBR experiments was consistently maintained at 100:5:1 in order to balance the process to run at maximum efficiency *(Zhang et al., 2005).* This procedure was repeated for each pH range in order to evaluate the yield of the Ca^{2+} bioleaching process on CLS samples.

At the end of each cycle of the DF A-MBBR pH range, the remains of the bioleached CLS samples were taken. The CLS samples were both physically and chemically characterized, and then stored until the end of the DF A-MBBR experiments.

3.2.3. Analytical Methods

Total and volatile solids of digestate and influent/effluent were measured by thermal processes at 105 °C and 600 °C, respectively, according to standard methods (*APHA, 1998*). CLS samples and reagents were weighed on RADWAG precision balance model AS/220/C/2. The total concentrations of Ca^{2+} ions in the CLS samples were obtained by an acidic mineralization process following the EPA *(Environmental Protection Agency)* method 3051. The concentrations of dissolved Ca^{2+} ions in the digestaste and CLS samples were evaluated through atomic adsorption spectrometry (AAS) using a Varian Model 55B SpectrAA (F-AAS) equipped with a flame (acetylene/air) and a deuterium lamp for background correction. The concentrations of organic acids were measured with a high-pressure liquid chromatography. Specifically, a Dionex LC 25 Chromatography Oven equipped with a polymer-based cation-exchanger column (Metrohm Metrosep Organic Acids - 250/7.8), a Dionex AD25 Absorbance Detector, and a Jasco RI-2031 refractive index detector were combined with a gradient pump (Dionex GP 50), eluting the samples with sulfuric acid 0.5 mM at the flow rate of 0.7 mL/min *(Glavan et al., 2023)*. The elution time was 21.5 min. Glucose content was measured using the total carbohydrates colorimetric method according to *Nielsen (2017)*. COD were measured via colorimetric analyses, according to standard methods (*American Public Health Association, 2005).* Biogas production was measured with RITTER Milli-Gas counter MGC-1 PMMA. Biogas composition was characterized by a Varian Star 3400 gas chromatograph equipped with ShinCarbon ST 80/100 column and a thermal conductivity detector. Argon was used as carrier gas with 1.4 bar front and rear end pressure *(Ferraro et al., 2018)*. All the analysis were carried out in triplicate.

3.3. Results and discussion

3.3.1. DF A-MBBR process: Production of VFAs and biogas at different pH stat ranges

The DF A-MBBR process was carried out at different pH stat ranges 6.0, 5.5, 5.0, 4.5 and 4.0 for a total duration of 21 days, relative to each pH stat range considered. The productions and compositions of VFAs and biogas were compared and analyzed as a function of the amount of glucose substrate that was used in concentration of 17 g/L and the variable pH ranges used in the experiment (*Tables 3.3. and 3.4.*).

pH range	*Influent/ Effluent [L]*	*Acetic Acid [$g/g_{glucose}$]*	*Butyric Acid [$g/g_{glucose}$]*	*Lactic Acid [$g/g_{glucose}$]*	*Formic Acid [$g/g_{glucose}$]*	*Propionic Acid [$g/g_{glucose}$]*	*Glucose [$g/g_{glucose}$]*
6.0 ± 0.1	33.080	0.228	0.298	0.046	0.020	<0.010	0.392
5.5 ± 0.1	26.210	0.295	0.249	0.027	0.016	<0.010	0.391
5.0 ± 0.1	21.530	0.367	0.289	0.036	0.021	<0.010	0.375
4.5 ± 0.1	9.870	0.209	0.181	0.029	0.015	<0.010	0.501
4.0 ± 0.1	4.220	0.151	0.120	0.025	0.013	<0.010	0.630

Table 3.3. *Comparison of VFAs production by different pH stat ranges*

pH range	*Biogas production [L]*	*[H_2] production*		*[CO_2] production*		*[CH_4] production*	
		[L]	*[$L/g_{glucose}$]*	*[L]*	*[$L/g_{glucose}$]*	*[L]*	*[$L/g_{glucose}$]*
6.0 ± 0.1	36.900	23.360	0.042	13.520	0,024	<0.030	$<0.010*10^{-5}$
5.5 ± 0.1	28.810	18.030	0.040	10.760	0,024	<0.030	$<0.010*10^{-5}$
5.0 ± 0.1	19.860	12.410	0.034	7.440	0,020	<0.030	$<0.010*10^{-5}$
4.5 ± 0.1	9.640	5.820	0.035	3.790	0,023	<0.030	$<0.010*10^{-5}$
4.0 ± 0.1	3.230	2.090	0.029	1.120	0,016	<0.030	$<0.010*10^{-5}$

Table 3.4. *Comparison of biogas production by different pH stat ranges*

The pH has a significant role in the production of VFAs during the DF A-MBBR process. After 21 days, at pH 6.0, were produced approximately 0.58 $g_{VFAs}/g_{glucose}$. The mixture of VFAs generated in this pH stat range was predominantly composed of acetic acid and butyric acid in concentrations about of 4000 mg/L and 5000 mg/L, respectively (*Fig.3.3.*), constituting a significant portion of the VFAs blend. Alongside these primary VFAs, small amounts of lactic acid and formic acid were also present, contributing to the overall composition. Additionally, traces of propionic acid were detected, although their concentrations were minimal compared to the dominant concentrations of acetic and butyric acids (*Fig.3.2.*). This pH stat range is considered to be neutral to slightly acidic, which allowed for efficient hydrolysis and acidogenesis. Generally in this pH stat range acidogenic microorganisms predominate, such as Clostridium and Enterobacter species, which lead to the production of VFAs such as acetic acid, butyric acid and propionic acid and Lactobacillus to the production of lactic acid *(Sivaramakrishnan et al., 2021)*. The overall yield of VFAs was not as high as in the lower pH ranges due to the probable presence of other competing microbial pathways, including acetogenic and H_2-producing microorganisms.

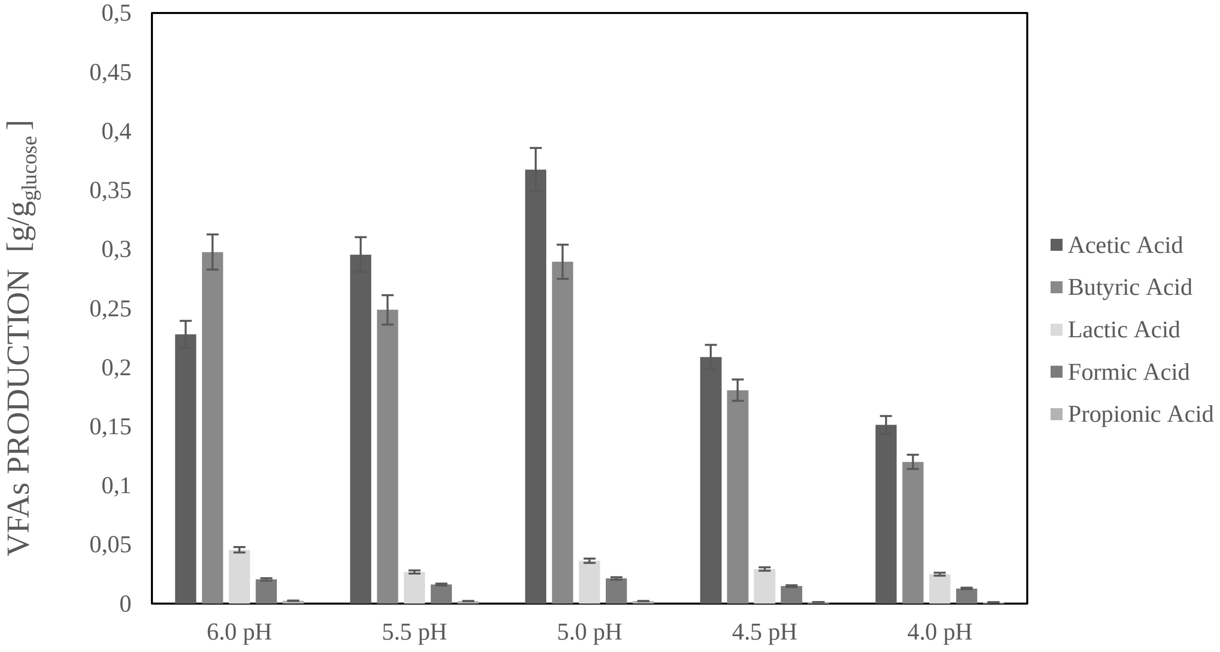

Figure 3.2. *VFAs production by different pH stat ranges*

Lower pH ranges 5.5-5.0 favored the activity of acid-producing microorganisms, with a consequent increase in the production of VFAs. At 21 days, about 0.59 $g_{VFAs}/g_{glucose}$ and 0.71 $g_{VFAs}/g_{glucose}$, respectively, were produced. These pH ranges favors acidogenesis and results in an increased production of VFAs (*Dareioti et al., 2021*). Acidogenic microorganisms, especially those belonging to the genus Clostridium, thrive under these conditions (*Wang et al., 2008*). The lower pH promotes enhanced hydrolysis and substrate conversion, resulting in higher production of VFAs. The major VFAs generated at these pH ranges include acetic acid and butyric acid, in concentrations about of 5000-6500 mg/L and 4000-4500 mg/L, respectively (*Fig.3.3.*).

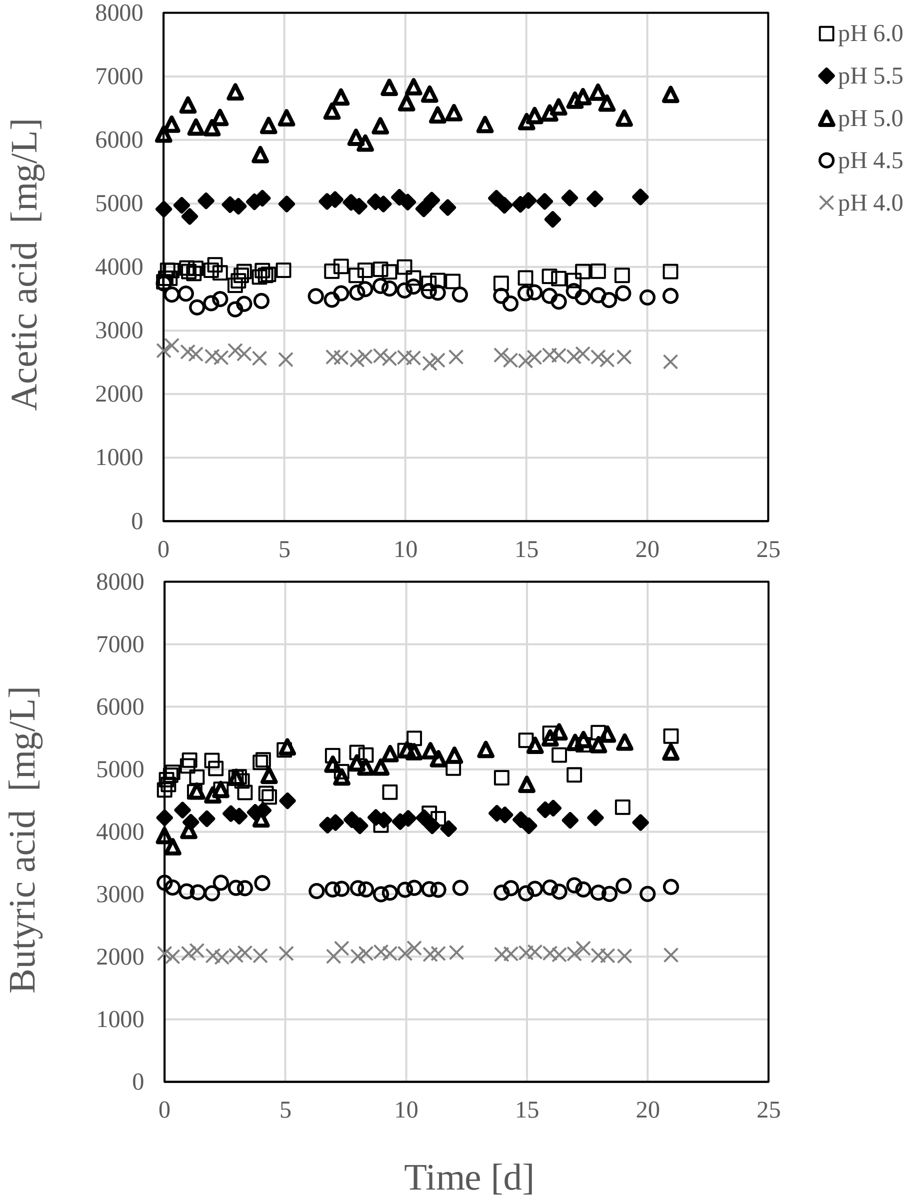

Figure 3.3 *Acetic and butyric acids concentration by different pH stat ranges*

However, extremely low pH values 4.5-4.0 inhibited microbial activity. Acidogenic microorganisms, particularly acid-tolerant strains, exhibit limited metabolic activities in this environment. The lower pH further improves the solubility of organic compounds and facilitates their breakdown into VFAs (*Namdarimonfared et al., 2023*). In these ranges about 0.43 $g_{VFAs}/g_{glucose}$ and 0.31 $g_{VFAs}/g_{glucose}$ were produced, mainly acetic acid and butyric acid in concentrations of about 3500-2800 mg/L and 3000-2000 mg/L, respectively (*Fig.3*). However, the extremely low pH limited and inhibited microbial acidogenic activity and reduced the overall yields of VFAs. The yield of VFAs production was lower than in the previous pH ranges 5.5-5.0 due to the increased acidic condition which favored a partial detachment of the biofilm from the K1 supports present in the reactor with a consequent reduction in microbial colonies and in the metabolic activity of the microorganisms acidogenic (*Saini et al., 2023*). Acidogenic, acetogenic and hydrogen-producing microorganisms that can tolerate extreme acidity in this environment are present in minimal quantities (*Fig.3.4.*).

Thus, maintaining an optimal pH range based on a specific microbial pathway and substrate is critical for maximizing yields of VFAs in DF A-MBBR processes.

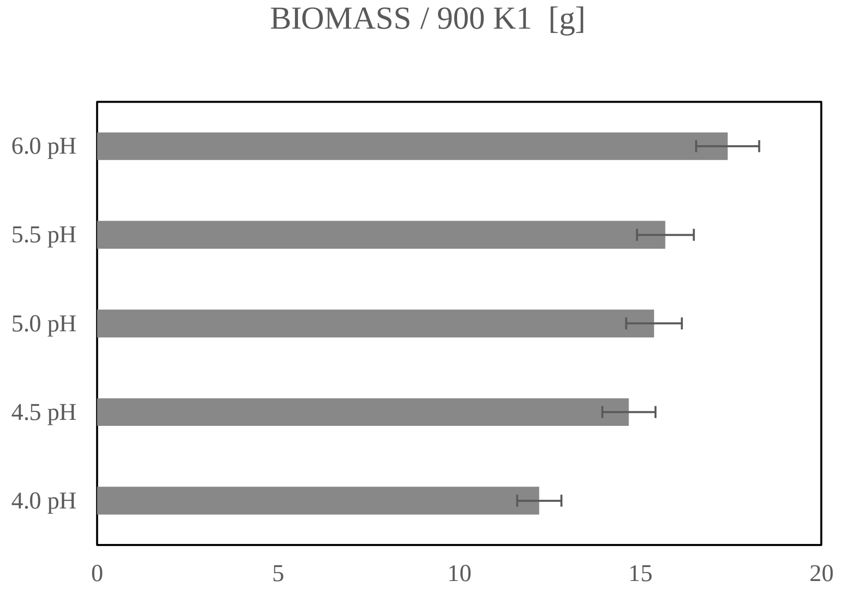

Figure 3.4. *Biomass on K1 carriers during the DF A-MBBR process by different pH stat ranges*

The pH stat ranges in the system significantly influenced the production of hydrogen-rich biogas during the DF A-MBBR process. After 21 days, at pH 6.0, the production of biogas reached about 37 L, consisting primarily of hydrogen (H_2) and carbon dioxide (CO_2), with low methane content due to inhibition heat treatment during the process start-up phase and F/M (food to microorganisms) ratio management *(Dahiya et al., 2021)*. The microbial community present at pH 6.0 favored the pathways that lead to the production of discrete quantities of H_2-rich biogas to the detriment of a lower production of VFAs. In the pH ranges of 5.5-5.0, the metabolic activity of H_2-producing microorganisms and acetogens was favored, resulting in biogas production yields of approximately 29 L and 20 L, respectively. The decrease in pH improved the solubility of organic acids, leading to significant H_2 production and making this pH range favorable for H_2-rich biogas production with respect to the amount of glucose converted during the process. Biogas produced in the pH ranges of 5.5-5.0 contained a percentage of bio-H2 between 55-60%. However, In the pH ranges of 4.5-4.0, the yield of produced biogas reduced to about 10 L and 4 L, respectively, indicating partial inhibition of the metabolic activity of acetogenic microorganisms. Highly acidic conditions discouraged efficient conversion of organic acids into H_2 biogas. Despite the high yield of bio-H_2 compared to the converted glucose substrate, the biogas production at pH 4.5-4.0 was lower overall compared to the other pH ranges in the DF A-MBBR process. These findings underscore the significance of pH control in H_2-rich biogas production during the DF A-MBBR process. Furthermore, in all conditions at different pH stat ranges, a linear production trend of bio-H_2 is highlighted due to the stability and efficiency of the process (*Kirtay E., 2011*).

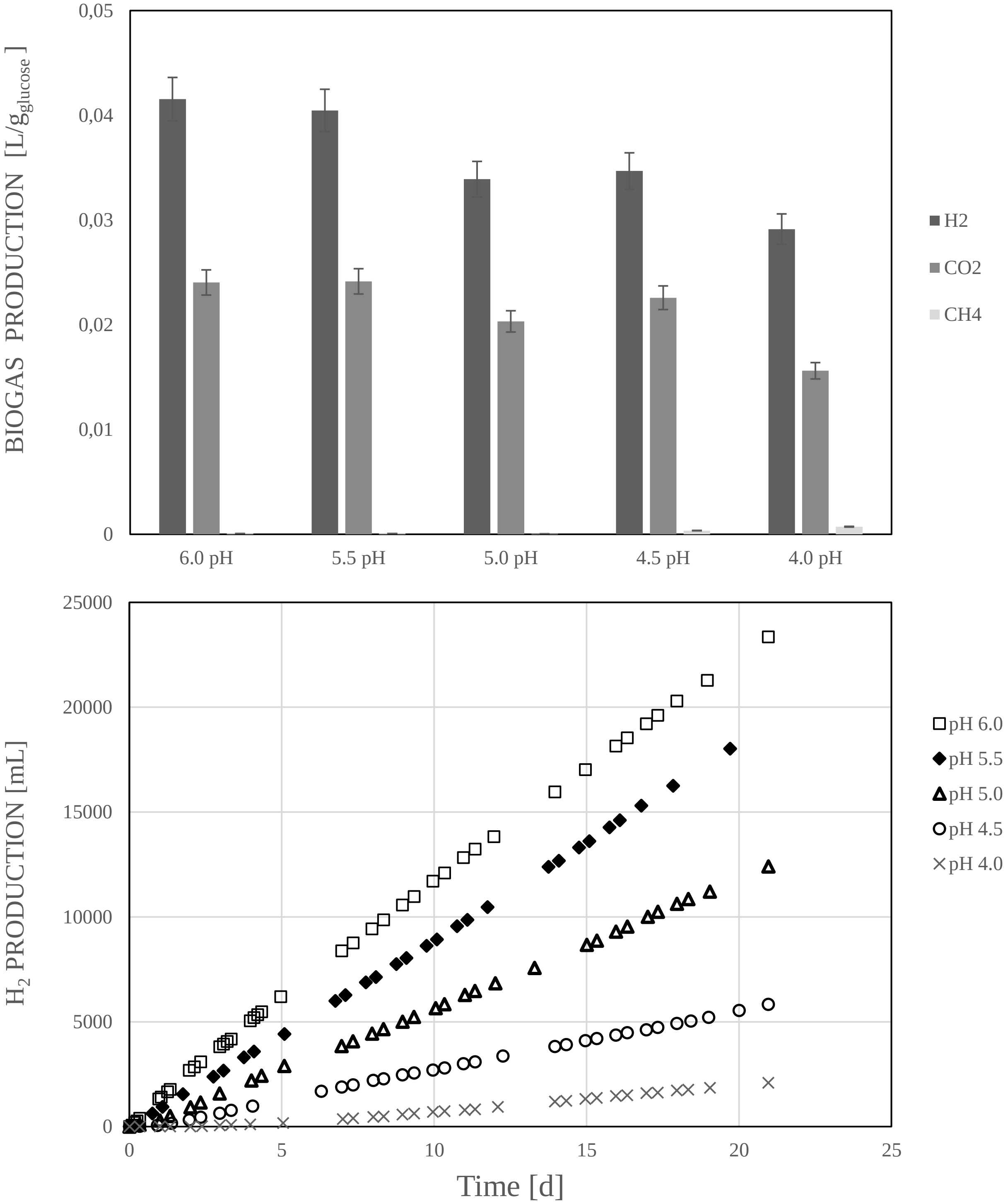

Figure 3.5. *bio-H_2 and CO_2 production by different pH stat ranges*

3.3.2. CLS dissolution at different pH stat ranges

During the DF A-MBBR process at different pH stat ranges (6.0, 5.5, 5.0, 4.5, and 4.0), concentrations of Ca^{2+}, the variations in volume and weight of the treated CLS samples were monitored at 7, 14 and 21 days. Observing the graph in figure (*Fig.3.6.*), it can be seen that the bioleaching mechanism can be structured in two phases: a first phase of direct attack at the external layer of the treated CLS samples by the VFAs, characterized by rapid kinetics, to then slow in the second phase related to diffusion processes. Diffusive effect that occurs between the external and internal part of the treated CLS sample, creating a gradient between the external and internal pore in terms of Ca quantity. Acetic acid, produced at variable concentrations at different pH stat ranges during the DF A-MBBR tests, has a selectivity towards the alkaline earth metals, in particular, it has a selectivity towards Ca with respect to the other alkaline earth metals of about 30% *(Santos et al., 2014*).

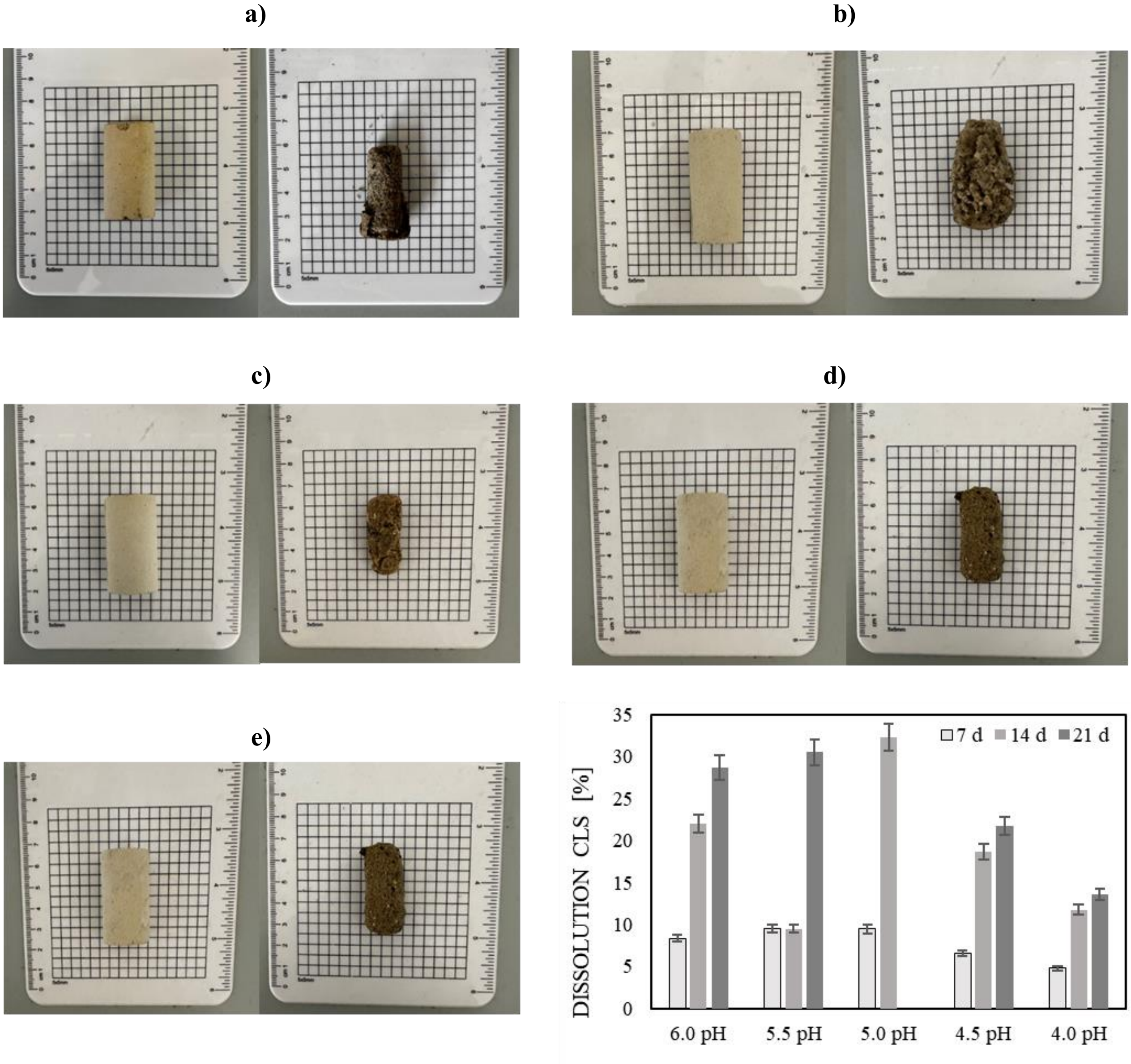

Figure 3.6. *Mass balance as a percentage of CLS samples leached during the DF A-MBBR process by different pH stat ranges: a) 6.0; b) 5.5; c) 5.0; d) 4.5; e) 4.0*

Different CLS samples were treated in order to evaluate the bioleaching yield of the variable mixtures of VFAs produced. The processes carried out on CLS samples revealed significant variations in both volume and weight reduction (*Fig.3.6.*). At pH 6.0, the bioleaching treatment resulted in approximately 28% weight reduction, showcasing a moderate level of efficiency. As the pH was lowered to 5.5 and 5.0, the efficiency of the bioleaching process improved, with weight reductions of about 30% and 32% respectively. However, at pH 4.5 and 4.0, the weight reduction decreased to 21% and 13% respectively, indicating a reduced efficacy in more acidic conditions. These differences in weight reduction of samples for CLS dissolution at different pH stat ranges are influenced by variable concentrations of VFAs produced during DF A-MBBR, as well as the diffusion processes and steric hindrance associated with these VFAs. The bioleaching mechanism is strongly dependent on the diffusion phenomenon which the mixture of VFAs undergoes (*Ukrainczyk N., 2021*). This penetrates inside the treated CLS samples which, being porous in nature, allows the passage to certain species of VFAs contained in the mixture.

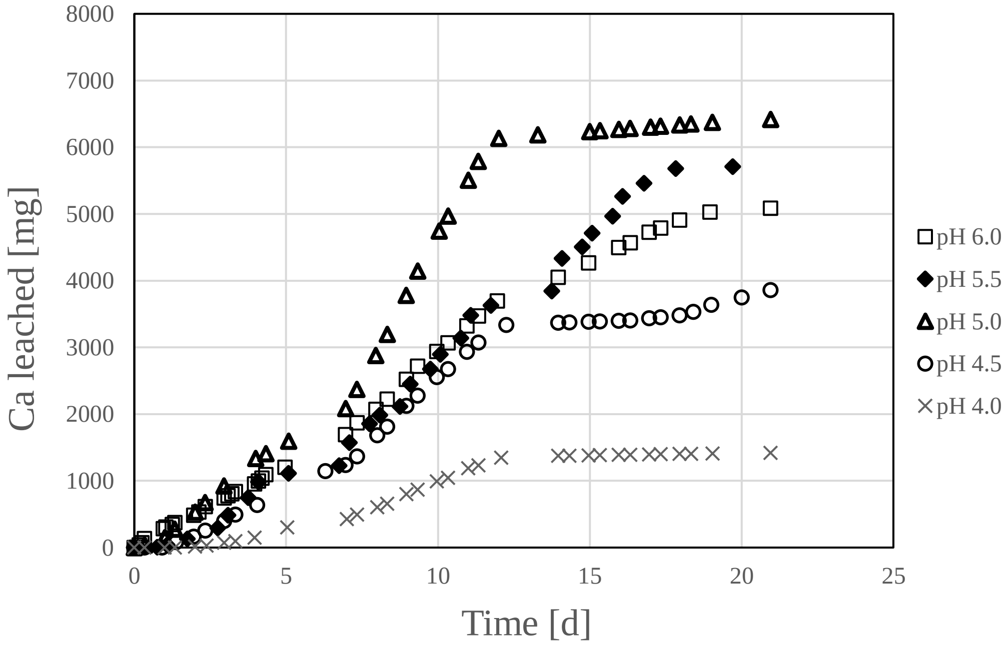

Figure 3.7. *Mass of Ca^{+2} ions leached during the DF A-MBBR process by different pH stat ranges*

The bioleaching processes conducted at different pH stat ranges on CLS samples showned distinct patterns regarding the amount of dissolved Ca^{+2} (*Fig.3.7.*). The initial 12 days of bioleaching showcase rapid kinetics attributed to the direct attack on the outer layer of the concrete, resulting in efficient dissolution of Ca. This aggressive phase allows for a significant release of Ca^{+2} ions due to the action of the VFAs produced during the treatment di DF A-MBBR. However, as the process progresses up to 21 days, the kinetics slow down due to the diffusion effect, where the VFAs find it more challenging to penetrate the inner layers of the concrete, resulting in a reduced rate of calcium dissolution.At pH 6.0, the bioleaching treatment resulted in a moderate dissolution of calcium, with about 5000 milligrams of Ca^{+2} being dissolved. As the pH decreased to 5.5 and 5.0, the efficiency of the bioleaching process improved significantly, leading to the dissolution of 6500 milligrams and 7000 milligrams about of Ca, respectively. However, at pH 4.5 and 4.0, the amount of dissolved calcium decreased about to 4000 milligrams and 1500 milligrams, respectively, indicating reduced efficiency in these more acidic conditions. The disparity in Ca^{+2} dissolution can be attributed to the varying mixtures and concentrations of volatile fatty acids (VFAs) involved in the bioleaching processes. Higher concentrations of acetic acid and butyric acid seem to promote a more efficient bioleaching process, as observed at pH 5.5 and 5.0, where the dissolution of Ca was notably higher. An explanation for this result can be related to the fact that the salts of these acids are either soluble or highly soluble in water, while complexation phenomena in solutions of cations, arising from the dissolution of cementitious paste, and anions, from acid dissociation, are governed by complexation constants. It can be observed that the reactions leading to the formation of complexes are predominant compared to those leading to the formation of salts (*Shi et al., 2000*). Furthermore, complexation tends to accelerate the kinetics of reactions between acids and the cementitious matrix of the CLS samples.

As reported in *Fig. 3.7.*, this condition caused the most rapid dissolution of suspended Ca^{+2} in the leaching solution. Ca is present in the 25 g of each CLS sample added to the reactor, as well as in the medium solution used, which contains micronutrients and minerals. In fact, this latter fraction contributed to increasing the amount of Ca in the mass balance. From the analysis of Ca concentrations, knowing the initial concentrations of calcium in the medium used, specific concentrations of leached Ca at the sampled contact time were determined, and subsequently, the quantity of leached Ca ($Ca_{leached}$) was calculated using the following relationship:

$$Ca_t = Ca_{analyzed} - Ca_0 \ \rightarrow Ca_{leached} = Ca_t * V_{effluent}$$

Where: Ca_t is the specific concentration of leached calcium at the contact time; $Ca_{analyzed}$ is the specific concentration of measured calcium in the effluent exiting the reactor; $V_{effluent}$ is the volume of effluent produced by the DF A-MBBR reactor at the given time.

3.4. Conclusions

The findings of this study highlight the significant advantages of bioleaching processes on CLS contained in CDW and its potential applications. Bioleaching offers an innovative and environmentally friendly approach to degrade CLS waste, reducing its volume and facilitating its disposal and recovery of materials. The controlled environment of A-MBBR provides an efficient means to promote the growth of acid-producing microorganisms and biofilms, enhancing the yield of bioleaching process. Moreover, the study suggests that bioleaching processes could be extended to other hazardous waste types, such as asbestos, offering a sustainable and effective method for their remediation and safe disposal. Additionally, the recovery of precious metals from electronic waste or other metal-rich hazardous materials represents a valuable application of bioleaching, contributing to resource conservation and minimizing environmental impacts. The versatility and eco-friendly nature of bioleaching make it a promising remediation for advancing waste management strategies and promoting circular economy.

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Chapter 4

Synergizing Construction and Demolition Waste Management with Dark Fermentation: Sustainable Resource Recovery and Waste Reduction

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Synergizing Construction and Demolition Waste Management with Dark Fermentation: Sustainable Resource Recovery and Waste Reduction

Abstract

This study explores an innovative approach to managing Construction and Demolition Waste (CDW) by integrating dark fermentation processes, traditionally applied for hydrogen production. The DF process also generates a liquid effluent (i.e. dark fermentation effluent) rich in organic acids. In this study, such effluents are re-evaluated for their potential in leaching processes to dissolve components of hardened cement paste, thereby reducing the volume of CDW requiring disposal. Experimental investigations looked into the leaching efficiency of various synthetic organic acids, usually produced during DF. Successively, the optimal operating conditions leading to the production of the desired organic acids, including the use of cheese whey as substrate, have been applied to DF and the leaching process has been assessed using the real effluent. Results showed that the most effective organic acids are lactic acid and acetic acid. The leaching process conducted using the real DF effluent led to a CDW reduction volume of the 80-90%. The process efficiency, compared to the traditional landfilling scenario, was also confirmed in terms of environmental sustainability through Life Cycle Assessment (LCA), and economic feasibility analysis.

4.1. Introduction

Construction and demolition waste (CDW) represents the predominant category of waste generated in contemporary society. China, the United States (US), and the European Union (EU) stand as the three largest economies globally and are concurrently the principal contributors to CDW generation (*Kabirifar et al., 2020*). Within Europe, the construction sector assumes a pivotal role in resource utilization and waste production, constituting half of all resource extraction and one-third of total waste output (*European Commission, 2018*).

As per the most recent available data, it is approximated that the EU generated approximately 333 million tons of CDW (excluding soils) in 2014, with inert waste accounting for 300 million tons (*Eurostat, 2023*). Despite the widespread implementation of established waste minimization principles, such as the 3Rs or 4Rs hierarchy (reduce, reuse, recycle, and recover), a substantial portion of construction and demolition materials is currently disposed of in landfills. Indeed, although the specific distribution varies among different countries, 35% of globally produced CDW is directed to landfills (*Menegaki and Damigos., 2018*).

An alternative approach could involve integrating the treatment of CDW to reduce the disposal volume (or facilitate future reuse) with other novel green processes. For instance, the Dark fermentation (DF) process, extensively researched for hydrogen production (*Mugnai et al., 2021; Wang and Yin, 2017*), could be synergistically combined with CDW treatment.

DF is a biological process, conducted by microorganisms capable of converting organic substrates into molecular hydrogen in an oxygen-free environment. Aside from hydrogen energy, the potential utilization of waste streams as organic substrates provides an additional advantage to DF, as it contributes to waste disposal in alignment with the Waste-to-Energy approach (*Policastro et al., 2024*). On the other hand, the DF process generates an acidic liquid effluent, i.e. Dark fermentation effluent (DFE), which is rich in organic acids (i.e. acetic, butyric, propionic, lactic acid) and, therefore, require further treatments to reduce its COD content (*Ghimire et al., 2015a*).

Nonetheless, the organic acids present in DFE can be considered an added value if managed and utilized appropriately. An example could be their use in a leaching processes applied to CDW. Indeed, acidic compounds have the capability to dissolve constituents of the hardened cement paste, such as calcium-based compounds, thereby reducing the final disposal volume (*Zhang and Moment, 2023*).

Such treatment has been previously tested by *Trancone et al., 2022*, who conducted a preliminary study for the treatment of asbestos cement waste. In particular, the authors studied mesophilic and thermophilic DF fed with glucose, to degrade asbestos fibers. Despite the positive results obtained, the scale-up of such leaching process require further studies.

In fact, for the process to be sustainable from both an economic and environmental point of view, it is necessary to optimize the production of the most efficient organic acids for this specific application, taking into consideration that the acids that are produced depend on the waste and operating conditions used. Furthermore, such optimization should occur using suitable organic waste materials, rather than synthetic substrates. *Table 4.1* presents research related to the use of various substrates in DF processes under different operating conditions for the production of OAs.

REACTOR TYPE	SUBSTRATE	OPERATING CONDITIONS	OAs	REFERENCE
Batch and cyclic mode V=80 ml	Date pulp waste	Controlled ph=6, HRT=48 h, pretratment enzymatic, 37 °, 150 rpm in rotary shaker, not inoculum	Lactic acid = 22,43 g/L	(Ahmad et al., 2021)
Batch mode; V=0,5 L	Sugary residue (sugar industry - cane sugar molasses) - Sugary wastewater	Inoculum digestate from a biogas plant like, uncontrolled pH, mesophilic and thermophilic Temperature	Acetic acid = 13,04 g/L; Propionic acid = 10,47 g/L; Butyric acid = 11,18 g/L	(Weide et al., 2019)
Batch and Feed-Batch V=1 L	Glucose medium	Inoculum digestate by AD plants dairy waste, 35 and 55 °C, uncontrolled pH	Acetic acid = 1,6 - 1,15 g/L; Butyric acid = 6,3 - 2,3 g/L; Lactic acid = 1,9 - 4,6 g/L	(Trancone et al., 2022)
Batch and Feed-Batch V=1 L	Co-fermentation of cheese whey and orange waste	Inoculum digestate by AD plants, 35 °C, uncontrolled pH	Acetic acid = 5 g/L; Butyric acid = 7,8 g/L; Lactic acid = 16 g/L	(Race et al., 2019)
Sequential Batch Reactor V=1 L	Kitchen waste	Inoculum garbage compost by soil plants, 37 °C, pH=6, HRT = 48h	Acetic acid = 3,9 g/L; Butyric acid = 6,7 g/L; Propionic acid = 1,85 g/L	(Ohnishi et al., 2010)
Semi-continuous V=1,5 L	Co-fermentation of cheese whey and buffalo manure	Inoculum digestate by AD plants, 55 °C, uncontrolled pH, HRT = variable, OLR = variable	Acetic acid = 3,43 (mM/gVS); Butiyric acid = 14,80 (mM/gVS); Propionic acid = 7,44 (mM/gVS)	(Ghimire et al., 2017)
Repeated-Batch Fermentation V=2 L	Cheese whey	Inoculum digestate by AD plants, 35 °C, uncontrolled pH, variable HRT	Lactic acid = 20 g/L	(Luongo et al., 2019)
Batch V=0,4 L	Winery wastewater	(AD) effluent consortia, batch V=0,4 L, thermal pretreatment, ph unc, mesofilia	Acetic acid = 4,45 g/L	(Policastro et al., 2022)

Table 4.1. *Studies relating to the application of DF processes for the production of OAs under varying reactor operating conditions and use of different substrates*

The objective of this study is to identify the most efficient organic acids for the CDW leaching process and assess their production through DF using a real waste. Moreover, the study aims at evaluating the environmental and economic sustainability of the proposed process. In particular, experimental tests were conducted with various organic acids usually produced in DF, to evaluate the efficiency of the leaching process. The study involved selecting the most effective acids and applying the necessary operational conditions for their production in a DF process utilizing real waste. The investigation further assessed the utilization of the real effluent for the leaching process, to evaluate: i) the process efficiency in terms of CDW volume reduction, ii) the environmental sustainability (Life Cycle Assessment - LCA).

4.2. Material and methods

4.2.1. Research plan

In this study, were conducted a laboratory-scale investigation of a bio-leaching process under acidic conditions, using acids derived from a DF process on solid and powdery concrete samples. The initial phase of the study focused on examining the variables of the leaching process using synthetic organic acid solutions and laboratory-made concrete samples. Based on the results from various conditions, we identified the optimal condition in terms of substrate/acid mixture for the process and the solid mass to liquid volume ratio. Subsequently, the DF processes was carried out to produce a real effluent, which was then used to study the bio-leaching process, under the optimal solid-liquid ratio. Finally, collected data were used for the environmental evaluation (Life Cycle Assessment, LCA) of the process and a preliminary economic assessment.

In the first phase of this study, the leaching process with organic acids, particularly acetic, propionic, butyric, and lactic acids, was studied on concrete samples to assess the dissolution kinetics. Building upon the preliminary study of adopting the DF process to dissolve a composite cement sample as proposed by *Spasiano et al., 2017*, an evaluation was made on possible DF processes considering various substrates, reactor types, and operational conditions to derive optimal conditions for the leaching process. The leaching capacity of each acid was assessed by varying the contact time, concentration of the synthetic acid solutions, the solid mass to liquid volume ratio (R [g/mL]), and the physical state (solid or powder) of the sample used in the trials. The tests were conducted for different solid-liquid ratios, i.e. 1/60 and 1/300, varying acid concentrations of 0.25M and 0.03M, and different contact times: 0.5h, 3h, 8h, 24h, 48h, and 96h. The same test was performed on solid CLS samples at different contact times with a fixed molar acid concentration of 0.25M and a fixed solid-liquid ratio of 1/60., Considering all variables combinations, a total numero of 20 tests were conducted. The summary of the experimental conditions tested during this first phase is reported in *Table 4.2*.

Organic acids	***Contact times [h]***	***Sample***	***Molar acid concentration [mol/L]***	***R = solid liquid ratio [g/mL]***
Acetic, Butyric, Propionic, Lactic	*0.5 - 3 - 8 - 24 - 48 - 96*	Powder	0.03	1/60
				1/300
			0.25	1/60
				1/300
		Solid	0.25	1/60

Table 4.2. *Operating conditions of experiments conducted using synthetic acid solutions*

In the second phase of this study, based on the outcomes from tests with synthetic acid solutions, we selected the most effective acids as target for the implementation in a DF process using real waste. This involved choosing the appropriate type of substrate (cheese-whey) for the DF processes and operating conditions, based on previous literature studies (*Ahmad et al., 2021; Policastro et al., 2022*). Subsequently, A DF reactor was start-up and operated for 10 days, to produce the real effluent needed for bio-leaching tests on concrete samples, comparing its efficiency with that of concrete samples. The leaching kinetics were determined by monitoring the pH and concentrations of Ca^{+2} over the previously mentioned contact times. Finally, collected data were used for the environmental evaluation (Life Cycle Assessment, LCA) of the process and a preliminary economic assessment.

4.2.2. Materials

In this study, the following organic acids were evaluated for synthetic tests: Acetic Acid (≥ 99.5 %) was purchesed from J.T Baker, Propionic Acid (≥ 99.5 %) and Butyric Acid (≥ 99.0 %) was purchased from Sigma-Aldrich, Lactic Acid (≥ 92.0 %) was purchased from Honeywell Fluka™.

Table 4.3 outlines the specific features of these organics. For testing purposes, they were suitably diluted in deionized water to achieve the desired concentrations. The pH values of these solutions were subsequently measured.

OAs	***Molecular Formula***	***Manufacturing company***	***PM [g/mol]***	***pKa***	***C_{max} [M]***	***pH***	***C_{min} [M]***	***pH***
Acetic	CH_3COOH	J.T. BAKER	60,05	4,80	0,25	2,63	0,03	3,25
Propionic	CH_3CH_2COOH	Sigma - Aldrich	74,08	4,88	0,25	2,76	0,03	3,76
Butyric	$CH_3CH_2CH_2COOH$	Sigma - Aldrich	88,11	4,82	0,25	2,70	0,03	3,70
Lactic	$CH_3CHOHCOOH$	Honeywell Fluka™	90,08	3,20	0,25	2,18	0,03	2,70

Table 4.3. *Synthetic organic acid characteristics, concentrations tested and pH measured*

The inoculum utilized for conducting the DF processes was sourced from a digestate obtained from an Anaerobic Digestion Plant. This plant, managed by Powerinasce srl, processes dairy and livestock waste and is situated in Santa Maria La Fossa, Caserta, Italy. Before use, inhibition of methanogenic bacteria was achieved by treating the digestate in an oven for 1 hour at 105 °C, as per Ghimire et al., 2015a. Cheese-whey (CW) substrate, a byproduct of ricotta cheese production, was sourced from Caseificio Artigianale Dei Fratelli Pezzullo, located at Via Tiziano, 43, 80024 Carditello (NA). After sampling, CW was preserved in 5-liter plastic containers, frozen at -4 °C and thawed for characterization prior to use. The digestate and cheese whey characterization is detailed in *Table 4.4*.

	pH	**C_{TS} [g/L]**	**C_{VS} [g/L]**	**CODs [g/L]**	**CODt [g/L]**	**Dissolved Ca [mg/L]**
Digestate	8,00	60,32	22,75	20,14	61,87	279,70
Cheese whey	6,03	55,83	8,17	42,35	94,86	90,50

Table 4.4. *Inoculum and substrate characterization*

Concrete samples were produced in laboratory using CaCEM IV/B 32.5 R pozzolanic cement and FINBOND fiber-reinforced siliquarzite sand in a 60:40 ratio, combined with demineralized water. Concrete samples produced had a cylindrical shape with a height of 10 cm and a diameter of 2 cm. Subsequently some samples were crushed in a steel mortar with a pestle, in order to make the sample powdery and more homogeneous. These concrete samples are characterized by a weight of 20 g approximately and a calcium percentage of 30% $w\ Ca^{2+}/w_{sample}$.

4.2.3. Experimental apparatus and operating conditions

For the synthetic acid solution tests, 5 g of concrete powder/concrete solid samples were introduced in 50 mL tubes. Based on R, 25 mL or 30 mL acidic solution was added. Tubes were placed in a container with demineralized water heated by integrated thermostatic probes to maintain a temperature of 35±1 °C.

An ARGO – LAB tilting plate, model SKO-D XL (Italy), was used for stirring, setting a mechanical agitation speed of 120 rpm. Both solid and powdery samples were weighed using a RADWAG precision scale, model AS/220/C/2 (Poland). At the start and end of each test, pH was measured using a HANNA instruments portable pH meter, model HI98100 (USA). The Falcon tubes containing the samples were centrifuged at 6000 rpm for 5 minutes using a HETTICH model Mikro 22R (Germany).

The collected supernatant was then filtered at 0.45 µm and diluted with deionized water composed of 5% nitric acid. Finally, Ca^{2+} present in the solution was measured using atomic absorption spectrometry.

Concerning the DF process, two 500 mL GL 45 transparent borosilicate glass bottles (Shott Duran, Germany) were used as reactors. The working volume of 300 mL was filled with 90 mL thermally pretreated inoculum, 150 mL distilled water, and 60 ml cheese-whey. This achieved a substrate/inoculum ratio (F/M) close to 2.6 (g substrate COD/g inoculum COD), as in the studies by *Race et al.,2019, Spasiano, 2018, and Trancone et al., 2022*. Before closing the bottles, a ten-minute argon purge was conducted to ensure anaerobic conditions. The reactors were sealed with airtight caps fitted with two sampling tubes. Each bio-reactor was operated in batch mode for the first day and then operated under semi-continuous mode, setting a hydraulic retention time (HRT) of 2 days. The reactors were placed on a five-station ARGO-LAB magnetic stirrer, model M2-A (Italy), set at 120 rpm and 35±1 °C. Everyday, liquid and gas samples were analyzed to measure pH, the concentration of produced OAs and biogas composition. Once the reactors reached steady state in terms of OAs production, the effluent was frozen and stored, then mixed and used for leaching tests with real effluent from DF with concrete samples.

Before conducting leaching tests, effluent were filtered using a VACUUBRAND vacuum pump, model PC 3001 VARIOpro (Germany), borosilicate glass flask, and a glass funnel with a 0.45 µm paper filter to eliminate all the biomass still present and avoid biological reactions during the leaching tests. 300 mL of effluent characterized in terms of pH, composition of OAs and Ca^{2+} was poured into 2 transparent 500 mL borosilicate glass bottles GL 45 (Shott Duran, Germany) with addition of concrete samples. The reactors were kept on the magnetic stirrer, at a controlled temperature. Sampling operations were conducted every day for 21 days. For each sampling time, the pH was measured and 5 mL of solution were centrifuged, filtered at 0.45µ and finally diluted and analyzed to determine the Ca^{2+} concentration.

4.2.4. Analytical methods and calculations

The determination of total and volatile solids in both the digestate and cheese-whey substrate was performed using thermal methods at temperatures of 105 °C for total solids and 600 °C for volatile solids, adhering to the guidelines set by the APHA (1998). To quantify the total Ca^{2+} ions in the concrete samples, an acid mineralization process was executed, following the protocol of the EPA's method 3051. For assessing the concentrations of dissolved Ca^{2+} ions in both digestate and concrete samples, atomic absorption spectrometry (AAS) was employed, utilizing a Varian Model 55B SpectrAA (F-AAS) with an acetylene/air flame and a deuterium lamp for background adjustment. The calcium percentage was then calculated using the following equation:

$$\%Ca_{leached} = \frac{Ca^{2+}_{measured}}{(Sample\ mass\ \times \%Ca^{2+}_{sample})}$$

Calcium analysis made it possible to determine its concentrations over time. Starting from the initial concentrations of calcium present in the wastewater, the specific concentrations of calcium leached at the various sampling times were calculated by difference. By applying the formula described below, it was possible to plot the kinetic curves relating to bio-leaching process:

$$Ca_t = Ca_{measured} - Ca_0 \ \rightarrow \%Ca_{leached} = \frac{Ca_t * V_{solution}}{m_{sample} * \%Ca_{sample}}$$

OAs concentrations were determined using high-pressure liquid chromatography. The setup included a Dionex LC 25 Chromatography Oven, a polymer-based cation-exchanger column (Metrohm Metrosep Organic Acids - 250/7.8), a Dionex AD25 Absorbance Detector, and a Jasco RI-2031 refractive index detector, combined with a Dionex GP 50 gradient pump. The samples were eluted with 0.5 mM sulfuric acid at a flow rate of 0.7 mL/min, as described by *Glavan et al.,2023*, with an elution duration of 21.5 minutes. COD levels were ascertained through colorimetric analysis, based on the procedures of the *American Public Health Association* (*2005*). Biogas volumetric production was quantified using the water displacement method, and the biogas composition in terms of Hydrogen and carbon dioxide was analyzed using a Varian Star 3400 gas chromatograph equipped with a ShinCarbon ST 80/100 column and a thermal conductivity detector, utilizing argon as the carrier gas at 1.4 bar front and rear end pressure, as reported by *Ferraro et al., 2018*. All analyses were conducted in triplicate to ensure accuracy and reproducibility.

4.2.5. Environmental and economic sustainability evaluation

4.2.5.1. Goal and scope definition

The analysis of environmental sustainability was conducted using the Life Cycle Assessment (LCA) methodology. The study was aimed at evaluating the proposed process to identify improvement opportunities as decision-making support for future studies focused on further optimizing the process and its scale-up. Additionally, to assess the environmental benefits of the proposed technology, the bioleaching process (scenario 1) was compared with the traditional disposal scenario (scenario 2) for CDW (i.e. landfilling). Considering the aforementioned objectives, the LCA analysis was carried out using the gate-to-gate system boundaries, considering both the dark fermentation and bioleaching phases. It has been considered that the organic acids resulting from the bioleaching process are treated via anaerobic digestion (AD), to produce biomethane. The digestate resulting from the AD process has been assumed to be used as concentrated fertilizer. The energy derived from the produced biohydrogen and biomethane has been used for reacors heating, with any surplus considered as electrical energy. Transportation processes, which would heavily depend on the location of the facilities, have been overlooked. The chosen functional unit was 1 kg of CDW. *Figure 1* reports the process flow chart.

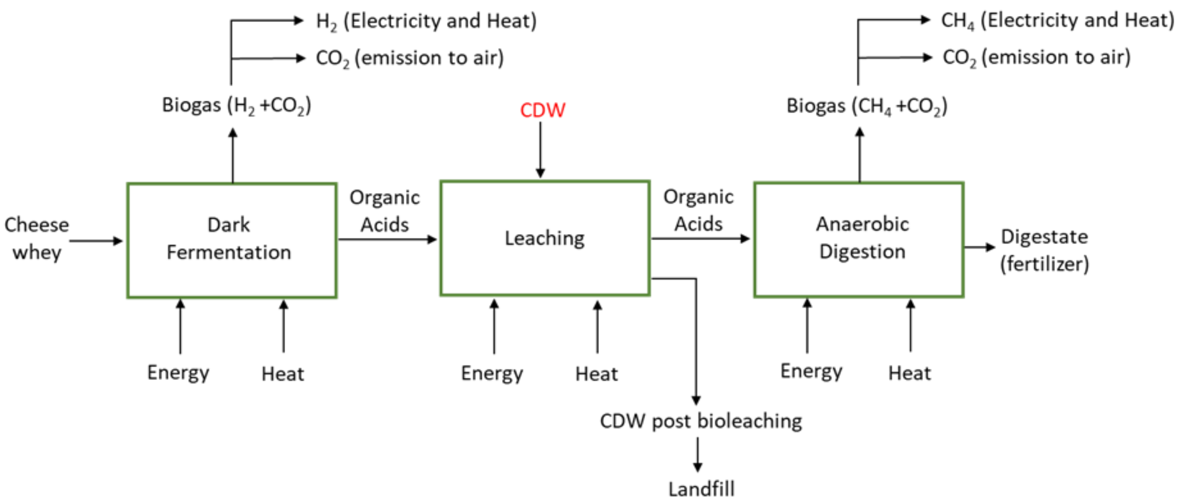

Figure 4.1. *Flow chart reporting Scenario 1 of the LCA study evaluating the environmental sustainability of a bioleaching process for the treatment of CDW*

4.2.5.2. Life cycle inventory and Life Cycle Impact Assessment

The life cycle inventory was compiled using data from experimental second phase. As cheese-whey is a by-product of the cheese production process, it has been considered burden free.

The biogas volume and methane percentage for the AD process have been obtained from *Trancone et al., 2022*. The volume of concentrated fertilizer is assumed to be the 10% of the initial digestate volume, according to *Camacho et al., 2022*. As all input/output have been calculated with respect to the functional unit, the DF and AD processes have been considered for the production/treatment of the same OAs quantity which was necessary for the bioleaching of 1Kg CDW. The estimation of electricity required for pumps and reactors agitation was conducted using literature data (*Camacho et al., 2022*) and considering the time lasting of the three processes. The estimation of the energy required for reactors heating over time has been performed using equations calculating warming energy and energy losses reported by *Ruggeri et al., 2010*. The estimation of the produced energy was conducted considering the lower heat values of hydrogen and methane. All calculations were performed by normalizing all material and energy flows in and out with respect to the functional unit. The LCI is presented in *Table 4.5*.

Process	Input/Output	Category	Unit per Kg/CDW	Value	Data base Input/Output
Cheese whey production	Milk production	Input	Kg	102.59	Cattle for slaughtering (RoW), milk production, from cow| APOS, S
	Cheese	Output	Kg	10	Created in this study
	Cheese whey	Output	Kg	92.59	Created in this study
Dark fermentation	Cheese whey	Input	Kg	92.59	Created in this study
	Electricity (DF)	Input	KWh	0.24	Electricity, medium voltage (GLO)| market group for| APOS, S
	Heat (DF)	Input	MJ	5.851	Heat, district or industrial, natural gas (RER)| market group for| APOS, S
	CO_2 emissions (DF)	Output	g	931	Carbon dioxide, biogenic
	Heat (Biohydrogen)	Output (avoided product)	MJ	8.1	Heat, district or industrial, natural gas (RER)| market group for| APOS, S
	Organic acids	Output	g	716.7	Created in this study
Anaerobic Digestion	Organic acids	Input	g	716.7	Created in this study
	Electricity (AD)	Input	KWh	1.07	Electricity, medium voltage (GLO)| market group for| APOS, S
	Heat (DF)	Input	MJ	5.996	Heat, district or industrial, natural gas (RER)| market group for| APOS, S
	CO_2 emissions (AD)	Output	g	405	Carbon dioxide, biogenic
	Electricity (Biomethane)	Output (avoided product)	KWh	3.31	Electricity, medium voltage (Glo)| market group for| APOS, S
	Heat (Biomethane)	Output (avoided product)	MJ	10.943	Heat, district or industrial, natural gas (RER)| market group for| APOS, S
	Digestate	Output (avoided product)	Kg	9.26	Organo-mineral nitrogen fertilizer (GLO), market for| APOS, S
Bioleaching	Organic acids	Input	g	716.7	Created in this study
	CDW	Input (functional unit)	Kg	1	Created in this study
	Electricity (Leaching)	Input	KWh	7.29	Electricity, medium voltage (Glo)| market group for| APOS, S
	Heat (Leaching)	Input	MJ	7.196	Heat, district or industrial, natural gas (RER)| market group for| APOS, S
	Residual CDW	Output (waste to treatment)	Kg	0.15	Waste concrete (RoW)| treatment of, inert material landfill| APOS, S

Table 4.5. *Life Cicle Inventory reporting Scenario 1 of the LCA study evaluating the environmental sustainability of a bioleaching process for the treatment of CDW*

Regarding scenario 2, it only involved the landfilling of 1 Kg CDW, which was modelled as: Waste concrete (RoW) | treatment of, inert material landfill | APOS, S. The analysis was carried out using the SimaPro software and the Ecoinvent 3 database. The ReCiPe 2016 Midpoint (H) method was chosen for calculating environmental impacts.

4.3. Results and discussion

4.3.1. Synthetic test: results of powdery and solid state concrete samples

The preliminary phase of this study focused on the kinetic analysis of the leaching process induced by organic acids, with the aim of deciphering the effect of specific operational variables. The variables examined include: the type of acid used (acetic, propionic, butyric and lactic), the concentration of the acid, the ratio between the solid and liquid phase, the duration of contact and the physical state of the samples (powdery or solid).

This initial investigation aimed to evaluate the kinetics of the leaching process, taking into consideration the variables mentioned above. Extending the work of *Spasiano et al., 2019*, which examined the effects of acetic, propionic, and butyric acids, the present study incorporated the analysis of lactic acid. The latter, recognized as a key metabolite in the DF process, suggests that the substrate has not been completely transformed, despite exerting a significant corrosive effect on the concrete, as highlighted by *Shi & Qian., 2000b*. *Figure 4.2* reports the results of the first experimental phase in terms of pH trends.

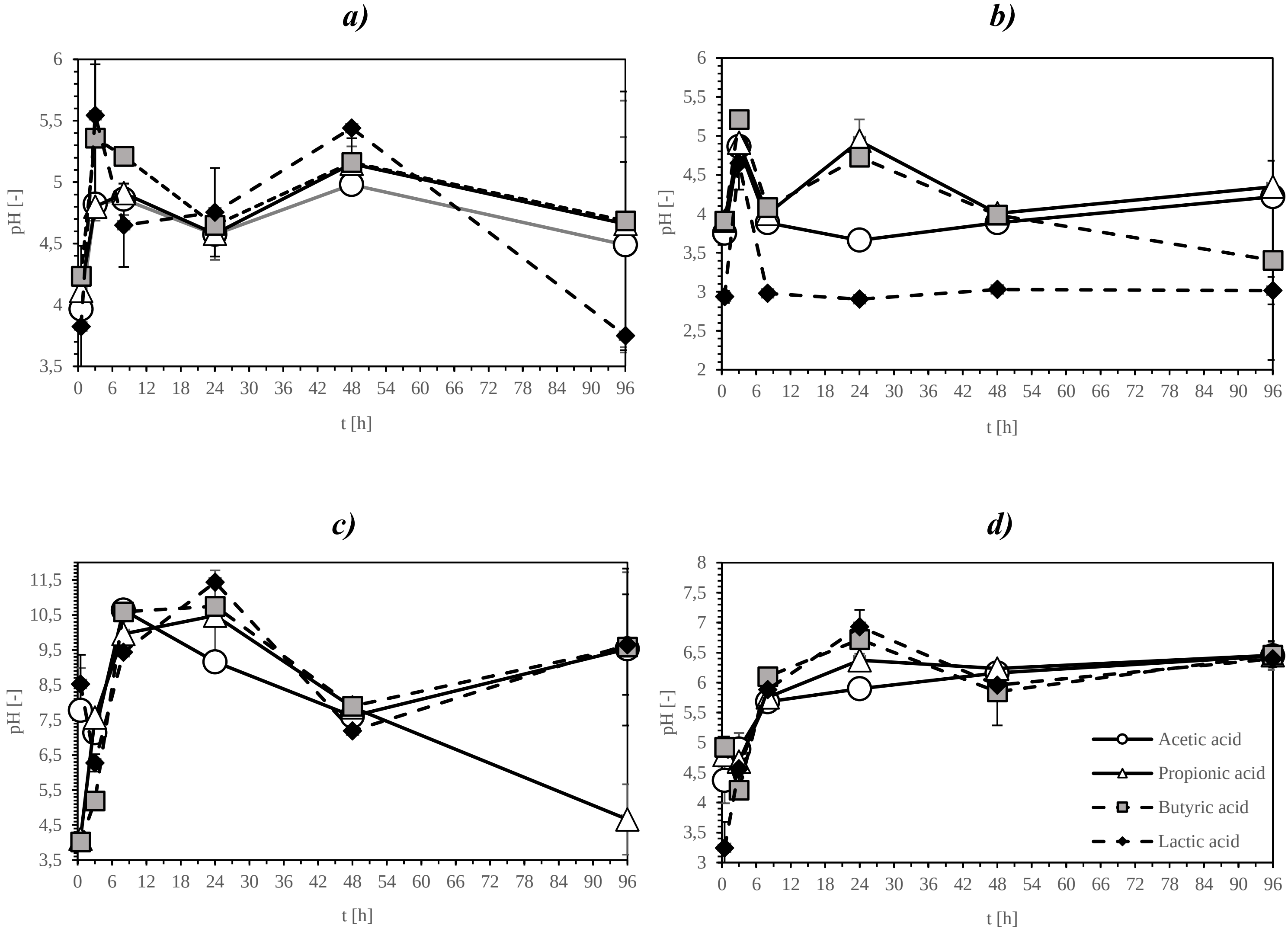

***Fig 4.2.** pH trends for leaching tests performed using the powder samples and different VFAs: **(a)** R=1/60 and C=0.25M, **(b)** R=1/300 and C=0.25M, **(c)** R=1/60 and C=0.03M and **(d)** R=1/300 and C=0.03M*

From the results it emerges that a contact time of 8 hours is sufficient to reach a pH plateau, indicating the exhaustion of the leaching effect. This phenomenon is particularly evident at the highest acid concentrations tested (0.25M), where the solid-liquid ratio of 1/60 shows a stabilized pH value between 4.5 and 5.5, as illustrated in Figure 1. In contrast, for a ratio of 1 /300, the pH remains in a lower range, varying between 3.0 and 4.5, due to less calcium leaching, as demonstrated in *Figure 4.2*.

For the lowest acid concentrations (0.03M) tested, we observed generally higher pH values. In all cases tested, the kinetics of the reactions quickly reached a stationary phase. This behavior is attributable to the inactivity of organic acids towards silicate components, such as silica (SiO_2), present in concrete, suggesting a clear slowdown of kinetic reactions, in accordance with what reported by *Shi & Qian., 2000a*.

Among the acids examined, lactic acid stands out for having consistently lower pH values than the others, in every condition of contact time, acid concentration and solid-liquid ratio tested. This difference is primarily attributable to its lower pKa value (*Siegumfeldt et al., 2000*). From *Figure 4.2c* and *Figure 4.2d* it can be observed that the solid-liquid ratio plays a crucial role. In fact, a greater solid load tends to result in a neutral-alkaline pH, interrupting the leaching process. This effect could have negative repercussions in the biological phase, leading to salt concentrations that exceed the tolerance thresholds of biological processes (*Gong et al., 2021*).

Below are the percentages of calcium leached:

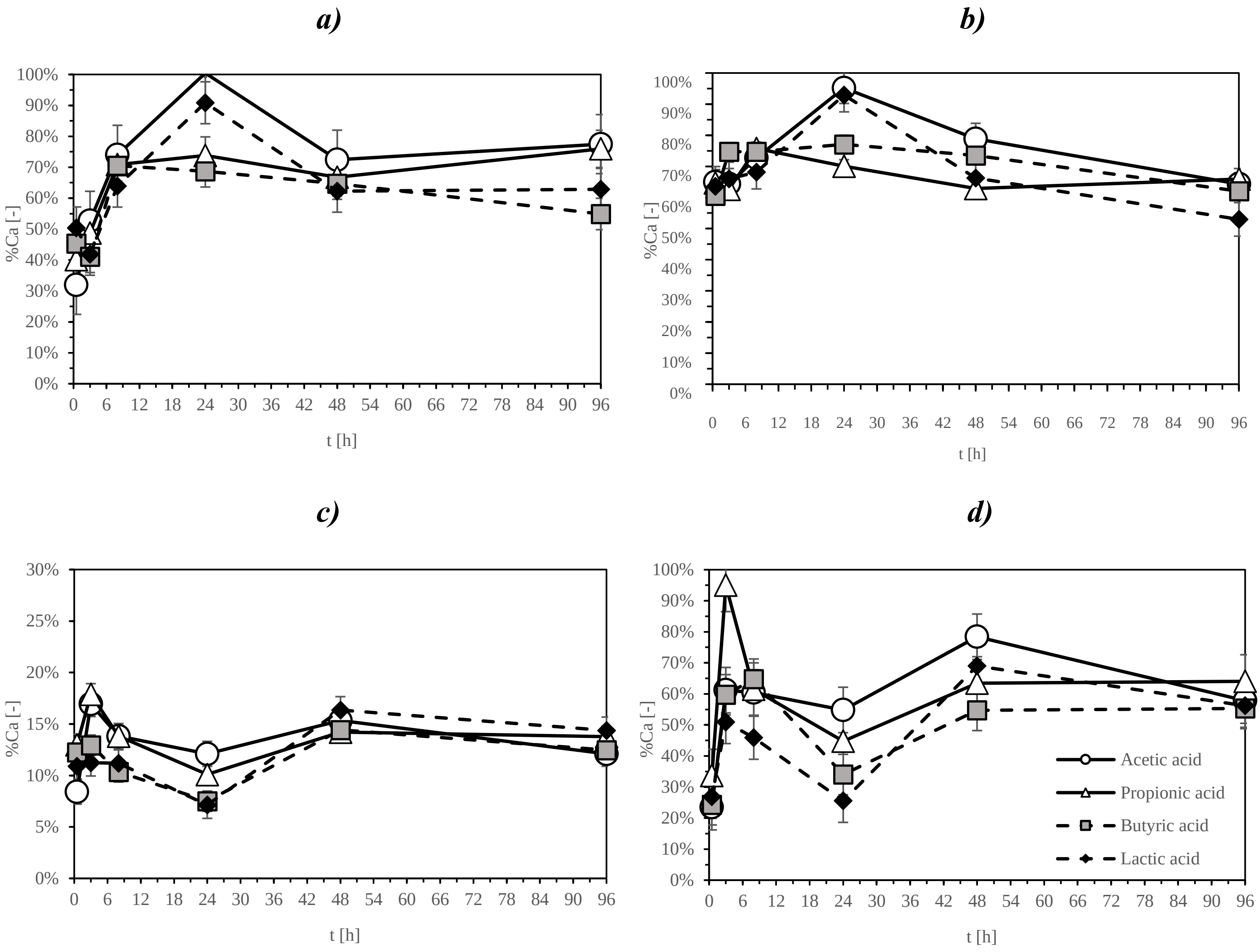

Fig 4.3. %Ca leached for leaching tests performed using the powder samples: ***(a)*** *R=1/60 and C=0.25M,* ***(b)*** *R=1/300 and C=0.25M,* ***(c)*** *R=1/60 and C=0.03M and* ***(d)*** *R=1/300 and C=0.03M*

Data analysis demonstrated that the maximum concentrations (0.25 M) tested were the most effective in terms of leaching, regardless of the solid-liquid ratio used. Specifically, we observed that removal efficiencies vary between 70% and 90% already after 8 hours of contact. This result is corroborated by the pH trend, which shows a stabilization plateau. No significant differences emerged in removal efficiency between the various acids tested, except for butyric acid, which proved to be the least efficient.

This phenomenon can be explained by considering the attachment mechanism to the sample. Unlike butyric acid, leaching in powdery samples occurs primarily through direct attack rather than diffusion, thus accelerating the kinetics of the process (*Perez et al., 2021*). Beyond 8 hours of contact, further time increments do not appear to significantly affect the efficiency of the process.

It was observed that at concentrations of 0.03M and with a solid-liquid ratio of 1/60, the lowest removal efficiency is recorded for each acid tested. This can be attributed to the low acid concentration and high alkaline content, which together tend to inhibit the leaching process. This is due to the resistance of cementitious materials in basic environments. However, as illustrated in *Figure 4.3*, even at these minimum concentrations, leaching efficiencies between 60% and 70% were obtained, thanks to a pH significantly lower than the 1/60 ratio, thus allowing the continuation of the leaching process, albeit with some degree of exhaustion.

Leached calcium is present in solution in the form of acetate, propionate, butyrate and lactate, in accordance with the chemical equilibria described by *Spasiano et al., 2017*.

$CH_3\text{-}CHOH\text{-}COOH_L \leftrightarrow CH_3\text{-}CHOH\text{-}COO^-_L + H^+$

$CH_3\text{-}COOH_L \leftrightarrow CH_3\text{-}COO^-_L + H^+$

$CH_3\text{-}CH_2\text{-}COOH_L \leftrightarrow CH_3\text{-}CH_2\text{-}COO^-_L + H^+$

$CH_3\text{-}CH_2\text{-}CH_2\text{-}COOH_L \leftrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}COO^-_L + H^+$

$Ca^{2+}_S + 2CH_3\text{-}CHOH\text{-}COOH_L \leftrightarrow Ca(CH_3\text{-}CHOH\text{-}COOH)_{2,L}$

$Ca^{2+}_S + 2CH_3\text{-}COO^-_L \leftrightarrow Ca(CH_3\text{-}COO)_{2,L}$

$Ca^{2+}_S + 2CH_3\text{-}CH_2\text{-}COO^-_L \leftrightarrow Ca(CH_3\text{-}CH_2\text{-}COO)_{2,L}$

$Ca^{2+}_S + 2CH_3\text{-}CH_2\text{-}CH_2\text{-}COO^-_L \leftrightarrow Ca(CH_3\text{-}CH_2\text{-}CH_2\text{-}COO)_{2,L}$

Based on the results obtained using powder samples, the study was carried out on solid state samples.

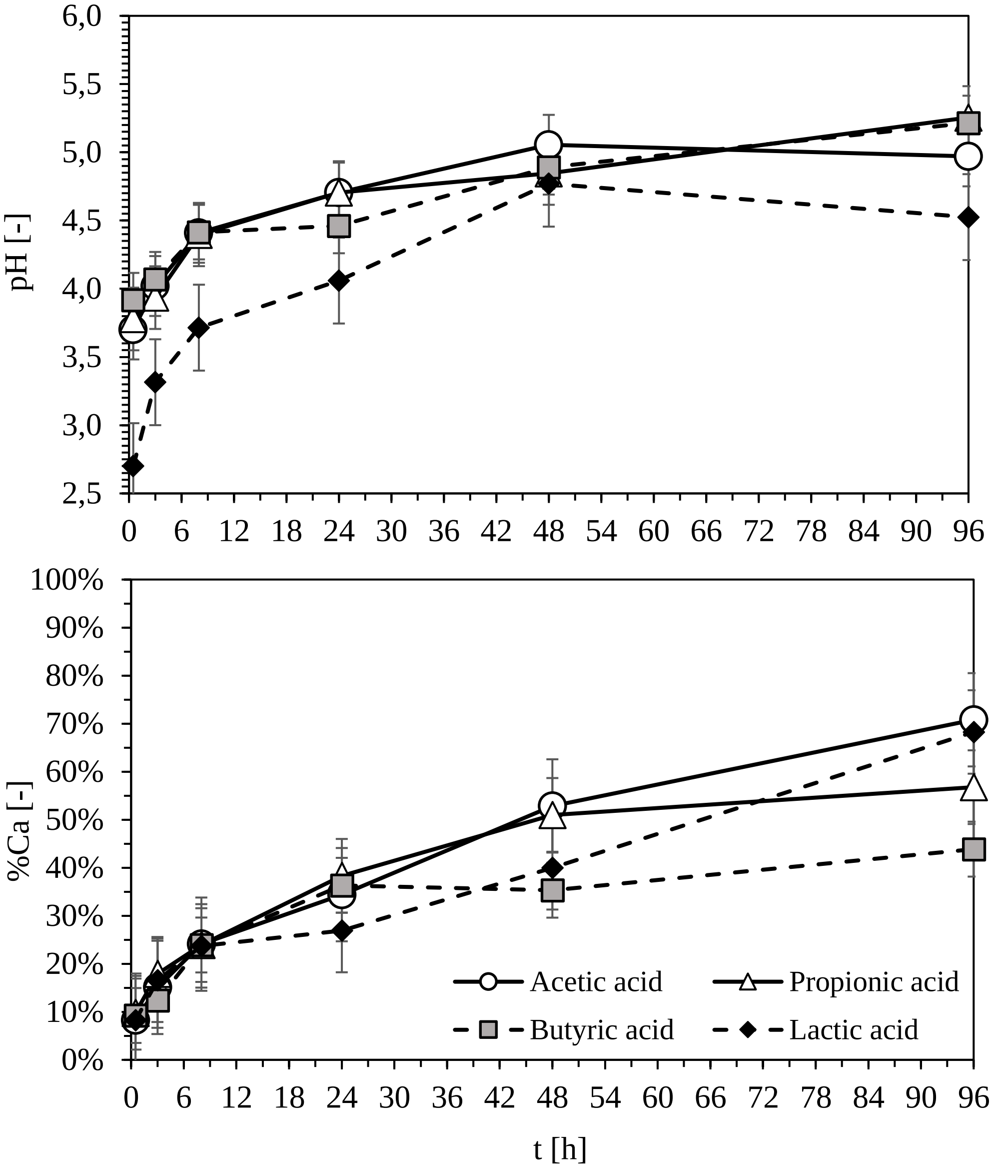

Figure 4.4. *pH trend and %Ca leached for tests with solid samples with R=1/60 and C=0,25M*

Results revealed that leaching in such conditions is primarily governed by diffusive mechanisms. The porous nature of the sample facilitates the selective passage of some chemical species, while others are hindered due to steric hindrance. Four main steps have been identified in the leaching process of solid samples. *Direct attack:* The external cement matrix is initially attacked by the acid solution. *Diffusion effect:* The porosity of the sample creates a calcium concentration gradient between the outside and the inside, influenced by the molecular size of the acids, which can limit their penetration due to steric hindrance. *Formation of calcium oxalate:* The interaction between some acids, such as oxalic acid, and the cement paste leads to the precipitation of calcium oxalate, an insoluble salt with an octagonal structure that can further obstruct the passage of acids, acting as a screen protective for the sample. *Complexation and cation extraction:* Chelating structures can accelerate leaching kinetics by extracting calcium from cement networks (*Garrabrants et al., 2004*).

Considering these dynamics, it becomes evident that solid samples, to achieve leaching efficiencies comparable to those of powdery samples, require significantly longer contact times, keeping the acid concentration and the solid-liquid ratio constant. This need is reflected in the pH trend during the experiments, conducted with an acid concentration of 0.25 M and a solid-liquid ratio of 1/60. This phase of the study allowed us to compare the leaching effectiveness of the acids and the contact time necessary to reach equilibrium.

The analysis of the pH trend reveals that the equilibrium of the leaching process is reached after 96 hours of contact. Significantly, as also observed in previous experiments, lactic acid stands out for its ability to maintain lower pH values compared to the other acids tested.

The examination of the leaching capacity highlighted acetic acid as the most effective, due to its smaller molecular size, reaching a leaching capacity of up to 71% after 96 hours of contact. Lactic acid came in next, with a capacity of 68%, followed by propionic and butyric acid, with 57% and 44% respectively. The reduced efficiency of butyric acid is attributable to its larger size, which however also makes it the least aggressive agent in powdery contexts. Previous studies (*Santos et al.,* *2014*) underlined a particular selectivity of acetic acid towards calcium ions, estimated at around 30%.

The comparison between the samples in solid and powdery states confirms that the contact times necessary to reach equilibrium are significantly longer. However, for practical applications it is preferable to treat solid matrix waste. Grinding waste into powder has economic and logistical disadvantages, making this option impractical. Furthermore, it was observed that the increase in contact time corresponds to an increase in the leaching percentage. The data analysis allowed us to identify two distinct phases in the process: a rapid initial kinetic linked to the attack of the external surface of the sample by the OAs, followed by a progressive slowdown due to the diffusion mechanism.

These results played a fundamental role in the study, guiding the choices relating to the type of substrate most suitable for DF processes and the determination of the optimal solid-liquid ratio to maintain an effective balance without excessively increasing the alkalinity of the leaching solution. In particular, CW was selected as a substrate for its rapid bioavailability and for the type of liquid metabolites it promotes, consistently with the acids analyzed. To generate both acetic acid and lactic acid, maintaining a controlled pH level is crucial. Indeed, the pH should not be too low, as this could hinder the activity of fermentative bacteria producing OAs and hydrogen, while favoring lactic acid bacteria exclusively (*Garcìa-Depraect et al., 2021*). The R ratio of 1/300 was chosen to mitigate the increase in alkalinity at the beginning of the process, which could hinder the effectiveness of the biological process.

4.3.2. *Tests with real effluent: results of solid state concrete samples*

From the results of previous synthetic tests, bio-leaching process was tested on a solid concrete sample using the real effluent of DF from CW and a solid-liquid ratio of 1/300. The results in terms of DF process and leaching performances are reported in *Figure 4.5* and *Figure 4.6*.

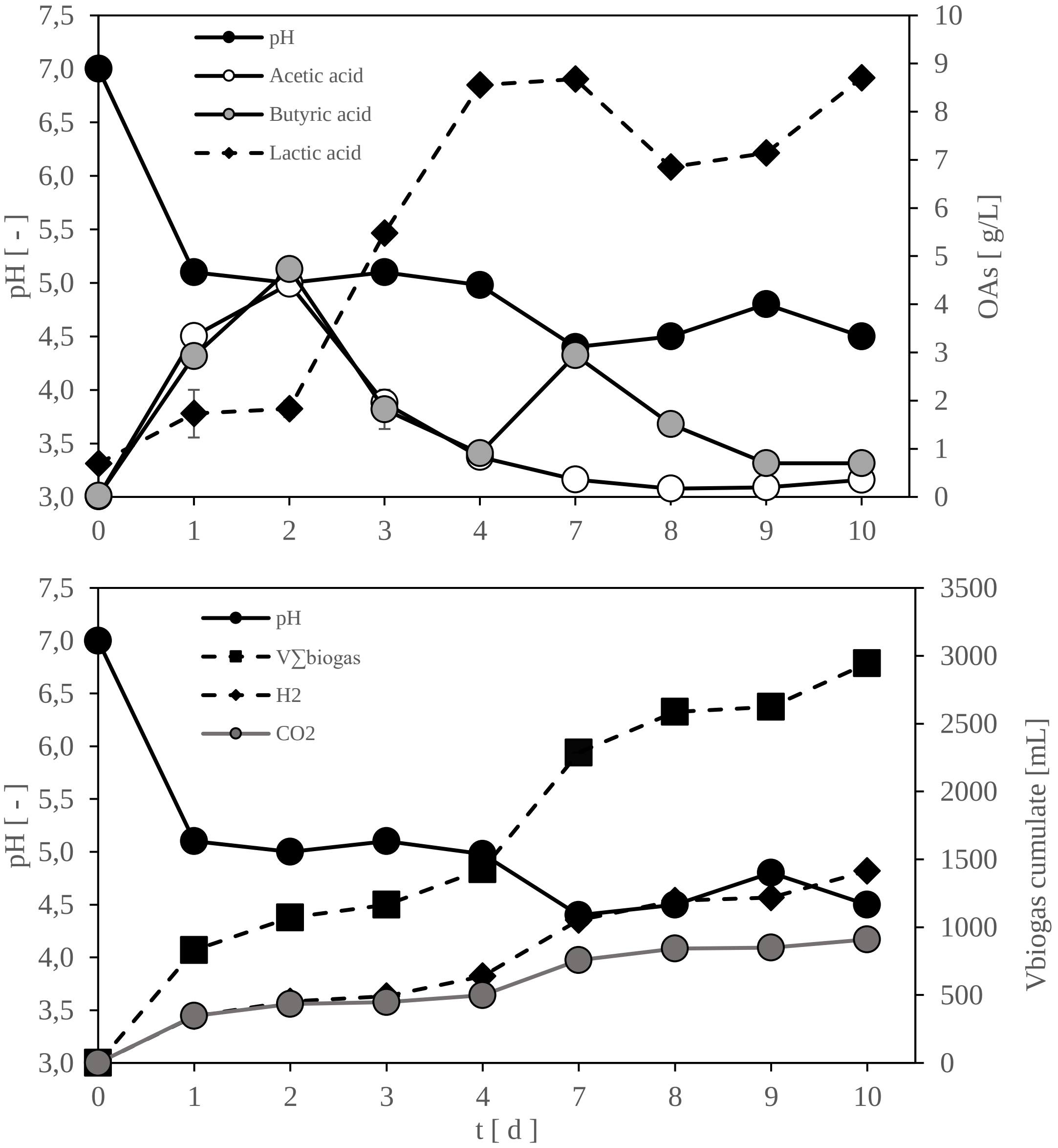

Figure 4.5. *Cumulative biogas and OAs production with pH trend in DF-CW reactors*

A rapid decrease in pH during the first two days was observed, followed by a more gradual decrease until stabilization around an average value of 4.2. This trend was correlated with the analysis of liquid samples, which indicated significant accumulation of OAs. Despite the use of phosphate buffer, the effluent still exhibited acidic characteristics due to the high production of organic acids. Nevertheless, the buffer enabled the production of hydrogen and other acids (i.e. acetic, butyric) besides lactic acid. Such phenomenon was not observed in previous studies conducted on the same DF process, without any pH correction (*Luongo et al., 2019*), confirming the beneficial effect of the buffer for applications aimed at hydrogen and acids mixtures production.

Effluents analysis revealed high concentrations of lactic acid (8.06 g/L at the end of the fermentation process), suggesting the presence of lactic acid bacteria contained in the CW, as highlighted by *Akhlaghi et al., 2017*. In addition to lactic acid, the presence of butyric and acetic acid was also detected (0.5 and 0.7 mg/L, respectively, at the end of the fermentation process), the accumulation of which was correlated to the production of H_2 gas, as documented in the literature (*Ghimire et al., 2017; Luongo et al., 2019; Policastro et al., 2021; Policastro et al., 2022*). It is interesting to note the absence of propionic acid production during the 10 days of operation of the reactors, probably due to the lack of propionate-producing saccharolytic clostridia, crucial for the H_2 consumption pathway (*Khanal et al., 2004*).

From the analysis of the data it emerges that, starting from the seventh day, there is a reduction in pH accompanied by an arrest in the production of H_2, a phenomenon attributable to the inhibitory effect due to the accumulation of OAs. The correlation between the quantitative and qualitative measurements of the biogas and the pH values detected highlights that the reactors produced approximately 400 mL/L d of biogas, of which 180 mL/L d of H_2. It should be underlined that, from the seventh day onwards, biogas production showed a tendency towards stationarity.

The initial pH value was 4.22, a typical level for an effluent derived from real wastewater, characterized by presence of salts that prevent excessive acidification of the cheese-whey. At the start of the process, a linear increase in pH was observed, which subsequently reached a stabilization phase. This phenomenon suggests that the concrete exerted a buffering effect during bio-leaching process, contributing to the increase in pH until an equilibrium state was reached. Although the acid concentration was relatively low, the increase in pH was not excessive, also thanks to the identification of an optimal solid-liquid ratio (R) previously determined.

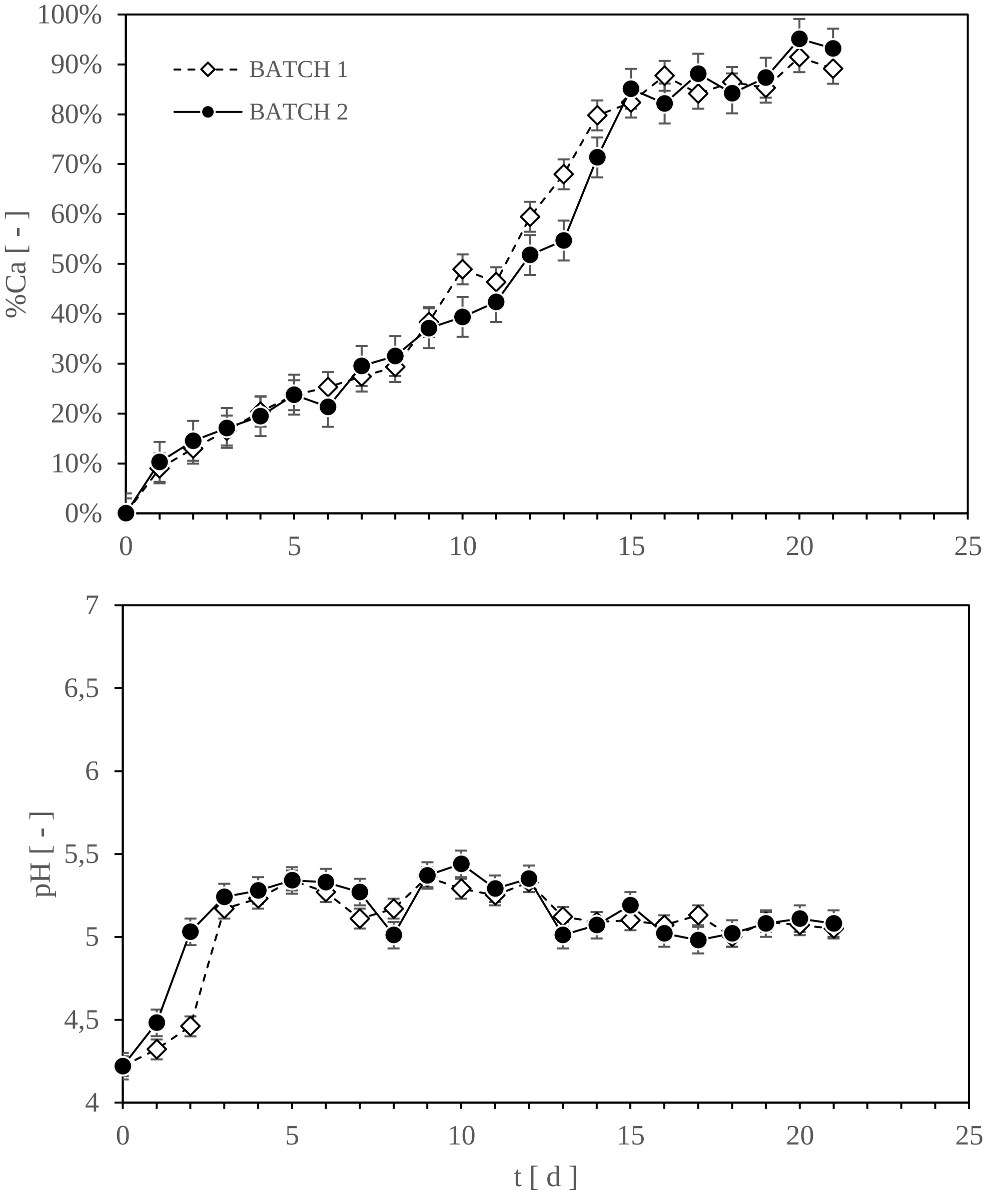

Figure 4.6. *%Ca leached and pH trend at various contact times in bio-leaching tests on concrete samples treated with real effluent*

From the analysis of the dynamics of calcium leaching over time, it emerges an increase of the pH value, which is attributable to the leaching of the concrete present in the treated samples. In particular, the acids present in the DF effluent effectively attacked the material, solubilizing the calcium from the concrete. In the first 5-10 days, the leaching trend appears almost linear, and then stabilizes at a plateau starting from 15th day. The leaching kinetics tends to slow down, a phenomenon that can be interpreted considering the relatively low concentrations of acid in solution, which are however sufficient to guarantee a leaching of the sample of at least 90-95%. Furthermore, the diffusion mechanisms, already observed in the tests with synthetic solutions, exerted an influence on the bio-leaching process, moderating the release of Ca^{+2} ions in solution.

These experiments confirm the feasibility of the bio-leaching process using OAs on solid state concrete samples and also highlight the buffer function of the concrete samples, with a solid-liquid ratio of 1/300. Since this study marks the first trial of this process, the phases of dark fermentation and leaching were tested sequentially to investigate each process independently. From the results obtained, which highlight the utility of the buffer in the DF phase and the buffering capacity of the concrete, it is evident that a prospective direction for this research would involve coupling the two phases into a single reactor.

4.3.3. Life Cycle Assessment (LCA) and preliminary economic evaluation

Figure 4.7 reports the total environmental impact of each process contributing to Scenario 1 of the LCA.

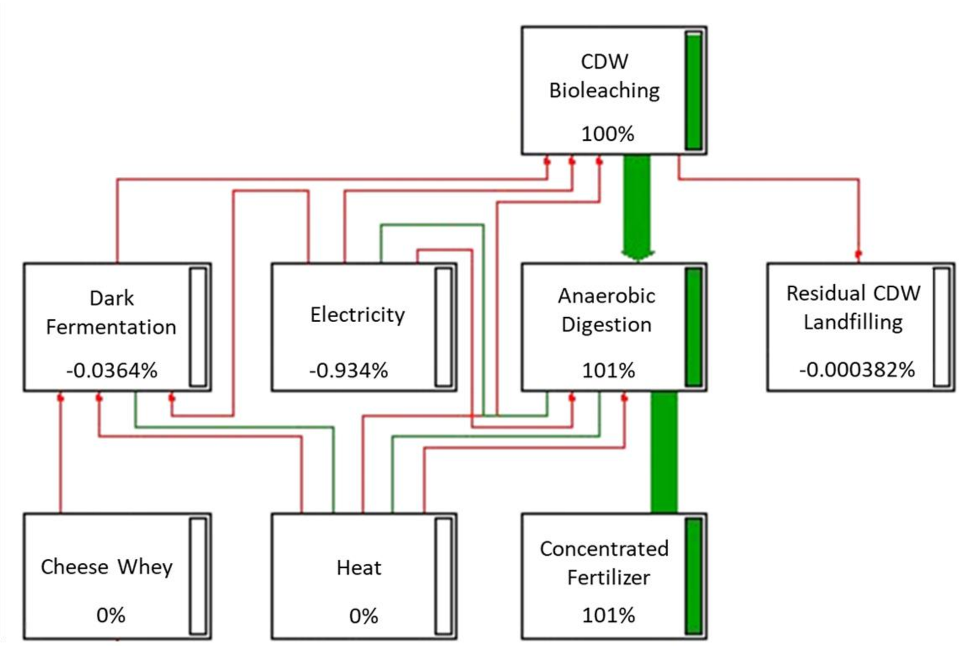

Figure 4.7. *Sankey diagram showing the normalised contributions to the total impact. Green arrows and red arrows represent positive and negative environmental burdens, respectively*

The analysis of the chart indicates that the process is environmentally advantageous (with a negative environmental impact). This positive outcome is attributed to the recovery of digestate as fertilizer. Specifically, the analysis considers that using the produced digestate as fertilizer helps avoid the production of an equivalent volume of organic-mineral nitrogen fertilizer. The production of such fertilizer is estimated to result in significant environmental burdens, as documented in the literature (*Skowrońska and Filipek, 2014*).

Regarding other contributions, it is noteworthy that the energy generated in both the DF and AD processes adequately meets the heating requirements. However, there is a shortfall in meeting the electricity demand. This discrepancy arises from the assumption in this study that the leaching phase occurs in a separate reactor. This separate reactor imposes a substantial demand for both heat and energy due to the prolonged duration of the process. If the bioleaching phase were to be conducted within the DF reactor, a positive energy balance would be achieved, leading to an even greater environmental advantage. Exploring this possibility should be the focus of future research on this technology, in line with the observations made regarding the experimental data in this study.

The results of the LCA characterization analysis for each impact category of both scenarios are reported in *Table 4.6*.

Impact Category	**Unit**	**Scenario 1 (bioleaching)**	**Scenario 2 (landfilling)**
Global warming	kg CO_2 eq	-56,8822	0,005217
Stratospheric ozone depletion	kg CFC11 eq	-0,00031	3,79E-09
Ionizing radiation	kBq Co-60 eq	-0,86212	0,000139
Ozone formation, Human health	kg NOx eq	-0,11319	4,53E-05
Fine particulate matter formation	kg $PM_{2.5}$ eq	-0,07538	1,3E-05
Ozone formation, Terrestrial ecosystems	kg NOx eq	-0,11584	4,62E-05
Terrestrial acidification	kg SO_2 eq	-0,23392	2,87E-05
Freshwater eutrophication	kg P eq	-0,0161	1,66E-06
Marine eutrophication	kg N eq	-0,00287	4,07E-08
Terrestrial ecotoxicity	kg 1,4-DCB	-355,821	0,017659
Freshwater ecotoxicity	kg 1,4-DCB	-3,39514	6,94E-05
Marine ecotoxicity	kg 1,4-DCB	-4,49286	0,000105
Human carcinogenic toxicity	kg 1,4-DCB	-3,0028	0,000252
Human non-carcinogenic toxicity	kg 1,4-DCB	-72,5065	0,001833
Land use	m^2 crop eq	-1,68931	0,00072
Mineral resource scarcity	kg Cu eq	-0,82454	1,05E-05
Fossil resource scarcity	kg oil eq	-15,625	0,003371
Water consumption	m^3	-1,32942	0,000158

***Table 4.6**. Life Cycle characterization results*

The traditional landfill scenario (Scenario 2) exhibits a detrimental environmental impact (positive burdens) across all impact categories, with a significant influence on freshwater ecotoxicity, marine eutrophication, and ozone formation. In contrast, the bioleaching process (Scenario 1) demonstrates a favourable environmental impact across all categories (negative burdens). Specifically, this innovative technology would primarily contribute to mitigating terrestrial ecotoxicity and global warming potential.

Looking ahead, the study opens several avenues for further research and development:

Scale-up Studies: There is a pressing need for scale-up studies to validate the efficiency and feasibility of applying DF-derived organic acids in CDW treatment on a larger scale. Such studies would help address the challenges of process optimization, including the selection of suitable organic waste materials and the refinement of operational conditions.

Technological Innovations: Future research should explore technological innovations that can enhance the efficiency of DF processes and the subsequent treatment of CDW. This includes advancements in bioreactor designs, microbial consortia optimization, and the development of more effective separation techniques for organic acids. *Economic Analysis:* Comprehensive economic analyses are essential to assess the viability of integrating DF with CDW treatment. This should include evaluations of cost-saving potentials, investment requirements, and long-term financial benefits associated with landfill diversion and resource recovery. *Environmental Impact Assessments:* Further studies should focus on detailed Life Cycle Assessments (LCA) to quantify the environmental benefits of this integrated approach. Assessments should consider the reduction in greenhouse gas emissions, energy consumption, and the overall environmental footprint compared to traditional CDW disposal methods. *Policy and Regulatory Frameworks:* The development of supportive policy and regulatory frameworks is crucial to facilitate the adoption of innovative waste management strategies. Policymakers should be informed about the benefits of DF and CDW treatment integration to encourage the implementation of policies that promote waste-to-energy initiatives and resource recovery. *Public and Industrial Engagement:* Engaging with the public and industries involved in construction and waste management is vital for the successful implementation of this approach. Awareness campaigns and demonstration projects could help showcase the benefits and practicality of integrating DF processes with CDW management.

In conclusion, the integration of DF with the treatment of CDW offers a promising pathway towards achieving sustainable waste management and resource recovery. Future efforts should focus on overcoming the technological, economic, and regulatory challenges to unlock the full potential of this innovative approach.

4.4. Conclusions

This study highlights the significant potential of integrating DF with the treatment of CDW as a novel and sustainable waste management strategy. By harnessing the biological process of DF to convert organic substrates into molecular hydrogen, we not only address the pressing issue of CDW disposal but also tap into the added value of generating renewable energy and valuable byproducts like organic acids. These acids have shown promise in leaching processes aimed at dissolving components of hardened cement paste, thus reducing the volume of CDW destined for landfills.

Our findings underscore the critical role of selecting the most efficient organic acids for CDW leaching and the importance of optimizing operational conditions to maximize both environmental and economic sustainability. The use of real waste as a substrate for DF has further demonstrated the feasibility of this approach, providing a dual benefit of waste reduction and resource recovery.

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Conclusions

The importance of CDW disposal is underlined by the study carried out on the different types of waste, which indicated the most relevant elements based on their economic importance and risk to human health. Different chemical, physical or biological processes can be applied for the treatment and recovery of CDW. In this thesis, the study and applications of bioleaching processes have been explored.

In chapter 2, the feasibility of applying bioleaching on W12B category CDW (mineral wastes containing asbestos) was studied. The VFAs produced through DF processes leached the Mg present in the brucitic layer of the chrysotile fibers contained in the ACW, effectively denaturing the asbestos present in the treated samples. During the tests the pH went from alkaline values to acidic values in all applied conditions. Different temperatures and solid-liquid ratios were tested, showing variable results and different productions of VFAs. The results of these first tests demonstrated the possibility of applying a bioleaching process for the integral treatment of an ACW: it was possible not only to denature the entire sample of treated ACW, but also to obtain a biogas CH_4-rich by converting the supernatants derived from the DF process in a subsequent AD process. In chapter 3, the possibility of using different mixtures of VFAs obtained through a DF process conducted in semi-continuously fed reactors at different pH value ranges for the treatment of CLS samples made in the laboratory (having the same characteristics as waste category W121 mineral wastes). The main parameters followed to evaluate its feasibility were the percentages of weight and volume reduction of the treated samples, pH monitoring and the quantity/composition of the biogas produced. Tests with pH 5.0-5.5 showed better results than other monitored pH ranges, indicating the ability of the attached biomass to produce a more effective mixture of VFAs. This is a very interesting aspect, since this experimentation constitutes a preliminary approach to subsequent studies aimed at optimizing the efficiency of the process. In chapter 4, experimental investigations evaluated the leaching efficiency of various synthetic organic acids, generally produced during DF. Subsequently, optimal operating conditions leading to the production of the desired organic acids, including the use of cheese whey as a substrate, were applied to the DF, and the bioleaching process was evaluated using the real effluent. The results showed that the most effective organic acids are lactic acid and acetic acid. The efficiency of the process, compared to the traditional landfill scenario, was also confirmed in terms of environmental sustainability through LCA and economic feasibility analysis.

Bioleaching has demonstrated its effectiveness as an environmentally sustainable method for treating various types of CDW. The findings presented in this thesis underscore the potential for future research endeavors to explore the introduction of organic waste as inoculants in DF and AD processes, particularly in fed-batch and semi-continuous reactors. This approach could enhance the efficiency of bioleaching treatments. Furthermore, there is room for further investigation into bioleaching treatments for the extraction of precious metals from different waste sources, such as spent mufflers and electronic boards, given the growing demand for recycling and resource recovery. In addition, future research should delve into the selectivity of waste types amenable to bioleaching processes, enabling tailored solutions for waste disposal. Bioleaching represents an emerging technique that finds application in waste management, particularly in the context of ACW. Depending on the different types and sizes of ACW, different treatment methods can be developed. The effectiveness of the process can vary based on the physical and chemical characteristics of the material to be treated. To optimize the treatment and ensure greater efficiency, different reactor configurations will be evaluated and considered. Among these, A-MBBR and MBR (Membrane Bio Reactor) stand out. These reactor configurations would allow to effectively retain ACW residues with dimensions d>0.1 micron, thus allowing a better treatment yield and effective biological degradation of ACW. These advances in bioleaching technology open up new perspectives for the sustainable management of asbestos and the reduction of the environmental impact of such waste.

To advance these research prospects into practical applications, the establishment of pilot plants in collaboration with specialized companies could play a pivotal role in developing concrete and scalable solutions for sustainable waste management. Such initiatives not only contribute to environmental protection but also promote resource conservation and economic growth.

Author information

Biography

Gennaro Trancone, born in Naples on 03.03.1986, obtained a three-year degree in Civil and Environmental Engineering from the University of Naples Parthenope on 14.12.2015. On 01.23.2020 he obtained a master's degree in Environmental and Territorial Engineering from the University of Naples Federico II with an experimental thesis carried out at the LARA (Laboratory of Environmental Analysis and Research) entitled "Biological treatment of cement waste containing asbestos" (Speakers: Ch.mo. Ing. F. Pirozzi; Co-rapporteurs: Prof. Ing. M. Race and Prof. Ing. D. Spasiano). After graduation, the candidate obtained the title of Safety Trainer on 11.02.2020 from the AIFES body (Italian Association of Expert Trainers in Safety at Work) (Decree 81/08 - Ministerial Decree 06.03.2013); he also obtained the Higher Education Master's Degree in Integrated Management Systems: Quality, Safety, Energy and Environment on 10.24.2020 at ALMA LABORIS Business School. Since 05.11.2020 he has been working as an Open Water Scuba Instructor and IDC Staff Instructor at PADI training centers, dealing with the planning and organization of recreational diving activities, environmental protection and scientific activities for monitoring microplastics and pollutants in the marine environment. Since 01.14.2021 he has been registered with the Order of Engineers of the Province of Naples, in section A of the civil and environmental sector with number 22658. Between 2020 and 2021 he carried out support activities for the design of purification plants suitable for the treatment of civil water and sewage systems for the company ETICA spa Environmental Technologies. During 2022 it carried out environmental monitoring activities on behalf of the Polytechnic of Bari.

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