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Detritus - Multidisciplinary Journal for Waste Resources and Residues - is aimed at extending the “waste” concept by opening up the field to other waste-related disciplines (e.g. earth science, applied microbiology, environmental science, architecture, art, law, etc.) welcoming strategic, review and opinion papers. **Detritus is indexed in Emerging Sources Citation Index (ESCI) Web of Science, Scopus, Elsevier and Google Scholar.** Detritus is an official journal of IRACE / International Research Association on Circular Economy ([www.irace.eco](http://www.irace.eco)) and IWWG / International Waste Working Group ([www.iwwg.eu](http://www.iwwg.eu)).

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## Editorial

# ENERGY POLYGENERATION AND CIRCULAR ECONOMY

Polygeneration (sometimes called multigeneration) is an energy process which extends simple generation systems for two products (e.g., cogeneration) and three products (e.g., trigeneration) to four or more products.

Polygeneration classifications of various types have been reported, including classifications by input (renewable energy, fossil fuel, waste, etc.) as well as classifications by outputs (electricity, heat, cool, desalinated water, synthetic fuels, etc.).

Polygeneration has considered as a component of sustainable engineering and has been examined from exergy, energy, environment and sustainable development perspectives.

Recent technology advances of various types have occurred for polygeneration energy systems, and reported in many countries.

Some of the more noteworthy of these follow:

- Advances in energy storage technologies to support polygeneration (e.g., thermal energy storage, batteries, pumped storage, hydrogen storage)
- Advances in district energy systems and distributed energy systems, that allow advantageous inputs to be selected, and products to be transported to where they are in demand and utilized in an effective manner.
- Developments in systems for waste-to-energy and renewable energy. The latter include systems that use biomass energy, solar energy geothermal energy wind energy and combinations of these.
- Development and commercialization of new technologies that can support polygeneration, including fuel cells (solid oxide fuel cells, PEM fuel cells, alkaline fuel cells, etc.) artificial intelligence and machine learning desalination technologies and nanotechnology systems.

## Integration of polygeneration within Circular Economy strategies

Sometimes, the inputs of polygeneration energy systems include waste in ways that yield viable systems that are often advantageous to more conventional systems.

Some examples of such systems follow:

- Jasim et al. (2024) performed a thermodynamic, environmental and economic assessment of a polygeneration system with waste heat recovery. The system for polygeneration includes CO<sub>2</sub> separation and water desalination sections. Fresh water is produced by the system at a rate of 3560 kmol/h while electricity is produced at a rate of 43 MW. The polygeneration efficien-

cies were reported to be 32% energy based on and 88% based on exergy.

- Taheripour et al. (2024) proposed and analyzed a polygeneration system for electricity and hydrogen from waste heat. The waste heat is sourced and recovered from a steel manufacturing plant. Components of the polygeneration energy system are: electrolyzer (proton exchange membrane type), Kalina power cycle and Rankine power. The economic return period for the polygeneration energy system is projected to be seven years. That projection is based on expected annual revenues of 3.6 MM\$ from sales of electricity and 3.8 MM\$ from sales of hydrogen is 3.6. The system exhibits an energy efficiency of 26%, but a much higher exergy efficiency, at 57%.
- Ratlamwala et al. (2024) examined for a community a polygeneration system. The outputs of the polygeneration energy system follow: electricity, desalinated water, space heating, space cooling, hot water, and waste heat for industry. The system is fed with non-renewable and renewable energy sources. Desalinated water is generated at a rate of 10.5 kg/s of for one of the working conditions considered.

The approaches and methods to attain such integrated polygeneration energy systems are varied, and often creative. For instance, Kalina and Pohl (2024) assessed technically and economically a polygeneration energy hub for buildings that addresses well multi-temperature heat demands. Important facets of the design were noted to be integration of waste and renewable energy inputs, as well as energy storage and decentralization. The system components include high-temperature heat pumps among other devices.

Advances in polygeneration energy systems and waste utilization often rely on economic methods to enhance economics. For example, Taheripour et al. (2024) performed a technoeconomic analysis of polygeneration using heat recovered from steel plant waste in order to provide electricity and hydrogen. The system initial capital cost was found to be \$36.6 million, while its annual revenues are \$3,600,000 from the sale of electricity and \$3,800,000 from hydrogen, respectively, leading to a return period of seven years.

The complexity of the design and operation of polygeneration systems integrated with waste often benefits from astute use of optimization. Ren et al. (2022), as a case in point, reviewed the optimization of distributed polygeneration energy systems. They considered numerous applica-

tions (cities, districts, neighborhoods and others) as well as relevant technologies (waste recovery, renewable energy, energy storage and others).

### Benefits of integrating polygeneration and waste recovery

There are many potential benefits of integrating polygeneration and waste recovery in appropriate manners. These include higher efficiencies than stand-alone processes for the corresponding separate products, as well as enhanced environmental performance and economics, and ultimately greater sustainability.

A good example is the investigation by Jasim et al. (2024) of a polygeneration system integrated with waste heat recovery. The system incorporates a carbon dioxide separation/liquefaction cycle, and seeks to reduce pollutants emissions and environmental impacts. Multiple factors are examined economics environmental impact, and energy and exergy usage. The system was shown to have a unit carbon dioxide release of 0.034 kg/kWh.

Another instructive example of the potential benefits of integrating polygeneration and waste recovery is for an application in industry. In particular, a steel manufacturing plant with waste heat recovery was investigated by Taheripour et al. (2024) for the incorporation of polygeneration of electricity and hydrogen.

With the system, 262 MW of waste energy is recovered from the steel plant, with an energy efficiency of 26% and an exergy efficiency of 57%, and with an economic investment payback period of about 7 years.

Given the steel industry constitutes a major portion of the industrial sector, the results can be extrapolated and seen as important.

### Conclusions

Polygeneration systems are increasingly applied across energy utilities, communities, industries, and other sectors

of the economy. When well-designed, these systems offer cleaner and more efficient alternatives compared to using separate processes for each output. In some cases, they also deliver improved economic performance.

However, the full potential of polygeneration is not always realized in practice. One effective way to enhance its performance is to integrate it into circular economy strategies by utilizing waste as an energy input. Such integration can significantly contribute to environmental protection and the transition toward sustainability.

Optimization plays a key role in advancing polygeneration, enabling the balancing of multiple objectives, including environmental impact, energy efficiency, and economic viability.

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# LANDFILL LEACHATE AMMONIA REMOVAL IN SUBMERGED AERATED FILTER: A FULL SCALE STUDY UNDER NON-ALKALINIZATION CONDITION

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## ABSTRACT

This study presents the performance of submerged aerated filter technology in landfill leachate treatment. The main objective was to evaluate ammonia removal. The investigation proposes the filter, without the use of chemical agents to alter the pH, as an applicable mechanism for nitrogen removal in the treatment. The research was developed in real-scale. The efficiencies obtained, for a hydraulic retention time of 56 days, were: 83% removal of ammoniacal nitrogen (influent concentration of 2,653 mg/L) and 78% removal of total Kjeldahl nitrogen (influent of 3,058 mg/L). The pH variation range was from 8.3 to 9.3. The alkalinity showed a reduction from 12,338 mg/L to 4,015 mg/L. The dissolved oxygen concentration ranged from 0 to 8.3 mg/L. Additionally, the efficiencies in removal organic matter were: 35% removal of COD (influent of 5,022 mg/L), 45% BOD removal (influent of 2,400 mg/L) and 40% TOC removal (influent of 2,141 mg/L). The expulsion of ammonia was great. The oxidation of organic matter, even after the establishment of a very favorable aerobic condition and despite the long liquid retention time, encountered difficulty in the extremely varied and complex composition of the leachate. The research hypothesis was positively confirmed: there is no need to alkalinize the medium to obtain high ammonia expulsion in the leachate. The removal, in terms of load, was quite significant: 2.6 tons.

## 1. INTRODUCTION

The concentration of ammoniacal nitrogen in landfill leachate generally reaches high values. In Chinese leachate, values of up to 3,100 mg/L were recorded (Ma et al., 2022). In Brazil, the leachate generated in the Bandeirantes and São João landfills, both in the state of São Paulo, presented concentrations of 2,390 mg/L and 2,870 mg/L, respectively (Mahler et al., 2020).

Ammoniacal nitrogen is composed of a gaseous fraction ( $\text{NH}_3$ ) and an ion (ammonium,  $\text{NH}_4^+$ ). The concentrations of each form depend on the pH of the liquid medium. For pH close to 9.2, there is 50%  $\text{NH}_3$ -N and 50%  $\text{NH}_4^+$ -N; for pH below 9.2,  $\text{NH}_3$ -N concentrations fall and  $\text{NH}_4^+$ -N rise proportionally; for pH greater than 9.2,  $\text{NH}_3$ -N concentrations rise and  $\text{NH}_4^+$ -N fall proportionally (Bidone, 2018). This behavior of chemical forms as a function of the variation in the pH can be seen in Figure 1.

The air stripping (or volatilization) of ammonia is a consequence of the forced introduction of air into the liquid medium. In this case, the physical effect of replacing, in the liquid mass, one gas ( $\text{NH}_3$ ) with another (air) prevails. The classic methodology consists of raising the pH of the

leachate to values close to 11 or higher (Ferraz et al., 2013), favoring the formation of ammoniacal nitrogen in the form of  $\text{NH}_3$ .

Alkalinization typically occurs under the action of the following agents: calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , and sodium hydroxide, NaOH (Gomes et al., 2023). After the appropriate pH condition has been established, the mechanical introduction of air into the liquid medium takes place, determining that, through the action of circulation of this mass of air, the expulsion or dragging of  $\text{NH}_3$  occurs.

The process is usually carried out in towers or lagoons (Souto and Povinelli, 2007). The positive aspect of this technology is the possibility of obtaining ammonia removal to the desired level. The efficiency in removing ammonia will basically depend on the amounts of alkalinizer and the hydraulic detention time used. One of the negative aspects is the need to adjust the pH to discharge the final treated effluent.

Calixto et al. (2021) carried out alkalinization of leachate. The study used calcium hydroxide and sodium hydroxide as alkalinizing agents. Both agents satisfactorily raised the pH. There was a reduction in color (clarification of the leachate). They concluded that alkalinization is, in-

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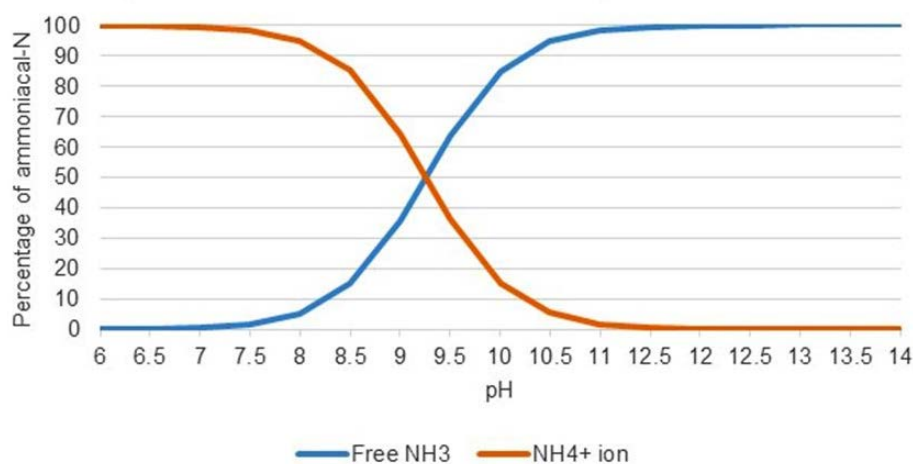


FIGURE 1: Proportion of  $\text{NH}_3$  and  $\text{NH}_4^+$  as a function of pH value variations (Bidone, 2018).

deed, an option to be considered for pre-treatment, especially when preceding stages that perform better at high pH.

Frederice (2019) studied air stripping removal of ammonia in leachate. The research was conducted on a laboratory scale. Two towers built with 150 mm diameter. The air stripping towers had a total height of 4 m; 3 m of which were filled with polypropylene. For  $\text{NH}_3\text{-N}$  initial concentrations of 2,874 mg/L and 2,415 mg/L, have been removed up to 83.4 and 85.5% of the ammonia, respectively, with pH equal to 11.4.

The subject of this study is the removal of ammonia from landfill leachate. The proposed technology is the submerged aerated filter. The main objective is to verify the level of efficiency of the filter in removing this form of nitrogen. The research hypothesis is that there is no need to alkalize the leachate to achieve high efficiencies. The data were generated on a real scale. The study materials are non-replicable.

The proposed ammonia removal is a clean technology. It does not use chemicals and does not propose dilution of leachate (which would require a huge volume of water). In addition, the electrical energy used to drive (operate) the aeration system is generated within the landfill itself: there is an energy generation unit on site that uses the biogas obtained from the decomposition of waste disposed of in the landfill. Finally, it provides the opportunity to obtain a large quantity of the nutrient nitrogen. The study takes place at a time when Brazil is seeking to become a world reference in sustainability (Bidone et al., 2025).

The Submerged Aerated Filter (SAF) was built to be part of a continuous flow process train comprising: Upflow Anaerobic Fixed Bed Filter → SAF → Constructed Wetland. It is anticipated that significant biological activity will develop on the surfaces of the aerated filter stone, over time. The initial construction of the SAF offered a one-off opportunity to carry out a single batch study of ammonia stripping at full scale in the absence of significant biological activity. This study will inform future interpretation of the mass balance of nitrogen removal from the leachate when the full process train is operational and biological activity has developed.

## 2. MATERIALS AND METHODS

### 2.1 Materials

#### 2.1.1 General description

The landfill from which the leachate was obtained is located in the municipality of Minas do Leão, in the state of Rio Grande do Sul, in the extreme south of Brazil. The state capital, Porto Alegre, is 80 km from the landfill. The landfill receives 50,000 tons of domestic solid waste from 150 municipalities per month.

The treatment of raw leachate is carried out in a system composed of two upflow anaerobic filters, operated in series, followed by a submerged aerated filter (unit in which this study was developed) and two constructed wetlands.

#### 2.1.2 Submerged aerated filter features

The main characteristics of the submerged aerated filter, the treatment unit analyzed in this study, are:

- Useful volume (discounting the volume of the support medium): 1,213 m<sup>3</sup>;
- Base area: 628 m<sup>2</sup>;
- Liquid surface area: 1,200 m<sup>2</sup>;
- Useful height: 2.7 m;
- Support medium (filter bed): gravel with the smallest dimension between 38 mm and 76 mm;
- Pipes for leachate distribution: in steel; 150 mm in diameter, perforated along the entire length;
- Number of blowers: 4 units (of 25 HP);
- Air distribution pipes: 4 in number; in stainless steel. Each of them, 150 mm in diameter, at the beginning of the aeration system (with reductions to 100 mm and 75 mm in diameter) and 50 mm in diameter at the end of the system (next to the bubble diffusers);
- Total installed power: 100 HP;
- Number of air diffusers (course bubble type): 360 units;
- Air flow through the tank: 117 m<sup>3</sup>/min;
- Air flow per diffuser: 0.325 m<sup>3</sup>/min;
- Hydraulic retention time for the batch: 56 days.

Table 1 presents a summary of the aeration conditions of the experiment.

**TABLE 1:** Summary of the aeration conditions of the experiment.

| Item                                                                                                                               | Value         | Units                                                                                           |
|------------------------------------------------------------------------------------------------------------------------------------|---------------|-------------------------------------------------------------------------------------------------|
| Aeration rate                                                                                                                      | 117           | m <sup>3</sup> /min                                                                             |
| Filter working volume (in integer values)                                                                                          | 1,200         | m <sup>3</sup>                                                                                  |
| Specific aeration rate $([117 \times 60] \div 1,200)$<br>$([117 \times 60 \times 24 \times 56 \text{ days}] \div 1,200\text{m}^3)$ | 5.85<br>7,862 | (m <sup>3</sup> air/m <sup>3</sup> leachate)/hour<br>m <sup>3</sup> air/m <sup>3</sup> leachate |
| Aeration power (4 x 25 HP motors)                                                                                                  | 100 (~75)     | HP (kW)                                                                                         |
| Specific aeration energy $([56\text{d} \times 24\text{h} \times 75\text{kW}] \div 1200\text{m}^3)$                                 | 84            | kWh/m <sup>3</sup> leachate                                                                     |

In Figure 2, it is possible to observe a daily service front of the landfill. In Figures 3, 4 and 5 it is possible to observe, in detail, the construction of the submerged aerated filter and its operation.

## 2.2 Methods

This article evaluates ammonia removal, under non-alkalinization condition, in a submerged aerated filter. The efficiencies obtained in the filter were calculated by comparing the effluent concentrations and the influent concentration (value verified on Day of sample 0), at the same collection point. The test results for Day of sample 0 constitute the raw leachate. This means that: the liquid introduced into the filter, for the purpose of this study, did not undergo any prior treatment. The concentrations mentioned are presented in Table 3, in the Results.

The control variables of the experiment, those whose analysis allows answering the research hypothesis, were pH and ammoniacal nitrogen (ammoniacal-N). The leachate characterization variables were organic matter (BOD, COD and TOC), dissolved oxygen (DO), total Kjeldahal nitrogen (TKN), nitrate (NO<sub>3</sub><sup>-</sup>) and alkalinity.

The filter operated in batch mode. The purpose of the batch mode was to determine the number of days required to achieve significant ammonia removal and, during this

period, the maximum pH value that the liquid could reach without alkalization.

From day 42 onwards, the possible removal began to show a tendency to stabilize. The pH also began to vary very little. To confirm this trend, observation of the experiment was continued until 56 days (eight full weeks) had been completed.

### 2.2.1 Physicochemical analysis

Table 2 presents the analytical methodology used in each physical-chemical analysis. The frequency and point of collection of the test samples are also included in the table. These analyses were performed by the Laboratory of Chemical Analysis Laborquímica Ltd. and followed the provisions of the Standard Methods for the Examination of Water and Wastewater (APHA, 2017).

## 3. RESULTS AND DISCUSSION

### 3.1 Influent and effluent concentrations

Table 3 presents the results of the experiment. All data generated for this article are listed there.

### 3.2 pH and alkalinity

The raw leachate had a pH of 8.3 (alkaline). On the 14th day of the experiment the pH had already reached 9.2. This



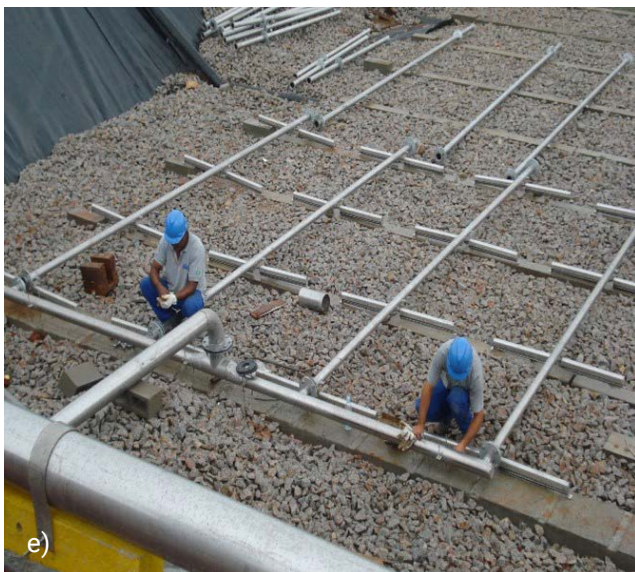
**FIGURE 2:** A daily service front of the landfill.





**FIGURE 3:** (a) Excavation and preparation of the base to begin construction of the filter; (b) start of installation of the waterproofing membrane; (c) welding of the membrane; (d) image of the progress of the waterproofing work; (e) preparation of forms for concreting the leachate pipe support; (f) spreading of gravel at the base of the filter.





**FIGURE 4:** (a) Leachate distribution piping and concrete beams (to support the air piping); (b) spreading of gravel over the liquid distribution piping; (c) image of the blower house; (d) view of the air distribution piping installation assembly; (e) installation of the last sections of the air piping; (f) detail of the bubble diffuser.





**FIGURE 5:** (a) Air distribution test and blower test; (b) filling the filter bed with gravel, after the successful aeration test; (c) another view of the air distribution piping, now with the filter completely filled with gravel; (d) view of the first author of this article, above the filter bed of the filter; (e) immediately after the beginning of operation at the filter.

**TABLE 2:** Analysis, frequency, collection point and method.

| Variable                                                 | Frequency | Collection point | Methodology                        |
|----------------------------------------------------------|-----------|------------------|------------------------------------|
| pH                                                       | Weekly    | Filter output    | Direct Potentiometry               |
| Ammoniacal-N (mgN.L <sup>-1</sup> )                      | Weekly    | Filter output    | Titrimetry with prior distillation |
| TKN (mgN.L <sup>-1</sup> )                               | Weekly    | Filter output    | Titrimetry with prior distillation |
| Nitrate (mgNO <sub>3</sub> .L <sup>-1</sup> )            | Weekly    | Filter output    | Ultraviolet Spectrophotometric     |
| DO (mgO <sub>2</sub> .L <sup>-1</sup> )                  | Weekly    | Filter output    | Titrimetry                         |
| Total alkalinity (mgCaCO <sub>3</sub> .L <sup>-1</sup> ) | Weekly    | Filter output    | Neutralization titrimetry          |
| BOD <sub>5,20</sub> (mgO <sub>2</sub> .L <sup>-1</sup> ) | Weekly    | Filter output    | Membrane electrode potentiometry   |
| COD (mgO <sub>2</sub> .L <sup>-1</sup> )                 | Weekly    | Filter output    | Open reflux dichromatometry        |
| TOC (mgC.L <sup>-1</sup> )                               | Weekly    | Filter output    | Titrimetry – permanganimetry       |

**TABLE 3:** Results of the analyses conducted during the batch process (results in mg/L, with the exception of pH).

| Day of sample | pH  | BOD   | COD   | TOC   | DO  | Ammoniacal-N | TKN   | NO <sub>3</sub> <sup>-</sup> | Alkal. |
|---------------|-----|-------|-------|-------|-----|--------------|-------|------------------------------|--------|
| 0             | 8.3 | 2,400 | 5,022 | 2,141 | 0   | 2,653        | 3,058 | 0                            | 12,338 |
| 7             | 8.9 | 1,800 | 4,247 | 1,750 | 6.3 | 2,734        | 3,035 | 0.5                          | 12,101 |
| 14            | 9.2 | 1,600 | 3,940 | 1,602 | 8   | 2,124        | 2,558 | 6.7                          | 11,233 |
| 21            | 9.2 | 1,500 | 3,885 | 1,621 | 7.2 | 2,102        | 2,161 | 28.3                         | 10,560 |
| 28            | 9.4 | 2,048 | 5,120 | 2,181 | 9   | 1,389        | 1,668 | 28.3                         | 9,987  |
| 35            | 9.3 | 1,700 | 3,740 | 1,595 | 7.9 | 1,147        | 1,411 | 18.7                         | 9,576  |
| 42            | 9.5 | 1,600 | 3,361 | 1,378 | 8.4 | 654          | 1,176 | 10.4                         | 5,348  |
| 49            | 9.3 | 1,250 | 3,293 | 1,517 | 8.4 | 645          | 796   | 8.6                          | 4,413  |
| 56            | 9.3 | 1,310 | 3,276 | 1,275 | 8.4 | 460          | 658   | 15.9                         | 4,015  |

increase occurred naturally/spontaneously (without the addition of alkalizing agents to the liquid medium). Values close to this (9.3, 9.4 and 9.5) were achieved and maintained consistently until the 56th day of the experiment. Aeration of the raw leachate, maintained for 56 days, induced an ion/gas imbalance ( $\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$ ). This shift in equilibrium to the right in the equation favored the formation of  $\text{NH}_3$  and allowed its subsequent dragging out of the liquid.

Alkalinity fell consistently over the 56 days, from 12,338 mg/L to 4,015 mg/L. It should be noted that a significant portion of the measured alkalinity is due to the presence of dissolved ammoniacal nitrogen. Therefore, the removal of  $\text{NH}_3$  inevitably results in a reduction in alkalinity. It is worth mentioning that, even to a small extent, the release of  $\text{H}^+$  ions, which occurs due to the small nitrification observed, also results in a reduction in alkalinity.

The pH values vary on a logarithmic scale and alkalinity on a decimal scale. Therefore, any increase in pH, even a small one, results in a not so small decrease in alkalinity.

The increase in pH observed in this research demonstrated that there is no need to use an alkalizing agent to reach a value of up to 9.5. This finding is quite important. Note that it was possible to remove 83% of ammoniacal nitrogen in the pH variation range of the experiment (between 8.3 and 9.3). This level of removal is quite significant.

The “traditional” ammonia removal would have consumed a large amount of alkalizing agent to obtain this percentage of removal. Worse still: the pH, through the “traditional” ammonia removal route, would have been raised

to values above 11. In Brazil, the emission standard for the discharge of treated final effluent requires a pH close to neutrality. In this case, even more chemical agents would be consumed, this time to reduce the pH of the treated leachate.

It is important to address the hydraulic retention time in this experiment. “Traditional” ammonia removal, conducted in towers, aims to remove  $\text{NH}_3$  in a short period of time (order of magnitude of hours). This is only possible because the pH is quite high (to values above 11) due to the use of a large amount of chemical agent, quickly making a lot of ammonia available for expulsion. It should be noted that the methodology studied in this article, in turn, demands a long liquid retention time (tens of days) because it advocates that no chemical agents are consumed. As a consequence of this, the maximum pH observed was equal to 9.5.

Therefore, there is no doubt that it is possible to raise pH without alkalization by chemical agents and that it can, in fact, be associated with high ammonia removal. Certainly, depending on the other units that will make up the leachate treatment plants, this discovery, verified on a real scale, is useful for the treatment of industrial effluents.

### 3.3 Ammoniacal-N, TKN and nitrate

It is important, preliminarily, to mention that the standards and conditions for effluent discharge in Brazil are set forth in CONAMA Resolution 430/2011. The maximum permitted concentration for ammoniacal- N is 20 mg/L. Dilutions of leachate are not permitted.



On the 42nd day of the batch, ammoniacal-N removal had already reached 75%. On the last day (56th), removal reached 83%. The close relationship between ammonia removal, pH and alkalinity is indisputable. The increase in pH stimulated the formation of  $\text{NH}_3\text{-N}$  in the liquid, enabling its removal (by the action of air) and the removal of alkalinity (verified by the enormous reduction in its concentration).

These results allow the following interpretations: (1) the ammoniacal-N dragging trend was consistent and uncontroversial, given the regularity of the decline in concentrations; (2) for a hydraulic retention time of 56 days, under the aeration conditions of the experiment, the ammoniacal-N removal exceeded 80%, without the need for alkalization of the leachate.

TKN showed a very similar decay behavior to ammoniacal-N. As expected, since TKN is the sum of organic nitrogen and ammoniacal-N. Its removal reached 78%.

Figure 6 shows the downward trends in ammoniacal-N and TKN. It also shows the rise in pH. The values are presented as a function of the 56 days of SAF operation.

Nitrate was generated in small quantities, considering the high availability of ammonia and the completely aerobic condition established in the liquid. However, it is important to note that there was some nitrification. This is not the subject of this article. The study of nitrification would involve the discussion of issues related to the active biomass in the filter and, in the case of leachate (extremely concentrated in terms of ammonia), the limiting concentrations of the pollutant. In this article, we focus on ammonia drag.

Regarding the 20 mg/L of ammoniacal-N, which is the effluent emission standard, it is worth noting that the landfill leachate treatment plant has two wetlands built downstream of the aerated filter. This is where the final stage of leachate treatment occurs. The macrophyte used in the wetlands is *Typha subulata*, a plant that avidly assimilates nitrogen. The design of this phytoremediation (treatment using wetlands) is another reason for not using chemical agents to remove ammonia. The performance of the macrophytes is not to be hindered/impaired. In the wetlands, the following are also expected: the physical effect of sedimentation of nitrogenous organic matter (because

**TABLE 4:** Ammoniacal-N removed charge.

| Item                                                                   | Value   | Units              |
|------------------------------------------------------------------------|---------|--------------------|
| Ammoniacal-N removed, in terms of concentration (2,653 - 460)          | 2,193   | mg/L               |
| $[2,193 \text{ mg/L} \div 1,000,000 = 0.002193 \text{ kg/L}]$          |         |                    |
| Filter working volume (in integer values)                              | 1,200   | $\text{m}^3$       |
| $[1,200 \text{ m}^3 \times 1,000 \text{ L/m}^3 = 1,200,000 \text{ L}]$ |         |                    |
| Removed charge $[(0.002193 \text{ kg/L} \times 1,200,000 \text{ L})]$  | 2,631.6 | kg of Ammoniacal-N |

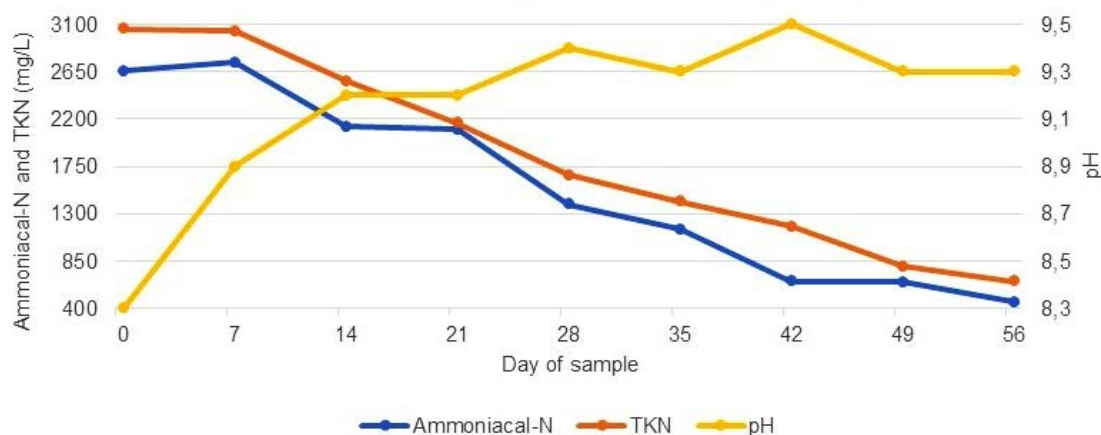
the wetlands are quite long and the flow velocity is low) and metabolization of soluble ammonium by the plants. The system, as a whole, will certainly generate treated leachate with an ammoniacal-N concentration of less than 20 mg/L.

Finally, regarding  $\text{NH}_3$ , it is important to emphasize that the gas extracted from the filter is not released into the atmosphere. It is recovered. The filter design included a cover for the unit. Under this cover there is a pipe that captures the  $\text{NH}_3$  that was expelled from the liquid mass. The photographic record in this article concerns the first days of operation and does not show the construction phase of the unit's cover.

### 3.4 Ammoniacal-N removed charge

The removal of ammoniacal-N reached 83%. This percentage, in itself, is already interesting. However, considering the very significant volume of the submerged aerated filter, how much would this removal represent in terms of charge? Table 4 shows the calculation of the ammoniacal-N charge removed.

The amount removed simply exceeds 2.6 tons of ammoniacal-N. It is very important to remember that all this ammonia can be converted into fertilizer. Therefore, it is no exaggeration to say that this result is extraordinary. There is hardly a more sustainable cycle than this: from landfill leachate (a liquid byproduct of solid waste from human activity), the macronutrient essential for food production is made available in this magnitude. Dos Santos et al. (2020)



**FIGURE 6:** Ammoniacal-N, TKN and pH as a function of day of sample.

successfully investigated the recovery of ammonia-N from the chemical absorption of ammonia in phosphoric acid, resulting in ammonium phosphate (a chemical compound widely used to induce plant growth).

### 3.5 BOD, COD and TOC

The removal of organic matter was monitored during the 56 days of experimentation. It can be observed that BOD, COD and TOC showed a downward trend. The removals reached, respectively, for COD, TOC and BOD: 35%, 40% and 45%.

The removals obtained in terms of BOD, COD and TOC were not greater, possibly because the highly biodegradable organic matter was quickly stabilized (in the first days of the experiment). It is quite noticeable that the substrate became refractory to biological treatment. Only this would justify that, in the presence of so much air and for such a long hydraulic retention time, the oxidation of the organic matter was so limited. The pH of the raw leachate was equal to 8.3. It should be noted that, under these conditions, in the first days of the experiment, the concentration of ammoniacal-N, although considered high, did not seem to completely inhibit the process. However, as the pH increased, even though the ammoniacal-N continued to decay, the liquid medium conditions for the biota became unequivocally more unfavorable. Furthermore, the substrate removal rate, in terms of organic matter, is expected to be higher at the beginning of the process.

### 3.6 DO

The dissolved oxygen quickly provided the environment with a fully aerobic condition. This condition was maintained throughout the experiment. On the 28th day, the concentration reached the maximum value verified during the experiment: 9 mgO<sub>2</sub>/L.

The air supply to the aerated filter was calculated so that it operates in continuous flow. This is the normal operating regime of the landfill. However, for the research hypothesis of this article (non-alkalinization of the leachate, naturally raising the pH and leading to a high ammonia removal) and taking advantage of the beginning of the filter operation, the batch experiment was evaluated as a unique opportunity.

It is true that the hydraulic retention time of the batch was high. This is because the batch would only be completed when a satisfactory level of ammonia removal was reached; this number of days was one of the research questions. The maximum value to be reached by the pH, without alkalinization by a chemical agent, was also a research question. The removal level established as satisfactory had been defined as 75%. This percentage was reached on the 42nd day of the batch.

Aeration was only maintained on the following days in order to ensure that the trend of the results would not be modified.

## 4. CONCLUSIONS

Thus, objectively, the number of days required to achieve a significant reduction (75%) of ammonia was

equal to 42. During this period, the maximum pH value was equal to 9.5. Maintaining the batch for 56 days confirmed the stability of the ammonia reduction trend (whose total removal, in the entire period of the experiment, was equal to 83%).

The research hypothesis was positively confirmed. There is no need to alkalinize the medium to obtain high ammonia expulsion in the leachate.

Any liquid that presents high concentrations of ammonia nitrogen could use an ammonia removal unit without alkalinization for subsequent recovery of the ammonia. The submerged aerated filter is a technology that deserves to be evaluated as part of a treatment system.

The removal of ammoniacal-N, in terms of charge, was quite significant: 2.6 tons. Only observation on a real scale allows verification of this magnitude.

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# IMPROVEMENT OF THE METHANE GENERATION POTENTIAL OF THE ANAEROBIC DIGESTION SOLID RESIDUE BY IMPLEMENTING A BIOLOGICAL POSTTREATMENT WITH THE BIOMYCETE *IRPEX LACTEUS* AT VARIOUS CONDITIONS

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## ABSTRACT

Biological pretreatment of different digestates with *Irpex lacteus* was employed to investigate the potential of the fungal strain to exploit any digestible organic matter in the spent anaerobic digestion effluent in methane recovery. In all cases, pretreatment of sludge with the non-selective *I. lacteus* promoted methane generation. Incubation of *I. lacteus* in digestate for 20 days at 28°C increased the methane generation potential of the sludge by 1.67-fold. Prolonging incubation time to 30 days led to an increment in methane yields (1.24-fold), however, the increase was lower than that accomplished at a shorter pretreatment period (20 days) due to a substantial loss of fermentable organics, especially cellulose. Regardless the digestate type, inoculation with *I. lacteus* enhanced the digestibility of sludge by at least 1.6-fold. The degree of improvement was depended on the amount of lipids and proteins supplied by the fungus when the modified sludge contained a small carbohydrate proportion and on the availability for digestion of cellulose when the pretreated digestate was rich in carbohydrates.

## 1. INTRODUCTION

Anaerobic digestion (AD) is the biological process in which microorganisms decompose an organic substance in an oxygen free environment to produce biogas and a solid effluent called digestate. Recently, AD was implemented for exploitation of a host of organic material streams ending up in a large number of biogas plants worldwide and global production of enormous quantities of digestate. Depending on process parameters, the AD by-product is generally composed of 80-97%wt. of liquid and 3-20%wt. of solid fraction, both of which are organic fertilizers with slight differences in their fertilization capacity. Storage expenses accompanied with additional costs of collection, handling and transportation obstruct its extensive valorisation in soil amelioration. Storage in open tanks may also contain concerns because of the existence of uncontrolled biogas release risks (Sambusiti et al., 2015). Depending on the source of feedstock, digestate may encloses heavy metals like Cu, Cr, Zn and As and pathogenic microorganisms such as *Escherichia coli*, *Salmonella spp.* etc. that can accumulate in the environment and due to their toxicity

hazard human health (Swain et al., 2016, Adamse et al., 2017). Despite the several studies conducted on exploitation of digestate in soil remediation and energy sector, the management of the AD effluent still comprises challenges that need to be addressed (Guilayn et al., 2020).

Digestate contains organic substances recalcitrant to AD of bacteria and non-degradable during the process. Lignin is non-degradable whereas by being chemically bonded to cellulose and hemicellulose it prevents the plant cell wall polymers degradation (Zanellati et al., 2020). In addition to lignin, cellulose degradation is limited by its crystallinity (Musatti et al., 2017). Therefore, cellulose and lignin accumulate in digestate while hemicellulose is the substance mostly removed from the material during AD (Sambusiti et al., 2015). In total, a 40-70%wt of biomass is converted to produce biogas throughout AD process whereas 35% of the organic matter remains in the final sludge (Uludag-Demirer and Demirer, 2022). White rot fungi (WRF) are considered to be the most effective lignin-degrading microorganisms in nature (Wan and Li, 2010) and their activity could destruct the complex structure of lignin and recover monomeric sugars existing in the



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carbohydrate fraction of a digestate that could be subsequently implemented in biogas production. Even though fungi grow at a slower rate in a digestate than in a raw biomass, methane generation potential of digestates has been observed to be altered with WRF treatment (López et al., 2013). It is indicative that a pretreatment of a digestate with *Trichoderma reesei*, *Myceliophthora thermophila* and *Phanerochaete chrysosporium* can rise methane yields by 35 to 50% (Götze et al., 2022), whereas an increment of 71.5% has also been reported for a solid fraction of digestate pretreated by *Cephalotrichum stemonitis* (Zanellati et al., 2021). In contrast, in a number of instances, inoculation of digestate with WRF such as *Pleurotus ostreatus* was reported to have an opposite impact reducing the capability of AD effluent to produce methane, whereas in other cases methane generation capability of a digestate was not influenced by the operation of fungi like *Phanerochaete flavidobrunnea* (Brémond et al., 2020). It is apparent, therefore, that the manner that a pretreatment with fungal species will impact the methane generation capacity of a digestate could not be easily predicted.

WRF can be classified as selective and non-selective, with the former mineralizing lignin and partly hemicellulose and cellulose and with the latter arbitrarily consuming all components of lignocellulose (Basinas et al., 2024; Wan and Li, 2010). Selectivity of a fungal strain is interconnected with the incubation time, both of which largely determine the influence of a fungus on the digestibility of a material (Albornoz et al., 2018). For non-selective species, a prolonged incubation time may lead to an excessive loss of digestible organics and eventually lessen the biodegradability of a substrate (Zanellati et al., 2020). Mustafa et al. (2016) pretreated rice straw with *T. reesei* ascertaining that methane yield rose by 45% with the increment of incubation time from 10 to 20 days, whilst methane output reduced with the extension of time to 30 days. Likewise, the non-selective basidiomycete *I. lacteus* showed a better potential to improve the biogas generation capacity of a biomass when pretreatment conducted for short periods and negatively affected the methane production potential of corn silage when pretreatment lasted between 10-30 days (Basinas et al., 2022; 2024). Digestate constitutes a spent AD effluent with a high proportion of lignin and a low fraction of available for anaerobic conversion soluble components. A pretreatment with *I. lacteus* at relatively short periods could provide a depolymerization of lignin and a recovery of other heteropolymers such as cellulose and hemicellulose that were bounded in the material. Nevertheless, the application of *I. lacteus* for the pretreatment and improvement of the AD performance of a digestate has attracted limited attention.

A parameter modifying the efficiency of a fungus to delignify a biomass material and improve its digestibility is related to the physicochemical properties of the parent lignocellulose (Xu et al., 2020). Individual AD effluents practically possess diverse physical and chemical characteristics due to the varying feedstocks and AD systems implemented for their production. Alike biomass, therefore, a treatment of two individual digestates with the same fungus would affect their methane generation capabilities at

a different extent. The level that the pretreatment of two differently derived digestates by *I. lacteus* methodology is influenced by the parent substrate used for the generation of digestates has not been investigated to any great extent.

In the current work, two AD effluents were treated with *I. lacteus* to determine the potential of biological treatment to eliminate the recalcitrance of a sludge in AD and improve the methane generation capacity of the spent AD effluent. One of the main objectives was to determine the pretreatment time required for the non-selective basidiomycete *I. lacteus* to bring an advancement in the digestibility of a digestate. Another aim was to clarify the impact of the pristine feedstock used for the production of a digestate on the efficiency of *I. lacteus* to improve the methane yields from the sludge. The proposed digestate treatment followed by recirculation of the modified digestate into a biogas reactor is expected to provide a significant advancement in anaerobic digestion efficiency.

## 2. MATERIALS AND METHODS

### 2.1 Fungus and digestate

The non-selective basidiomycete *Irpex lacteus* 617/93 used for the modification of digestates was provided by the Czech Collection of Basidiomycetes (Institute of Microbiology, Academy of Sciences of the Czech Republic, Prague) whereas cultivated on malt extract/glucose (MEG) agar plates (5 g.L<sup>-1</sup> malt extract, 10 g.L<sup>-1</sup> glucose, 20 g.L<sup>-1</sup> agar).

The reference digestate referred to as the mixed (industrial) digestate (MD) was a residue obtained from an agricultural biogas plant (Pustějov II - Zemspol Studénka Ltd). The plant was operated at mesophilic conditions (40°C) with a mixture of corn silage and cattle slurry and with an organic loading rate (OLR) at 3.30 kg<sub>VS</sub>·m<sup>-3</sup>·d<sup>-1</sup> and hydraulic retention time (HRT) at 36 days. A second digestate (CSD) was prepared from mono-digestion of corn silage in a laboratory 60 L reactor at similar conditions to the biogas plant, i.e. mesophilic temperature (40°C), OLR at 3.37 kg<sub>VS</sub>·m<sup>-3</sup>·d<sup>-1</sup> and HRT at 36 days.

### 2.2 Fungus cultivation

20 g of digestate particles were placed in 250-mL Erlenmeyer flasks, moisturized and sterilized at 121°C for 60 min (Systec VX-5, Germany). Digestates were inoculated with 1 mL of fungal inoculum, preparation of which was described in an earlier study (Basinas et al., 2022). Following a method described by Rouches et al. (2016), 25 mg of glucose and 2.5 mg of diammonium tartrate per g of total solids (TS) were added in flasks which sealed with cotton plugs. Solid state fermentation (SSF) cultures were incubated statically for 20 and 30 days at a temperature of 28°C.

### 2.3 Methane yields and biodegradability determination

#### 2.3.1 Inoculum

Inoculum for the AD tests was a liquid effluent from the first stage of the same biogas plant that provided the MD. A centrifuge (BEHO CHC-61A) operated at 25°C and 1200



rpm was used to reduce the TS concentration in inoculum from 7.22 (as received) to 2.65%wt. Inoculum main properties were: volatile solid (VS) concentration at 74.31%wt<sub>TS</sub>, C/N ratio at 11.42 and pH at 7.51. Prior to AD assays inoculum was stored at 4°C.

### 2.3.2 Biochemical methane potential (BMP) assays

BMP tests were conducted in 1-L glass bottles connected with burettes allowing for a volumetric measurement of the produced biogas (Figure 1). AD tests were performed at mesophilic conditions (40±0.5°C) for 40 days. Stirring was applied for all experiments. For the BMP assays, 800 g of inoculum were placed in a glass reactor and mixed with 30 g of substrate. MD and the same material pretreated with *I. lacteus*, at 28°C for 20 and 30 days were the substrates utilized for the investigation of the impact of the pretreatment time on the methane generation capacity of digestate. The impact of digestate type and origin was assessed in a glass reactor using a second AD effluent (CSD) as the substrate and an additional run using as the feedstock the same sludge after pretreatment with *I. lacteus* (28°C, 20 days). Biogas generation potential of inoculum was determined in a blank run with 800 g of inoculum in a reactor and was considered in the estimation of the amount of gas that actually was produced from each substrate. Biogas production potential of fungus was considered insignificant given the low growth and the limited quantity in reactors compared to the substrate and AD inoculum. To validate tests repeatability each experiment was triplicated. Deviations among recurring tests were minimal in all cases and the mean values were used in graphs. Before tests, reactors were purged with nitrogen for sufficient time to ensure that anaerobic conditions were established. A gas analyser (Geotechnical Instruments Biogas5000) equipped with dual-wavelength IR sensors was utilized for determination of biogas composition (CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>S). Biogas

volume and composition were monitored on a daily basis and the obtained data was normalized to 0°C, 1 atm and dry conditions.

## 2.4 Physico-chemical analyses

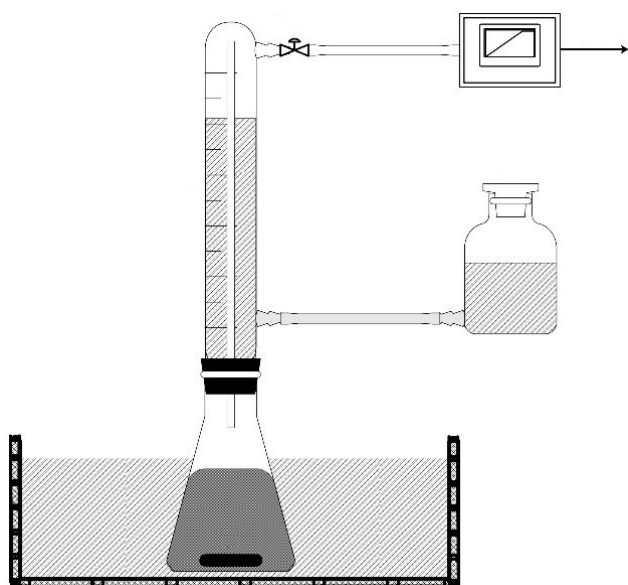
A laboratory mill (IKA Tube Mill Control) was used for the homogenization of digestates. The pH was measured in a WTW 340i pH-meter with SenTix 410 sensor. TS concentration was determined in a KERN DLB 160 3A moisture analyser (EN 15934:2012 standard). VS content was determined in a LECO TGA 701 thermogravimetric analyser by measuring the loss on ignition of the material at 550°C. Elemental analysis (C, H, N, S) for the determination of the C/N ratio was conducted in a LECO Truspec CHN and S628 elemental analyser (ASTM D5373-16 standard). Lipids were determined by the EN ISO 6492:1999 standard, carbohydrates according to the ASTM D5896-96, proteins by titration based on the EN ISO 5983:1997, starch content by applying the EN ISO 6493:2000 and fibers following the EN ISO 6865:2000 standard method. Cellulose, hemicellulose and lignin concentrations were assessed according to a method proposed by Van Soest (1991).

## 3. RESULTS AND DISCUSSION

### 3.1 Digestate properties and degradation with fungal pretreatment

The results for the main physicochemical characteristics of untreated digestates appear in Table 1. VS and TS proportion in MD (71.59%wt<sub>TS</sub> and 7.22%wt) and CSD (68.28%wt<sub>TS</sub> and 8.24%wt) (as received) agreed with values appear in the literature for similar digestates (Sambusiti et al., 2015; Zanellati et al., 2020; 2021; Zhong et al., 2016). TS fraction increased to 94.08 and 93.69%wt. in digestate MD and CSD, respectively with the drying applied prior to the treatment with the fungus (Table 1). The pH values of MD (8.61) and CSD (8.14) (as received), were inside an alkaline range, which is typical for AD effluents (Brémond et al., 2020; Zanellati et al., 2020; 2021). The pH of MD and CSD dropped with drying to 6.63 and 6.97, respectively and sludges converted to neutral or slightly acidic before treatment with the fungus. According to earlier reports (Brémond et al., 2020), the pH intervals facilitating fungal growth encompass a neutral and a part of the alkaline range (6.5-8.7), hence the dried sludges would be foreseen to be suitably colonized by *I. lacteus*.

MD and CSD contained a great proportion of holocellulose (cellulose and hemicellulose) (23.22 and 26.22%wt<sub>TS</sub>, respectively) indicating that a significant quantity of digestible organic substances remained unconverted in the precedent AD. Lignin and cellulose prevailed in digestates consistent with results for biomass- and waste- sludges (Zanellati et al., 2020; Zhong et al., 2016). Lignin fraction at 15.28 and 14.62%wt<sub>TS</sub> in MD and CSD, respectively was also consistent with proportions reported for sludges generated from mono-digestion and co-processing of biomass with other substrates (Musatti et al., 2017; Rodriguez Correa et al., 2017; Zhong et al., 2016). Digestates contained a high concentration of lignin as a consequence of polymer's recalcitrance to AD microorganisms (Fang et al., 2020),



**FIGURE 1:** Representation of the experimental setup for BMP tests (Basinas et al., 2024).

**TABLE 1:** Main characteristics of untreated and pretreated with *I. lacteus* digestates.

| Parameter                                       | MD    |         |       | CSD   |         |
|-------------------------------------------------|-------|---------|-------|-------|---------|
|                                                 | Raw   | Treated |       | Raw   | Treated |
|                                                 |       | 20d     | 30d   |       | 20d     |
| pH                                              | 6.63  | 8.94    | 8.20  | 6.97  | 6.40    |
| TS (%wt.)                                       | 94.08 | 16.29   | 16.77 | 93.69 | 16.56   |
| VS (%wt <sub>TS</sub> )                         | 71.59 | 73.43   | 73.83 | 68.28 | 75.86   |
| <b>Elemental composition (%wt<sub>TS</sub>)</b> |       |         |       |       |         |
| H                                               | 5.15  | 4.91    | 4.90  | 4.86  | 5.12    |
| N                                               | 3.05  | 3.25    | 3.19  | 2.45  | 3.03    |
| S                                               | 0.38  | 0.36    | 0.36  | 0.22  | 0.31    |
| O*                                              | 24.82 | 29.02   | 28.72 | 25.55 | 28.73   |
| C/N ratio                                       | 15.41 | 13.70   | 13.93 | 18.01 | 15.56   |
| <b>Main components (%wt<sub>TS</sub>)</b>       |       |         |       |       |         |
| Lipids                                          | 3.39  | 3.93    | 3.17  | 2.76  | 2.81    |
| Carbohydrates                                   | <0.05 | 2.98    | 2.26  | <0.05 | 0.43    |
| Proteins                                        | 14.20 | 16.60   | 13.10 | 11.90 | 12.70   |
| Starch                                          | <0.5  | 1.09    | 1.63  | 0.64  | 1.14    |
| Fibers                                          | 11.54 | 4.54    | 3.30  | 15.35 | 7.40    |
| Cellulose                                       | 16.22 | 12.28   | 11.08 | 16.80 | 13.92   |
| Hemicellulose                                   | 7.00  | <0.25   | <0.25 | 9.42  | <0.25   |
| Lignin                                          | 15.28 | 10.94   | 12.40 | 14.62 | 9.42    |
| Cellulose/Lignin ratio                          | 1.06  | 1.12    | 0.89  | 1.15  | 1.48    |

\* by subtraction, TS=Total solids (105°C), VS=Loss on ignition (550°C)

which suggests that the AD performance of sludges could likely be advanced by a WRF pretreatment.

Incubation of WRF in digestates modified the composition of sludges (Table 1). Concentration of TS decreased 5.6 and 5.8-fold with SSF treatment likely due to a consumption of polymers, proteins, soluble sugars and volatile fatty acids (VFA) by the fungus (Zanellati et al., 2021). The water quantity contained in fungal inoculum may also affect the proportion of TS in an incubated material. Contrary to TS, the fraction of VS slightly increased (2.5 and 3.0%) with cultivation of *I. lacteus* in MD and 1.1-fold in CSD (20 days). The small amendment in VS concentration resembles to those reported for the treatment of agricultural digestates by the basidiomycete *C. stemonitis* (Zanellati et al., 2021). Cultivation of a fungal strain in a material would normally expected to introduce a reduction in VS concentration due to removal of polysaccharides. However, organic fraction is possible to maintain stable or increase due to the organic matter contained in fungal mass that is formed on substrate because of mycelia growth. The latter could counterbalance a part or even exceed the quantity of VS consumed by WRF (Zanellati et al., 2021).

*I. lacteus* amended the fraction of plant cell wall polymers in digestates (Table 1). Based on the theory (Sun et al., 2011), lignin cannot serve as carbon and energy source for fungal survival, as such WRF hydrolyse part of the available cellulose and hemicellulose to support their growth, metabolism and lignin degradation activity. Colonization of MD by *I. lacteus* led not only to a reduction in lignin con-

centration (18.8-28.4%), but also to a complete removal of hemicellulose (>97.3%) and a significant loss of cellulose (24.3-31.7%). Lignin mineralization was sufficient, however, the specific fungal strain belongs to the non-selective category and the quantities of cellulose and hemicellulose, consumed by the basidiomycete for retrieving nutrients for its growth and metabolism, were also significant (Sun et al., 2011). WRF colonization in CSD for 20 days influenced the concentration of polysaccharides in a similar manner with that in the case of MD. In particular, *I. lacteus* caused all polymers degradation with cellulose loss reaching a 17%, hemicellulose approaching complete removal (>97.3%) and lignin being depleted by 36%. A significant part of holocellulose, especially hemicellulose, was lost from both digestates, however, the delignification was also sufficient and could potentially lead to elevated methane yields from digestates provided that the absence of lignin could provide passages for AD microorganisms to reach the available holocelluloses in substrate that constitute suppliers of carbon to methanogenic archaea for their growth and activity (Abraham et al., 2020; Vasco-Correa et al., 2016).

### 3.2 BMP

#### 3.2.1 Biogas and methane production from untreated digestate

Figure 2 shows cumulative biogas and methane generation curves for the inoculum and digestates. Biogas and methane yield attained a sufficient value during the first three days. Produced gas early in process suggests

that AD microorganisms were promptly adapted to the substrates and exploited part of organics in digestates to generate gas (Hosseini Koupaie et al., 2019), which was considered reasonable, bearing in mind that both inoculum and sludges were generated by AD of biomass-based substrates. Besides, the production temperature for inoculum was within the mesophilic range which also favoured a prompt acclimatization of AD microorganisms to the conditions of BMPs.

Total methane generation from MD ( $0.119 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$ ) was essentially equal, with insignificant statistical difference ( $p > 0.05$ ) to that from the inoculum ( $0.111 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$ ) and CSD ( $0.132 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$ ). Methane production from digestates and inoculum resembled with those found in the literature for AD effluents ( $0.117\text{--}0.134 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$ ) (Menardo et al., 2011a; Ruile et al., 2015). Nevertheless, lower methane generation in the order of  $0.023$  to  $0.087 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$  was also reported for digestates deriving from typical AD feedstocks like animal manure, food waste and agricultural crops (Lindner et al., 2015; Uludag-Demirer and Demirer, 2022). In these cases, the low values were relevant to the AD system from which the digestate was derived and particularly to the operating conditions like the HRT (Menardo et al., 2011b). Ammonia concentrations larger than  $2.5 \text{ g L}^{-1}$  in an AD medium could be also capable to hamper the activity of methanogens and limit methane yields from digestates ( $0.003\text{--}0.070 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$ ) (Menardo et al., 2011b; Sambusiti et al., 2015).

### 3.2.2 Effect of *I. lacteus* on methane production from digestates

Figure 3 provides total biogas and methane production results for the untreated and modified by *I. lacteus* ( $28^\circ\text{C}$ , 20 days) MD. For biomass materials, pretreatment with non-selective WRF such as *I. lacteus* and *C. subvermispura* was reported to moderately or negatively influence the AD performance of the lignocellulose (Basinas et al., 2022).

However, few reports (García-Torreiro et al., 2016; Wan and Li, 2011) existed where the impact of non-selective WRF on biomass degradability was reported to be positive. This is agreement with the observations in the current assays, where incubation of the non-selective *I. lacteus* in MD enhanced the total methane yields from the sludge by 67.2% (Figure 3). The same trend was observed for the CSD with the rise being at 59.1% (Basinas et al., 2025). *I. lacteus* activity for 20 days induced an almost complete removal of hemicellulose from the MD ( $>96.4\%$ ), provoked a mild cellulose reduction (from 16.22 to  $12.28\% \text{ wt}_{\text{TS}}$ ) and an extensive metabolization of lignin (28%) (Table 1). As such, the remaining quantity of cellulose was presumably the principal source of organics for AD microorganisms to produce biogas. Evidently, lignin polymerization was efficient to provide additional proportions of the available cellulose for digestion and promote methane production at a level that covered any depletion in methane yield provoked by the consumption of cellulose and hemicellulose by *I. lacteus* (Fang et al., 2018; Zanellati et al., 2021). In addition, despite the pH of the treated MD with *I. lacteus* was at a high level (8.94 for a treatment of 20 days) (Table 1) that would be expected to promote a generation of free ammonia inhibiting AD, the pH of reactor sludge after blending with inoculum was at 7.81 leading to insignificant ammonia inhibition effects.

### 3.2.3 Effect of incubation time on the AD performance of digestate

For the investigation of the influence of incubation time on the methane generation potential of a digestate, MD was inoculated with *I. lacteus* for 20 (baseline) and 30 days and the modified materials were subjected to AD for 40 days. Cumulative methane generation results for modified digestates appear in Figure 4. Methane production results for the untreated MD are also included for comparison.

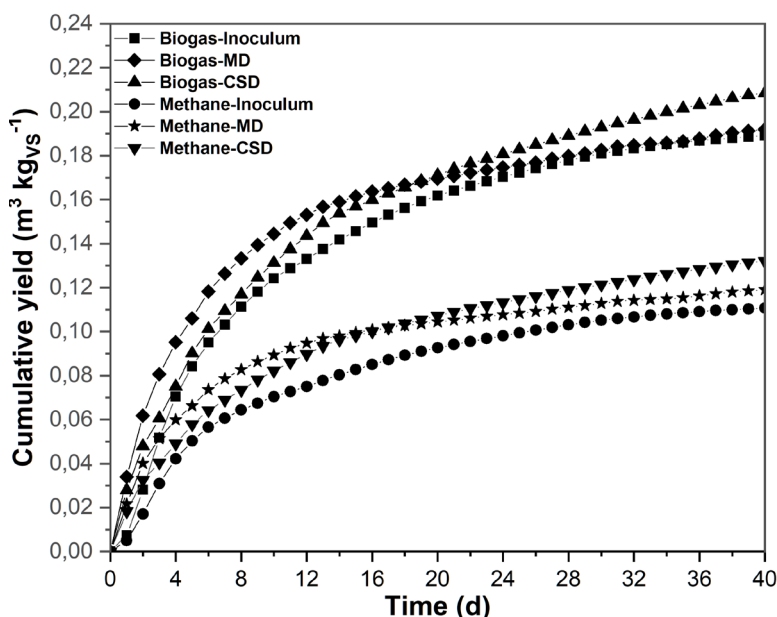
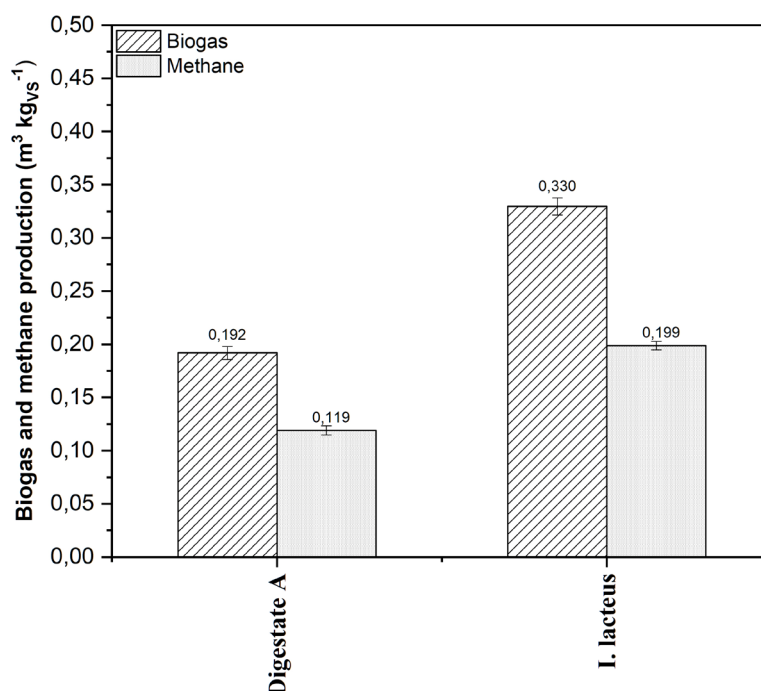


FIGURE 2: Biogas and methane production from non-treated digestates.





**FIGURE 3:** Effect of pretreatment with *I. lacteus* on biogas and methane generation potential of MD under mesophilic AD conditions (mean values±standard deviations from three replicates). Conditions of pretreatment: 28°C and 20 days.

Despite that the methane production from MD increased 1.24-fold with incubation for 30 days, the increment was lower ( $p < 0.05$ ) than the rise achieved with pretreatment for 20 days (1.67-fold). Given the non-selective characteristics of *I. lacteus*, the elongated time of 30 days resulted in a greater loss of cellulose by 31.7% and a lower reduction in lignin concentration (18.8%) with regard to the modification for 20 days where the corresponding decrease in concentration was at 24.3% and 28.4%, respectively (Table 1). As such, an extensive abatement in cellulose and a modest depolymerization of lignin by *I. lacteus* during the 30 days treatment were presumably reasons for the lower methane generation ability of the sludge sustained a prolong modification (Mustafa et al., 2017).

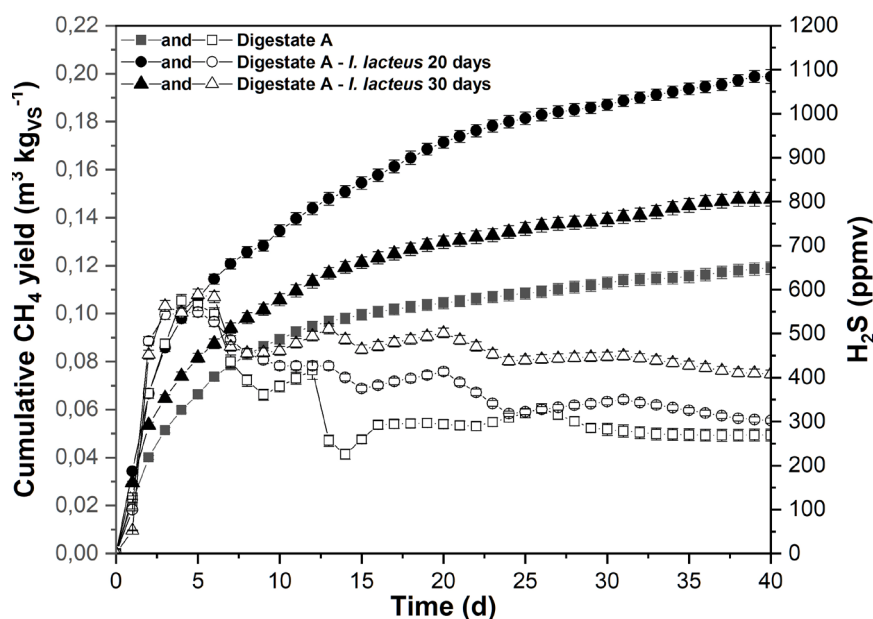
According to theory (Chen et al., 2008), the manner that  $H_2S$  inhibits the biochemical conversion of a substrate is related to the production of  $H_2S$  and a competitive consumption of intermediate fermenters by sulphate reducing bacteria in order to conduct a reduction of sulphates ( $SO_4^{2-}$ ) to sulphides ( $S^{2-}$ ) and a final conversion of sulphides to  $H_2S$ . A second way is relevant to the molecular form of  $H_2S$  and a toxic effect that can exert on methanogenic bacteria leading to a restriction of their methane generation capacity which becomes more intense when concentration of dissolved  $H_2S$  in the AD sludge exceeds  $400 \text{ mg L}^{-1}$  (Cai et al., 2021; Zhou et al., 2016). The proportion of  $H_2S$  in biogas liberated from the 30-day pretreated digestate was permanently greater than those from the untreated and 20-day pretreated sludge while concurrently surpassed the 400 ppmv throughout the AD process (Figure 4). This level likely corresponds to significantly low dissolved concentrations, well below the cited inhibitory threshold. While an inhibition by  $H_2S$  was unlikely, a mild inhibitory effect cannot

be entirely ruled out and might even barely contributed to the lower methane yield from the 30-day modified sludge than that from the digestate pretreated for a short period. The total methane production that was significantly greater than that from the untreated digestate and the fact that the difference in yields from the 20-day treated sludge could be justified by the non-selective delignification of the material by *I. lacteus* further support the conclusion for a minimal inhibition effect.

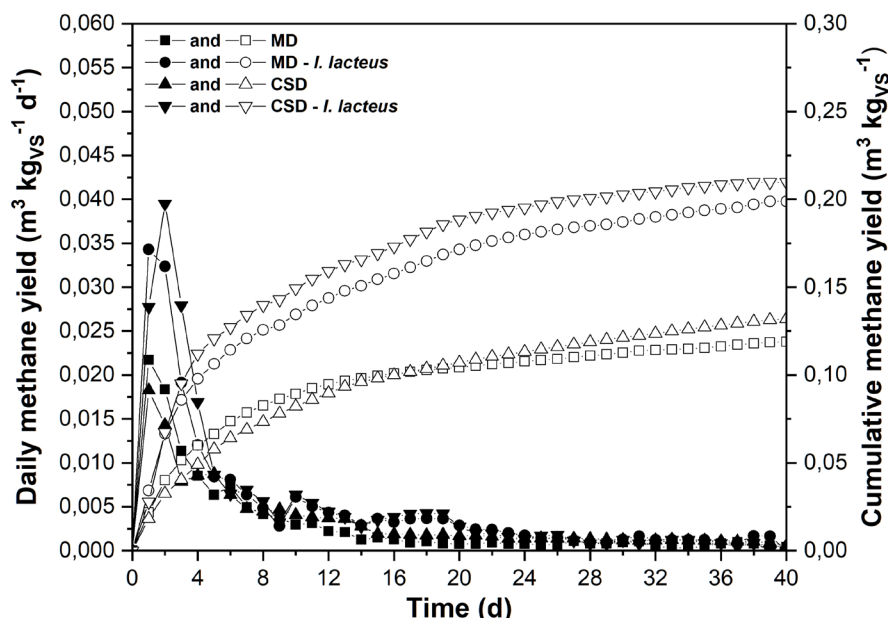
#### 3.2.4 Fungal efficiency dependence on digestate origin

The type of material fed in a digester defines at a great extent the properties of an AD effluent (Ruile et al., 2015; Tišma et al., 2018; Uludag-Demirer and Demirer, 2022). The way, therefore, that a fungus modifies the methane production capacity of a digestate is presumably influenced by the origin of sludge. A second sludge (CSD) was employed to be incubated with *I. lacteus* at baseline conditions (28°C – 20 days) and the AD performance of the pretreated material was examined in BMP assays (Figure 5).

Modification of CSD induced a rise in the total methane production by 1.6-fold. As discussed above, *I. lacteus* impacted the composition of CSD in a similar way with MD, provoking an appreciable removal of lignin (36%) from the CSD and a relatively modest loss of cellulose (17%) (Table 1). Hence, the amount of cellulose remaining in the material could presumably be considered as major supplier of organics to AD microorganisms and together with the delignification effect principal reasons for the advancement in methane production from the sludge (Abraham et al., 2020). Nevertheless, total concentration of carbohydrates despite increased from  $<0.05\% \text{ wt}_{TS}$  in untreated CSD to  $0.43\% \text{ wt}_{TS}$  in treated sludge was significantly small (Ta-



**FIGURE 4:** Effect of the length of pretreatment on cumulative methane (close points) and H<sub>2</sub>S (open points) production during AD of digestates pretreated with the non-selective *I. lacteus* at 28°C.



**FIGURE 5:** Daily (filled points) and cumulative (open points) methane production during AD of different digestates and their pretreated samples with *I. lacteus* at 28°C for 20 days.

ble 1) to comprehensively justify an increment of 59% in methane generation potential. Notwithstanding the carbohydrates proportion, concentration of lipids and proteins were increased from 2.76 and 11.90 in untreated digestate to 2.81 and 12.70%wt<sub>TS</sub>, respectively in its pretreated counterpart. Fungal mass encloses amounts of lipids and proteins, and therefore mycelial growth on digestate fibres could be regarded responsible for the augmented concentration of the specific components and considered complementary to delignification for the increase in methane generation from the sludge (Zanellati et al., 2021). Comparison of cumulative methane generation from MD and CSD

before and after treatment (Figure 5) indicates that the gas yields from the two untreated substrates were comparable (statistically insignificant difference,  $p > 0.05$ ) and subsequently the increment in methane release attained with inoculation of MD was merely 7.6% greater than that accomplished with modification of CSD. As discussed above, the advancement in AD performance of modified MD was likely related to a metabolization of lignin during the rotting process that improved the proportion of carbohydrates and the accessibility of AD microorganisms to the available cellulose. Therefore, it would be reasonable to be assumed that pretreatment with *I. lacteus* at certain conditions fea-

sibly enhanced the biodegradability of both sludge types, however, the degree of improvement in methane production was depended on the increment in lipid and protein concentration in the case of a modified sludge with a small carbohydrate fraction and on the available for digestion cellulose in the case of a pretreated digestate rich in carbohydrates.

## 4. CONCLUSIONS

Digestates produced from different substrates were subjected to treatment with the basidiomycete *I. lacteus* and the methane generation potential of the modified materials was examined in AD assays to determine the influence of the fungal strain, modification time and digestate type on the AD performance of sludge. Pretreatment of sludge with the non-selective *I. lacteus* for 20 days at 28°C increased the methane generation potential of the sludge by 1.67-fold. For the non-selective fungus, prolonging incubation time to 30 days led to an increment in methane yields (1.24-fold), which, however, was lower than that accomplished at a shorter pretreatment period due to a substantial loss of fermentable organics, especially cellulose. Independently of the digestate type, pretreatment of digestate with *I. lacteus* enhanced the digestibility of sludge by at least 1.6-fold. The degree of improvement was depended on the amount of lipids and proteins supplied by the fungus when the modified sludge contained an insignificant carbohydrate proportion and on the available for digestion cellulose when the pretreated digestate was rich in carbohydrates. A combination of biological fermentation post-treatment and recirculation of the modified digestate into the biogas reactor could alter the overall efficiency of the anaerobic digestion of organic materials.

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# PRELIMINARY DEVELOPMENT OF A COMPOSITE INDICATOR OF CIRCULARITY IN THE CONSTRUCTION AND DEMOLITION WASTE (CDW) SECTOR

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## ABSTRACT

The circular economy is central to promoting sustainability in the construction sector, especially in the management of Construction and Demolition Waste (CDW). This article explores the importance of circularity indicators as key tools to assess and improve practices in this sector, with a particular focus on the proposed Integrated Circularity Index for CDW (ICICDW), which would provide a comprehensive view in the framework of the Circular Economy. In the EU, indicators like energy use, waste management, and recycled content help assess the environmental impact of construction. However, growing waste and emissions, along with a lack of standardised methods, highlight the need for a more holistic approach. This article reviews thirteen EU-proposed indicators for the construction sector, evaluating their relevance to CDW and emphasizing the need for new composite indicators that also consider material use and economic factors. The Integrated Circularity Index for CDW (ICICDW) is introduced as a tool that combines specific indicators from the CDW sector with economic aspects. This integration allows for a comprehensive assessment of circular economy performance within the CDW sector. This approach seeks to address crucial challenges, thereby driving the transition towards a more sustainable model. The implementation of circular economy indicators brings significant benefits, including improved waste management, reduced environmental impact, optimised resources and costs, promotion of the circular economy and compliance with current regulations. In this context, this paper highlights the fundamental importance of developing indicators that integrate various dimensions in order to move effectively towards sustainability and more environmentally friendly construction.

## 1. INTRODUCTION

The European Union faces significant challenges related to waste generation and greenhouse gas emissions, producing over 2.2 billion tons of waste annually and exceeding 2.5 billion tons of CO<sub>2</sub> emissions. In response to climate change, the European Parliament adopted the EU Climate Law, which sets the target of reducing net greenhouse gas emissions by at least 55% by 2030 (European Commission, 2024a; European Commission 2023; European Parliamentary Research Service, 2021). This effort aligns with the goal of achieving climate neutrality by 2050, a central aim of the European Green Deal. This deal, in turn, drives the new Circular Economy Action Plan, launched by the European Commission on March 25, 2020, which iden-

tifies the construction sector as a priority area (European Commission 2019; European Commission 2020). This prioritization is not arbitrary, as the construction sector is a major consumer of resources in Europe, using approximately half of all extracted materials, nearly half of the energy consumed, and a third of all water used, in addition to generating a third of the total waste, Figure 1 (Avintia 2021; European Commission, 2024b).

In this context, also in March 2022, the European Commission presented a package of measures designed to accelerate the transition to a circular economy, as detailed in the Circular Economy Action Plan, with the aim of transforming the current “take, make and dispose” model into a fully circular, environmentally sustainable and toxin-free economy by 2050 (European Commission 2020).

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**FIGURE 1:** Consumption in the construction sector.

The circular economy has established itself as a fundamental approach to promoting sustainability, especially in sectors with a high environmental impact such as construction. This model seeks to reduce dependence on virgin resources and minimise waste production through reuse and recycling. In recent years, significant progress has been made at the political, methodological and scientific levels in the analysis and implementation of circular practices. However, there is still a lack of a comprehensive and agreed methodology to enable effective monitoring of processes related to the circular economy. The construction industry is rapidly shifting its focus towards sustainability and more environmentally friendly practices. Institutions have developed tools for the circular economy and adopted a monitoring framework to assess progress towards it. However, there is currently no universally recognised indicator of 'circularity' and the number of reliable indicators to describe the most important trends is limited. Further research is therefore needed to develop a set of relevant indicators to define an appropriate monitoring framework (Avintia 2021; Sacyr 2021).

As a result of this need, the European Commission developed a monitoring framework based on ten key indicators, broken down into sub-indicators and organised into four categories: (1) production and consumption, (2) waste management, (3) secondary raw materials, and (4) competitiveness and innovation. These indicators were subsequently revised in 2023 to include metrics related to material footprint and resource productivity, with the aim of monitoring material efficiency and assessing whether EU consumption remains within planetary boundaries (European Commission 2023). This new framework strengthened the EU's circular economy and climate neutrality ambitions, aligning them with the objectives of the European Green Deal.

In this way, circularity indicators are crucial tools for evaluating progress towards the adoption of sustainable and circular practices in both organisations and production systems. In this context, a longevity indicator has been developed that quantifies the contribution to material retention based on the total time a resource remains in use, considering its initial useful life, extended useful life through remanufacturing, and additional useful life achieved through recycling (Franklin-Johnson et al. 2016). However, while these indicators provide valuable information on material retention and progress towards the circular economy, it is essential to recognise that sustainability encompasses a broader perspective (Ghisellini et al 2018, Franklin-Johnson et al. 2016). It is therefore essential to complement these circularity indicators with others that assess aspects such as energy consumption, integrated waste manage-

ment and resource efficiency, thus enabling a more comprehensive assessment of environmental and economic performance. Additionally, the lack of comprehensive data on the impacts of circular practices highlights the need to develop a more complete and effective set of indicators (Franklin-Johnson et al. 2016; Kirchher et al 2018).

With regard to Construction and Demolition Waste (CDW), the European Union has established the importance of moving towards high circularity in the construction sector, recognizing that this is the biggest driver of resource consumption and waste generation in Europe. While the EU Waste Framework Directive introduced a waste hierarchy and set a 70% recovery target for CDW by 2020, the inclusion of practices such as backfilling within recovery rates raises questions about the true contribution to a circular economy, as this practice does not preserve the value of materials. Although, as indicated, the EU revised the circular economy monitoring framework in 2023 by adding new indicators to monitor material efficiency and consumption footprint, a more comprehensive assessment of the effectiveness of the circular economy in the construction and demolition sector is still needed due to the lack of specific and adequate metrics (Zhang et al 2022). It is therefore crucial to develop more robust and specific indicators that allow effective monitoring of progress towards the targets set out in the EU Circular Economy Action Plan and go beyond traditional recovery metrics (European Commission 2020).

The CDW is composed of a variety of materials, including concrete, bricks, gypsum, wood, glass and metals, many of which have a high potential for recycling and reuse. The European Union has identified CDW as a priority waste stream, and despite the potential for recycling, the increasing amount of material stockpiles in cities driven by the consumption of raw materials for construction underlines the need to consider further recycling of construction and demolition waste as an option for resource conservation. Conventional practices, based on continuous resource extraction and waste generation, are being challenged in favour of a European recycling society with a high level of resource efficiency (Lederer et al 2020; European Commission 2024a).

In this context, the transition towards a Circular Economy (CE) model in the construction and demolition waste (CDW) sector is presented as a key solution whose environmental challenges could be mitigated through the adoption of circular economy practices as Menegaki et al. point out that, globally, increasing efforts are being made to recycle and reuse CDW as a means to avoid the environmental impacts associated with landfilling (Murray et al. 2017; Royal Decree 105/2008; Papargyropoulou et al 2011; Menegaki and Damigos 2018).

Ma et al. 2023 focuses on identifying the critical success factors (CSFs) for achieving a closed-loop circular economy in CDW management in China, seeking to move beyond the traditional 3R approach and stimulate a transition to a more sustainable model.

Ghisellini et al. 2018 analysed the environmental and economic costs and benefits of the circular economy (CE) in the construction and demolition (CD) sector. Their liter-



ature review found that circular strategies (reuse and recycling) decrease waste generation. The reviewed studies showed that reusing and recycling construction and demolition waste (CDW) generally provides environmental and economic benefits, reducing environmental impacts by decreasing raw material extraction and waste volume.

Also, Ghisellini et al. 2018 and Kirchherr et al. 2018, addressed the evaluation of CE by pointing out the need for better metrics and flow accounting to assess the effectiveness of CE and identified the lack of data, as a technological barrier. This lack of data makes it difficult to fully assess the effectiveness of EC in the C&D sector. Therefore, the difficulty of evaluating EC in this sector due to the lack of specific metrics is supported by both studies. Meanwhile Menegaki and Damigos 2018 conducted a review on construction and demolition waste (CDW) management. Their study focuses on the factors, barriers and motivations that influence the generation and management of CDW. The authors calculated CDW indicators for selected countries and developed an explanatory model to identify key factors. In addition, they created a conceptual map with 36 components that represents the existing knowledge about the CDW system and its interrelationships. The main objective of their work is to provide an overview of the challenges in CDW management, including the policy framework. Lederer et al. (2020) conducted a material flow analysis in Vienna, showing that reuse and recycling of construction minerals could reduce material imports by 32%. This example highlights the potential of CE to decrease dependence on virgin resources and improve the resilience of building systems (Leader et al 2020b). However, significant barriers remain. Murray et al. 2017 and Sauvé et al. 2016 identified a lack of clarity regarding the fundamental principles and objectives of the circular economy, which hinders its assessment and widespread adoption in the sector.

Despite advances in CDW recovery and recycling, the integration of the circular economy on a large scale remains limited due to the absence of specific indicators that accurately measure progress towards circularity. Thus Mayer et al. 2019, improvements in statistical data collection, knowledge on material stockpiles and the development of criteria for ecological cycle closure are needed to advance the assessment of CE. Parchomenko et al. 2019 also emphasize the fragmentation of CE measurement approaches and the need for more comprehensive metrics.

It is therefore clear that in order to effectively implement the circular economy in the field of construction and demolition waste (CDW), multiple interrelated social, governmental, economic, behavioural, technological and environmental dimensions that influence the adoption of circular strategies need to be addressed in an integrated manner. In this context, the development of specific metrics and indicators to assess and optimize the use of CDW, improve quality control during dismantling, encourage efficient material handling and facilitate a more sustainable management that maximizes ecological and economic benefits, thus driving the transition towards a circular economy in the construction sector, is of particular relevance. The implementation of the circular economy in the management

of CDW requires a combination of technical, political and economic strategies, supported by specific indicators that reflect progress towards sustainability. These efforts will not only minimize environmental impacts, but also maximize the value of materials and foster a more resilient and sustainable model in the construction sector.

This work aims to contribute to the preliminary development of a composite circularity indicator focused on waste from the construction and demolition sector, which is considered crucial for the global economy.

## 2. CIRCULARITY INDICATORS

### 2.1 Indicators of the construction sector in the EU

Public and private entities have published reports on what the indicators for the circular economy measurement framework should be. Despite these efforts, there is still no stable and recognized framework of indicators unique to the construction sector. The European Commission in 2014 proposed a set of areas to assess the environmental performance of the construction sector (European Commission 2014):

1. Total energy consumption: energy from material manufacturing processes added to construction processes and building operation and use;
2. Use of materials and their environmental impact;
3. Durability of construction products;
4. Demolition planning;
5. Construction and demolition waste management;
6. Recycled content of building materials;
7. Possibility of recycling and reuse of building materials and products;
8. Total water consumption;
9. Intensity of use of buildings: flexibility, resilience, possibility of change of typology and use, degree of space occupation, etc;
10. Interior comfort.

Subsequently the European Commission published the Level(s) report establishing a common EU framework of core sustainability indicators for residential and office buildings proposing indicators for measuring sustainability in the building sector (European Commission 2014).

Based on this work, the Green Council Building Spain (GCBs) published the report: Indicators for measuring circularity in the construction sector at the beginning of 2020 (summary in figure 2). This work, initiated jointly with the Working Group GT-6 National Environmental Congress, Conama Foundation divides the indicators into two groups (Green Building Council Spain 2023; Conama 2018):

1. Short-term indicators, those that are currently capable of being accounted for by valid and credible sources, as they are based on existing indicators that are similar or for which data are already collected, and could therefore be implemented with some ease;
2. Long-term indicators. Indicators that are recognised as strategic, but for which today we do not have the necessary reliable sources for their measurement, nor do we have solid references.

Table 1 summarises all the proposed key indicators and the aspects that each one assesses, and where defined, the units of measurement, analysing the advantages and disadvantages of each one.

From analysis of the indicators in Table 1, it can be deduced that the availability and reliability of the data needed for their calculation is important, as they are essential for the effective application of these indicators. Efforts are needed to improve data collection and harmonise calculation criteria at the national level.

In the specific case of construction and demolition waste, based on previous studies analysing the construction sector, a series of key indicators have been identified that enable the degree of circularity in the management of construction and demolition waste (CDW) to be accurately assessed. These indicators not only quantify material flows but also provide operational and strategic information for the design of public policies and the continuous improvement of sustainable construction projects. Analysing their usefulness and relevance on a scale of 1 (minimum) to 5 (maximum), we find that (Green Building Council Spain 2023; Conama 2018):

- a. The indicator of CDW management per built-up area ( $\text{Kg}/\text{m}^2\text{year}$ ) is considered one of the most complete and relevant. Its high usefulness (5) is due to the fact that it makes it possible to normalise the waste generated according to the construction activity, facilitating comparisons between projects, regions or periods. By differentiating between hazardous and non-hazardous waste and classifying their final destination, this indicator provides a global and detailed vision that is indispensable for establishing baselines and measuring the impact of reduction and recovery strategies. Its relevance (5) is equally high, as it is aligned with European and national objectives to minimise waste generation and maximise waste recovery.
- b. The percentage of CDW at each destination is another key indicator. With a usefulness valued at 4, it allows the efficiency of waste treatment to be assessed by quantifying the fractions destined for material recovery,

energy, landfill or landfill. Its relevance (5) lies in its direct alignment with the principles of the circular economy, which promote the reintroduction of materials into the value chain and the minimisation of final disposal.

- c. Recycled content in building materials, measured in  $\text{kg}/\text{m}^2$  or as a percentage of the total, has a high utility (4), as it evidences the demand for secondary raw materials and can influence green public procurement criteria and environmental certifications. Its relevance (5) is unquestionable, as the use of recycled materials reduces pressure on natural resources and fosters circular markets.
- d. The CDW Recovery Rate, defined as the proportion of waste prepared for reuse, recycling or recovery, has both a usefulness and relevance of 4 and 5 respectively. This indicator, adopted by Eurostat (cei\_wm04038) and institutions such as IHOBE 2018, provides an aggregate measure of the efficiency of waste management systems and allows the assessment of compliance with legislative targets (Conama 2018; IHOBE 2028; Ghisellini et al 2016; OECD, European Union, & EC-JRC, 2008).
- e. The CDW generation per built area indicator is proposed as a direct metric of prevention. Its usefulness (4) lies in its ability to monitor material efficiency from design, while its relevance (5) lies in its connection with the waste hierarchy, which prioritises reduction at source (Conama 2018, Ghisellini et al 2016).
- f. On the other hand, the Absolute amount of CDW generated in buildings is of moderate usefulness (3), as it provides gross volume without contextualising it with the activity. Even so, its relevance (4) is significant for understanding the full magnitude of the problem and guiding macro strategies (Green Building Council Spain 2023).
- g. The percentage of recovered waste, aligned with Eurostat frameworks, is useful (4) to understand the aggregate performance of the management system and very relevant (5) for its contribution to circular economy and landfill reduction objectives (Green Building Council Spain 2023).

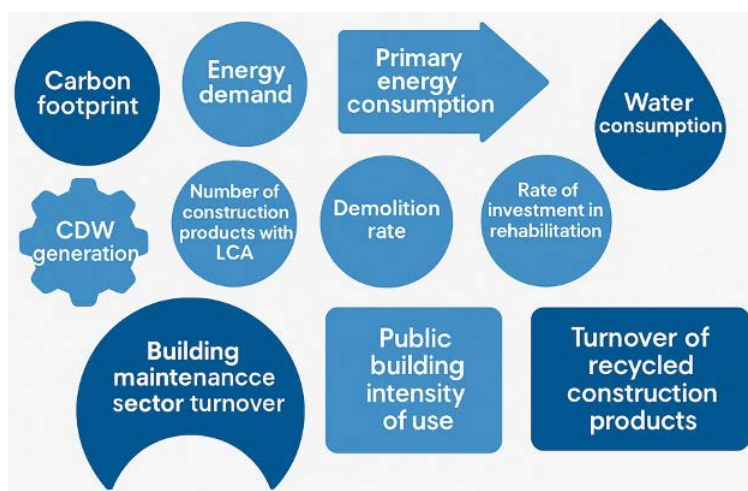


FIGURE 2: Summary of indicators.

**TABLE 1:** Summary of the proposed key indicators.

| Indicator           | Target                                                          | Advantages                                                     | Disadvantages                                              | Units                                   |
|---------------------|-----------------------------------------------------------------|----------------------------------------------------------------|------------------------------------------------------------|-----------------------------------------|
| Carbon footprint    | Track GHG emissions and promote low-impact strategies           | Shows impact evolution; encourages efficiency and renewables   | May omit transport and end-of-life stages                  | kgCO <sub>2</sub> /m <sup>2</sup> -year |
| Energy demand       | Evaluate building envelope efficiency and long-term performance | Highlights efficiency and supports 2050 savings goals          | Risk of theoretical values being disconnected from reality | kWh/m <sup>2</sup> -year                |
| Primary energy      | Better represent energy flows in Circular Economy               | Reflects system/source efficiency; closer to real use          | Risk of disconnect with real consumption                   | kWh/m <sup>2</sup> -year                |
| Water use           | Promote reduction and efficient management                      | Supports sustainable water use and resource synergy            | No major drawback noted                                    | m <sup>3</sup> /occupant-year           |
| Material use        | Promote efficient material use and prioritise refurbishment     | Encourages efficiency, durability, and environmental awareness | Data reliability and standardisation issues                | (kg, T)/m <sup>2</sup> -year            |
| CDW generation      | Monitor and reduce construction and demolition waste            | Encourages reuse, recycling, and controls illegal dumping      | Hard to track rehabilitation without permits               | (kg, T)/m <sup>2</sup>                  |
| Products with LCA   | Encourage use of EPD/LCA for sustainability assessment          | Facilitates sustainability at product/building levels          | Limited by market maturity                                 | N° of EPDs/LCAs                         |
| Refurbishment ratio | Track refurbishment vs. new construction                        | Supports life extension and performance improvement            | Lacks unified refurbishment data                           | m <sup>2</sup> /m <sup>2</sup> (%)      |
| Demolition rate     | Discourage unnecessary demolitions                              | Emphasises preference for refurbishment                        | Indirect; requires interpretation                          | m <sup>2</sup> /m <sup>2</sup> (%)      |
| Rehab investment    | Track economic trends and quality of rehab                      | Shows value generation and depth of interventions              | Data may mix different rehab types                         | €/m <sup>2</sup>                        |
| Maintenance sector  | Define and size the building maintenance market                 | Clarifies sector scope and aids CNAE classificatio             | No major drawback noted                                    | € or workers                            |
| Public building use | Avoid underuse of public buildings                              | Promotes efficient space use                                   | No major drawback noted                                    | Not specified                           |

h. Finally, the Level of on-site segregation, measured by the percentage of mixed waste LER 17 09 04, is one of the most practical and operational indicators. Its usefulness is maximal (5), as it allows the quality of on-site management to be assessed, and its relevance (5), as good segregation is a precondition for efficient and high-quality recovery (Green Building Council Spain 2023).

Figure 3 shows a comparative assessment of the key indicators for the construction and demolition waste sector.

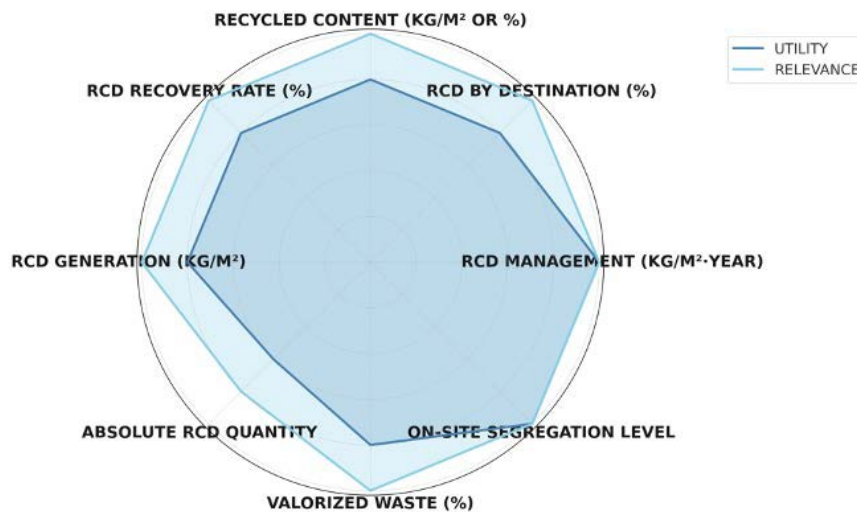
Together, these indicators form a robust and coherent framework for monitoring circularity in the construction sector, allowing an assessment of the environmental and operational performance of current practices, and identifying opportunities for improvement for a real transition towards the circular economy. But for an effective implementation of the circular economy in the construction and demolition waste (CDW) sector, it is essential to propose indicators that integrate environmental and economic aspects in a balanced way. While the circular economy seeks to increase resource efficiency and promote closed-loop production patterns, with a particular focus on industrial and municipal waste, measuring progress towards these goals requires going beyond traditional resource efficiency metrics (Parpomenko et al 2029, Ghisellini 2026). Approaches purely focused on reducing resource consumption may not capture the main objective of the circular

economy, which is to maintain the value of products and materials for as long as possible. The integration of environmental dimensions, such as environmental burden reduction and prevention of impacts, with economic dimensions, such as value creation through material retention, is crucial to guide decision-making and assess performance in the CDW sector within a circular economy framework (Franklin-Johnson 2010, Ghisellini 2016). The current lack of specific indicators that combine material environmental and economic aspects and the need for further research in this area highlight the importance of developing tools that enable comprehensive monitoring and facilitate the transition to a circular model in the construction sector (Parpomenko et al., 2029; Ghisellini, 2026).

### 3. PRELIMINARY DEVELOPMENT OF A CIRCULARITY INDICATOR IN THE CONSTRUCTION AND DEMOLITION WASTE SECTOR. DEVELOPMENT METHODOLOGY

The evaluation of the circular economy in the construction and demolition waste (CDW) sector has traditionally focused on material and environmental indicators. However, as seen in the previous section, in order to promote an effective and realistic transition towards circular models, it is also necessary to incorporate economic variables that reflect the viability and financial impact of the strategies applied. In this context, the preliminary development of a





**FIGURE 3:** Benchmarking circular economy indicators applied to the construction and demolition sector.

new composite indicator integrating environmental and economic aspects is proposed, allowing for a more comprehensive assessment of the circular performance of the sector. The transition towards the circular economy in the CDW sector faces several barriers (European Commission 2020; Parpomenko et al 2029):

1. Technical barriers: There is significant variability in the quality of recycled materials, as well as a lack of advanced technologies for efficient processing;
2. Economic barriers: The high costs associated with recycling, coupled with the lack of financial incentives, make it difficult for recycled materials to compete with virgin materials;
3. Regulatory barriers: Insufficient, inadequate or complex regulations limit the adoption of circular practices, increasing bureaucracy for companies;
4. Social and behavioural barriers: Resistance to change and lack of knowledge about circular economy practices hinder its implementation in the sector;
5. Logistical barriers: Limited infrastructure to manage CDW and difficulties in the supply chain increase costs and make it difficult to incorporate recycled materials into processes.

Overcoming these barriers requires a combination of financial incentives, technological advances, targeted regulations and increased sustainability education.

A key first step is the development of simplified and measurable indicators to assess progress towards the circular economy. Based on the indicators analysed and following the recommendations on how to design, develop and disseminate a composite indicator from the OECD Handbook on constructing composite indicators: methodology and user guide, a composite indicator is proposed, the Integrated Circularity Index for RCD (ICICDW), which simplifies and combines these key dimensions into a single framework of analysis by adding the economic dimension (OECD, European Union, & EC-JRC, 2008).

The creation of an Integrated Circularity Index for CDW (ICICDW) addresses the above-mentioned barriers and

allows for a comprehensive assessment of the circular performance of CDW management. The proposed index combines three key dimensions: (1) the recycling rate of CDW, (2) the environmental impact avoided through the substitution of virgin materials by recycled materials, and (3) the relative economic benefit derived from the efficient reuse of recycled materials in new construction. Thus, the proposed indicator will combine material circularity with the economic benefits generated by waste recovery, incentivising sustainable practices that are also economically viable.

### 3.1 Development methodology

This methodology is based on a sequence of steps adapted from the "Handbook on Constructing Composite Indicators" for the creation of a composite indicator to assess circularity, applied to the construction and demolition waste (CDW) sector (OECD, European Union, & EC-JRC, 2008).

#### 3.1.1 Stage 1: Developing a Theoretical Framework

This step is fundamental. The ICICDW aims to provide a comprehensive and multidimensional view of circular performance in CDW management, combining material circularity (MC), avoided environmental impact (AEI) and relative economic benefit (REB).

The theoretical framework recognises that an effective transition to the circular economy in the CDW sector requires consideration not only of material and environmental aspects, but also of financial viability and impact.

The selected ICICDW components are:

- Material Circularity (MC): Measures the proportion of CDW that is reintegrated into the production cycle through reuse, recycling and recovery, in relation to the total amount of CDW generated;
- Avoided Environmental Impact (AEI): Evaluates the environmental benefit of replacing virgin materials with recycled materials by comparing the avoided impact with a theoretical baseline impact;

- **Relative Economic Benefit (REB):** Quantifies the economic value recovered from CDW in relation to the total cost of its management.

This framework seeks to encourage sustainable practices that are also economically viable.

Defining the ICICDW as:

$$ICICDW = w_1 * MC + w_2 * AEI + w_3 * REB \quad (1)$$

with  $w_1 + w_2 + w_3 = 1$

### 3.1.2 Stage 2: Selection of Variables

At this stage, the individual indicators that make up each dimension of the ICICDW are defined.

In this step, the data necessary to calculate each component of the index are collected:

#### Material Circularity (MC)

$$MC = \frac{CDW_{reused} + CDW_{recycled} + CDW_{valorized}}{CDW_{generated}} \quad (2)$$

The data should be obtained from authorised manager's certificates, site reports, waste management platforms.

#### Avoided Environmental Impact (AEI)

Calculated from an estimate of the savings in CO<sub>2</sub> emissions, water, energy or raw material use by replacing virgin materials with recycled materials

$$AEI = \frac{Impact_{avoided}}{Impact_{theoretical}} \quad (3)$$

The AEI can be calculated using LCA databases (Ecoinvent, Simapro, One Click LCA) or references.

#### Relative Economic Benefit (REB)

$$REB = \frac{Recovered\ economic\ value}{Total\ management\ cost\ CDW} \quad (4)$$

Includes revenues from sale of materials, savings from reuse, treatment and transport costs.

It can be calculated on the basis of invoices, sales contracts, cost bases, construction budgets.

### 3.1.3 Step 3: Imputation of Missing Data (Simplified)

As this is a preliminary development, priority will be given to collecting complete data for the selected study units. If there are missing data, a simple imputation, such as using the mean of the indicator for similar cases, could be considered, always documenting this decision. A more complex imputation strategy (such as multiple imputation) could be implemented at later stages if the amount of missing data is significant and may generate important biases.

### 3.1.4 Step 4: Multivariate analysis

In a preliminary development with a small number of dimensions clearly defined by a theoretical framework, this step can be omitted to simplify the initial methodology. A more in-depth analysis of the relationships between the individual indicators could be carried out at later stages with a larger dataset.

### 3.1.5 Stage 5: Data Normalisation

Since MC, AEI and REB will have different units and scales, it is necessary to normalise their values to make them comparable before aggregation. As this is a preliminary design, simple standardisation has been chosen, using the Min-Max method for all dimensions and scaling them to a range of 0 to 1.

### 3.1.6 Step 6: Weighting and Aggregation

In this stage, the weights ( $w_1$ ,  $w_2$ ,  $w_3$ ) are assigned to each of the three dimensions of the ICICDW. The sum of the weights must equal 1 ( $w_1 + w_2 + w_3 = 1$ ).

The allocation of weights can be based on different criteria: a) technical if they give more weight to the dimension considered most relevant to sustainability objectives or normative e.g., more weight to the AEI if environmental impact is prioritised. b) Expert judgement, through stakeholder consultations or surveys to reflect their priorities (Budget Allocation Process) or c) sensitivity analysis, exploring different combinations of weights to assess their impact on the ICICDW.

### 3.1.7 Stage 7: Robustness and Sensitivity Analysis (Initial)

A preliminary robustness and sensitivity analysis is necessary to assess the reliability of the ICICDW in the face of different methodological choices.

In this initial phase, it will be analysed how these variations affect the final value of the ICICDW and the relative ranking of the study units, if a comparison is made. Further sensitivity analysis could include methods such as Monte Carlo analysis in later stages.

### 3.1.8 Stage 8: Component Analysis

It is important to analyse the contribution of each dimension (MC, AEI, REB) to the final value of the ICICDW. This allows identifying which aspects are driving better or worse circular performance.

### 3.1.9 Step 9: Linkages to Other Variables

In a preliminary development, the analysis of the linkages of the ICICDW with other relevant variables (such as policy indicators, infrastructure investment, etc.) should be postponed until the indicator is consolidated and more data are available.

### 3.1.10 Stage 10: Presentation and Dissemination

The presentation of the ICICDW should be clear and precise. The overall value is proposed to be visualised through graphs of its components to facilitate interpretation.

In addition, the limitations inherent in this preliminary phase of indicator development shall be clearly communicated.

This simplified methodology allows the ICICDW to be properly formulated at a preliminary stage, focusing on the essential steps of definition, data selection, normalisation, weighting, aggregation and an initial robustness assessment. The more complex steps can be incorporated in future developments of the indicator. The summary of ICICDW development methodology stages is shown in Figure 4 (OECD, European Union, & EC-JRC, 2008).

## 4. CONCLUSIONS

It is concluded that effective implementation of the circular economy in the management of CDW requires a combination of technical, political and economic strategies, supported by specific indicators that reflect progress towards sustainability. These efforts will not only minimise environmental impacts, but also maximise the value of materials and foster a more resilient and sustainable model in the construction sector.

The paper is presented as a contribution to the preliminary development of circularity indicators focusing on waste generated in the construction sector, an area considered crucial for the global economy.

Despite the efforts of public and private entities, there is still no stable and recognised framework of indicators exclusively for the construction sector. Therefore, it is concluded that there is a need to formulate new comprehensive indicators that not only address environmental aspects, but also material consumption and/or economic aspects.

The Integrated Circularity Index for CDW (ICICDW) is introduced as an approach to address challenges such as material contamination, environmental impact while encouraging economic transition towards a more sustainable model. The formulation of indicators that integrate different aspects is considered crucial to move towards sustainability and more sustainable construction.

Finally, for an effective implementation of the circular economy in the CDW sector, it is concluded that it is essential to propose indicators that integrate environmental and economic aspects in a balanced way. Measuring progress towards circular economy objectives requires going beyond traditional resource efficiency metrics by integrating environmental and economic dimensions to guide decision-making and assess performance in the CDW sector. The current lack of specific indicators and the need for further research in this area underlines the importance of developing tools that enable comprehensive monitoring and facilitate the transition towards a circular model in the construction sector. The preliminary development of the ICICDW is proposed as a key step in this direction.

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# CIRCULAR BUSINESS MODEL FOR SMALLHOLDER FARMERS: UTILIZING BANANA FARMING WASTE FOR TEXTILE PRODUCTION

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## ABSTRACT

Sustainability, aligned with the principles of the Circular Economy, emerges as an alternative for waste reduction and the mitigation of environmental impacts. In the banana cultivation sector, large quantities of pseudostems are discarded after harvest, representing not only an environmental challenge but also an opportunity for the production of sustainable textile fibers. Simultaneously, the textile industry, one of the most polluting in the world, demands innovative solutions to reduce the consumption of natural resources, as well as the emission of pollutants and greenhouse gases. Based on an integrative literature review, this study examines the feasibility of a Circular Business Model (CBM) designed for smallholder farmers, utilizing banana crop residues for textile production. The final review portfolio consisted of 46 scientific articles, selected based on relevance, temporal scope, and methodological rigor. The results indicate that this approach can mitigate environmental impacts, create new income opportunities, and strengthen the circular bioeconomy. Furthermore, the adoption of this model fosters symbiosis between sectors, promoting integration between agriculture and the textile industry in the pursuit of more sustainable solutions. Ultimately, the transition toward a more responsible production model aligns with international initiatives and regulations that promote biomaterials and reduce dependence on synthetic fibers.

## 1. INTRODUCTION

Sustainability in both agriculture and the textile industry has become a central theme in discussions surrounding innovative, circular, and inclusive business models. The emergence of the Circular Economy (CE) as an alternative to the linear model of production and consumption has driven new approaches to resource management and waste reduction. In the context of banana cultivation, a globally significant agricultural sector, the generation of waste, such as the disposal of tons of pseudostems after harvest, may pose a significant environmental challenge (Brühl et al., 2023). However, such residues can also be repurposed as inputs for the production of biomaterials, including more sustainable textile fibers (Anafack et al., 2023; Fiallos-Cárdenas et al., 2022).

The food industry is one of the main drivers of environmental degradation, contributing to impacts such as deforestation, water resource depletion, and greenhouse gas emissions. Intensive food production generates large volumes of waste and organic residues, and their improper disposal contributes to soil and water contamination (Ghosh & Pramanik, 2023). Moreover, global food waste

accounts for approximately one-third of all food produced, representing not only a failure in the distribution system but also a significant source of environmental pollution and biodiversity loss (Abdullah et al., 2023).

Although the environmental impacts of agriculture and the textile industry have been widely discussed, practical strategies that link small-scale farming with sustainable textile production remain underexplored in the literature. This study addresses this gap by proposing a circular business model that utilizes banana cultivation residues, specifically the pseudostem, for the production of textile fibers. The model is designed to support smallholder farmers and aims to foster resource circularity, environmental mitigation, and social inclusion in rural areas. This approach has the potential to contribute to waste reduction, resource optimization, and the generation of employment and income in vulnerable rural communities (Korsunova et al., 2022). Furthermore, the use of banana fibers in the textile industry offers advantages such as high tensile strength, durability, and biodegradability, thereby reducing dependence on synthetic fibers and minimizing the sector's environmental impact (Subash & Perumalsamy, 2024).

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The development of appropriate Business Models (BMs) helps transform environmental challenges into economic and social opportunities. According to Cullen and De Angelis (2021), a well-structured BM functions as a bridge between innovation and value creation, enabling the identification of promising opportunities. While traditional business models describe how a company creates, delivers, and captures value, encompassing elements such as value proposition, customer segmentation, distribution channels, and revenue streams (Dembek et al., 2022; Vatankhah et al., 2023), the implementation of such models in rural communities requires adaptations that consider local socioeconomic and cultural factors (Iheanachor et al., 2021).

The Circular Business Model (CBM) represents a promising approach grounded in the principles of the Circular Economy, aiming to maximize resource value through the reuse, recycling, and recovery of materials within a regenerative system (Daou et al., 2020; Rosa et al., 2019). When applied to banana cultivation, this concept enables the conversion of agricultural residues into textile fibers, contributing to the mitigation of environmental impacts in the sector while creating economic opportunities for smallholder farmers.

An illustrative example can be found in agricultural cooperatives that repurpose crop residues into biomaterials or textile fibers, representing tangible cases of CBMs. Such initiatives demonstrate how shifting from traditional to regenerative practices can simultaneously generate economic value and reduce environmental impact (Korsunova et al., 2022).

It is also noteworthy that the literature highlights a gap in the practical application of the circular economy, particularly within the context of rural entrepreneurship (Maher et al., 2023). Therefore, this research also aims to address

this gap by proposing a circular business model focused on smallholder farmers, promoting a more sustainable and equitable approach to natural resource management. To this end, an integrative literature review will be conducted to consolidate knowledge and evidence regarding the potential use of banana cultivation residues for textile production.

## 2. METHOD

The approach of this article consisted of an integrative literature review, aimed at providing new theoretical and conceptual insights derived from existing syntheses or critiques (Annosi et al., 2022). According to Torracco (2005, 2016), integrative reviews are a specific review method that summarizes empirical or theoretical literature to offer a more comprehensive understanding of a particular phenomenon, while simultaneously reviewing, critiquing, and synthesizing the representative literature on a topic, thereby generating new frameworks and perspectives on the subject.

It is noteworthy that, despite being widely used in scientific studies, the integrative literature review does not yet have a standardized protocol. Therefore, the next step involved employing the PRISMA method, an important tool to enhance the eligibility of selected studies as well as to ensure transparency, reproducibility, credibility, and efficiency (Costa et al., 2020; Oliveira Neto et al., 2023), as demonstrated in Figure 1.

As shown in Figure 1, after searching the databases and applying filters alongside the inclusion and exclusion criteria, 46 research articles comprised the final portfolio for the development of this integrative review article. It is noteworthy that the Scopus and Web of Science databases were selected due to their extensive multidisciplinary

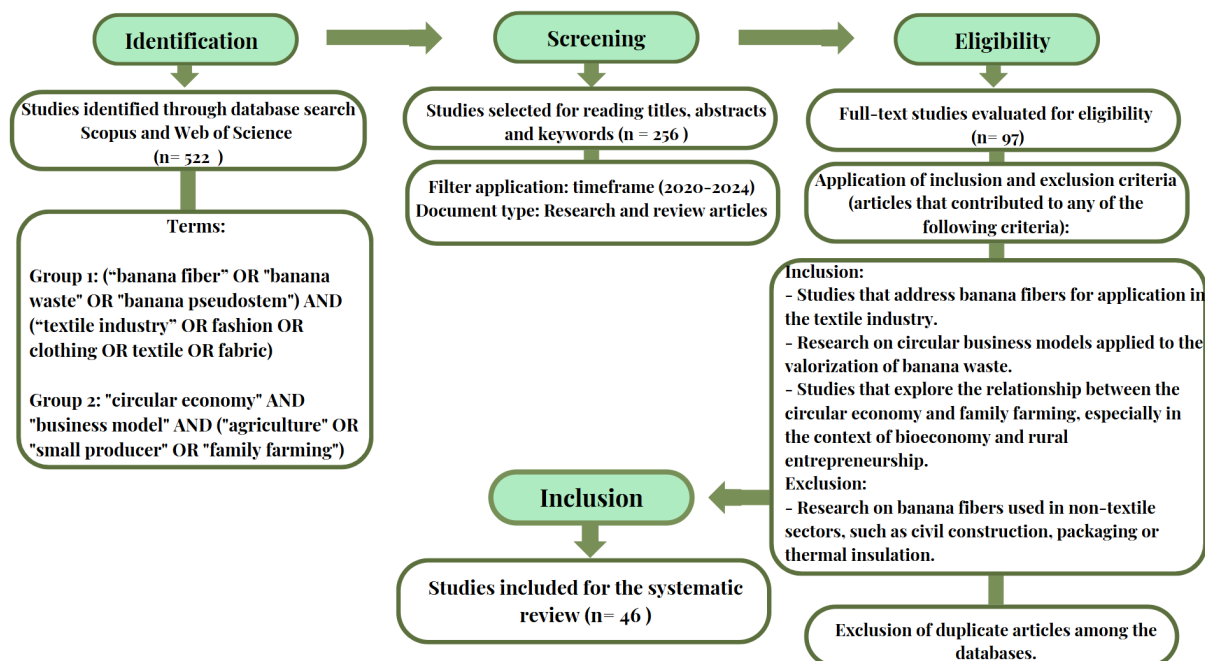


FIGURE 1: Selection and evaluation of studies using the PRISMA method. Source: Authors, 2025.



**TABLE 1:** Search Results in Scopus and Web of Science Databases.

| Term Groups                                                                                                                    | Initial Search                     | 1st Filter: Time Frame             | 2nd Filter: Document Type         |
|--------------------------------------------------------------------------------------------------------------------------------|------------------------------------|------------------------------------|-----------------------------------|
| ("banana fiber" OR "banana waste" OR "banana pseudostem") AND ("textile industry" OR fashion OR clothing OR textile OR fabric) | Scopus: 278<br>Web of Science: 156 | Scopus: 160<br>Web of Science: 103 | Scopus: 114<br>Web of Science: 90 |
| "circular economy" AND "business model" AND ("agriculture" OR "small producer" OR "family farming")                            | Scopus: 67<br>Web of Science: 21   | Scopus: 56<br>Web of Science: 19   | Scopus: 34<br>Web of Science: 18  |

Source: Authors, 2025

coverage and rigorous indexing, ensuring the inclusion of studies with high scientific relevance.

However, it is important to emphasize that an integrative literature review allows for the inclusion of supplementary documents to enrich the findings obtained from the databases. Therefore, in addition to scientific articles, the following documents were used to support Section "4. Discussions": 1) A Sustainable Bioeconomy for Europe: Strengthening the Connection between Economy, Society, and Environment; 2) Circular Economy Action Plan: For a Cleaner and More Competitive Europe; 3) BIT II Bioeconomy in Italy; 4) Economic Instruments for the Circular Economy in Italy; 5) Sustainable Bioeconomy Action Plan (PABS - original acronym); 6) Decree No. 12,044, dated June 5, 2024, which establishes the National Bioeconomy Strategy in Brazil, and Decree No. 12,082, dated June 27, 2024, which establishes the National Circular Economy Strategy in Brazil; 7) National Program for Strengthening Family Farming, Brazil; and 8) the book *The Fortune at the Bottom of The Pyramid: Eradicating Poverty through Profits* by C. K. Prahalad.

### 3. RESULTS

#### 3.1 Search and Selection of Articles in Databases

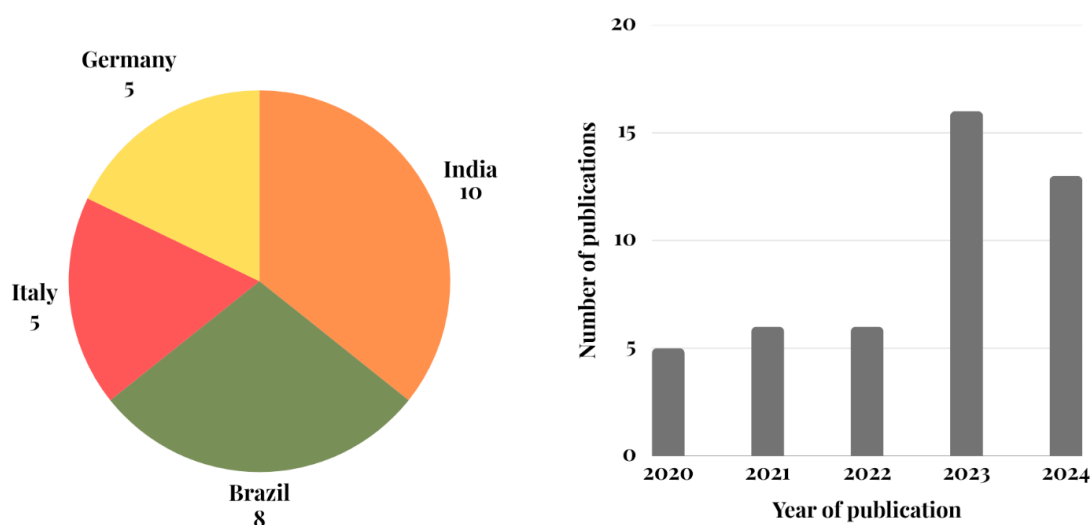
Regarding the search for research and review articles in the Scopus and Web of Science databases, Table 1 presents the number of documents identified through the two sets of terms, both in the initial search without applying filters and after applying the pre-established filters.

A greater number of results was observed with the first group of terms, with the Scopus database accounting for the highest number of retrieved publications for both the first and second groups of descriptors. After applying the defined filters, a total of 256 documents were identified across the two databases. Subsequently, titles, abstracts, and keywords were screened, resulting in the selection of 97 articles for full-text reading. Following this stage, 46 studies were identified as consistent with the topic according to the inclusion and exclusion criteria and were included in the final portfolio of the present integrative literature review.

#### 3.2 Analysis and Classification of Articles

Data from the 46 articles comprising the final portfolio were collected, considering the countries with the highest number of publications on the topic and the year with the greatest number of publications, respecting the time frame established between 2020 and 2024. Figure 2 presents the countries with the highest number of publications on the subject, as well as the year with the highest concentration of studies within the analyzed period.

Figure 2 presents the countries with the highest participation in the analyzed publications, with India being the most recurrent, contributing ten articles, followed by Brazil (8), Italy (5), and Germany (5). For the country count, all institutional affiliations of the authors in each article were considered, regardless of authorship order or corresponding author status. Thus, each country represented among the co-authors was counted once per article, reflecting col-



**FIGURE 2:** Distribution of the Number of Publications by Country and Year (2020–2024). Source: Authors, 2025.

laborative and multinational participation in scientific production. This approach acknowledges the contribution of all involved authors and enhances the representativeness of the data.

The predominance of India and Brazil may be related to the fact that both are among the world's largest banana producers, in addition to having extensive rural areas and significant socio-environmental challenges related to agricultural waste management. As developing countries, both have also been investing in sustainable and accessible solutions that promote income generation in rural areas.

The presence of European countries such as Italy and Germany may reflect academic and technological interest in circular economy models, biomaterials, and sustainable innovations, despite these countries not being major banana producers. Regarding temporal distribution, there is a marked increase in publications starting in 2022, peaking in 2023 (16 articles), and continuing this trend in 2024 (13 articles), demonstrating an intensification of academic debate on circular business models, particularly in the context of the bioeconomy and rural sustainability.

A co-occurrence term analysis was also conducted using the VOSviewer software, applied to the 46 selected articles, as shown in Figure 3. This tool is widely used in the scientific field due to its ability to map and visualize networks of keywords, authors, institutions, and other bibliometric elements based on data extracted from publications. The analysis enabled the identification of the most recurring terms within the analyzed corpus, contributing to the recognition of thematic patterns.

In Figure 3, it can be observed that the terms "circular economy," "sustainability," "bioeconomy," and "banana" form the most robust conceptual core, indicating the cen-

trality of these themes in scientific discussions related to the reuse of agricultural residues. The direct connection between "circular economy" and terms such as "biowastes," "apparel," and "banana" demonstrates the growing relevance of utilizing agricultural by-products in the textile industry. Furthermore, although some terms appear isolated or with low connectivity, such as "family agriculture," "family farm," "bottom-of-the-pyramid," and "rural development", they indicate potential gaps and opportunities for greater integration of social and economic aspects in the academic debate.

The sparse presence of these concepts reinforces the need to expand discussions on circular business models aimed at small producers and rural communities. In this context, the adoption of two distinct groups of search terms is justified: (1) "banana fiber" OR "banana waste" OR "banana pseudostem" combined with "textile industry" OR fashion OR clothing OR textile OR fabric; and (2) "circular economy" AND "business model" AND ("agriculture" OR "small producer" OR "family farming"). This strategy allowed the identification of studies aligned with the proposal of this article, promoting a linkage between research involving sustainability, social innovation, and valorization of agricultural residues. Additionally, it highlights the lack of interdisciplinary approaches that systematically integrate these thematic axes.

Finally, it was observed that the proposal of a circular business model for small farmers based on the use of banana cultivation residues has great potential to transform environmental challenges into sustainable economic solutions, as shown in Figure 4.

Although banana production residues serve as an example, this model could be adapted to other food waste

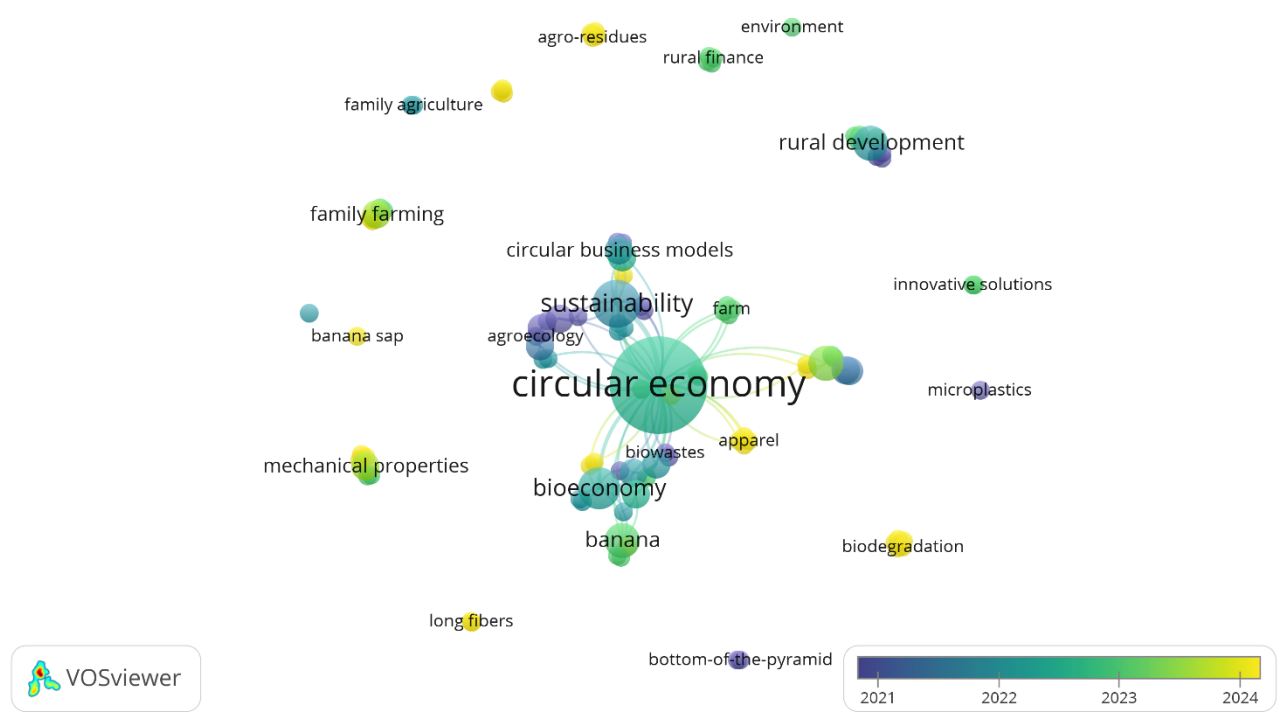


FIGURE 3: Term co-occurrence map in the 46 analyzed articles. Source: Authors, 2025.



**FIGURE 4:** Diagram of the circular model for the valorization of banana cultivation residues in the textile industry. Source: Authors, 2025.

streams and implemented symbiotically with different industries, creating new opportunities for the circular bio-economy. In addition to reducing pollution and waste, this approach can strengthen local production chains and promote more equitable and resilient rural development.

## 4. DISCUSSION

### 4.1 The Rural Base of the Pyramid and Family Farming as Drivers of Sustainability

The strengthening of family farming has been identified as one of the strategies to reduce social inequalities and improve the quality of life in rural areas. The United Nations (UN) emphasizes the importance of family farming for global food security and its contribution to reducing hunger and poverty. However, the need for innovation and productive diversification emerges as a critical agenda to ensure the economic sustainability of small-scale producers (Zahaikevitch et al., 2022).

The base of the pyramid is predominantly found in developing countries, encompassing both urban and rural areas. Prahalad (2005), in his work *The Fortune at the Bottom of the Pyramid: Eradicating Poverty Through Profits*, addresses the issue of rural communities and argues that poverty is a major challenge to be tackled by businesses and organizations. He highlights the importance of directing efforts toward this neglected segment, recognizing its potential for socioeconomic development.

Cui et al. (2023) emphasize that approximately 698 million people live below the global poverty line, predominantly in rural areas. In these regions, poverty manifests as economic vulnerability and a lack of resilience, making the strengthening of these capacities crucial for achieving rural revitalization and sustainable development. In this context, the promotion of self-development and resilience of rural communities in the face of economic, social, and environmental transformations is imperative.

It is important to note that the rural base of the pyramid is predominantly located in developing regions, characterized by populations with limited access to adequate

infrastructure, markets, and financial services (Cui et al., 2023). According to Villalba et al. (2023), smallholder farmers face challenges such as limited credit availability, high transaction costs, and vulnerability to market fluctuations. Access to appropriate credit is identified as a key factor to improve agricultural efficiency and liquidity; however, many development programs overlook the resources necessary to ensure their long-term viability. Furthermore, studies on Financial Service Agents (FSAs) indicate that a significant portion of these initiatives operate beyond the financial sector, extending into commercial activities, and highlight the need for alternative channels to provide financial services in rural areas, emphasizing low-cost solutions and qualified professionals (Iheanachor et al., 2021).

It is worth recalling that the rural population at the base of the pyramid is also composed of family farmers. Thus, it is highlighted that family farming is responsible for approximately 80% of the food consumed in major urban centers (Zahaikevitch et al., 2022). However, despite its importance, structural challenges persist, such as rural succession and the exodus of young people from rural areas. The intense rural-to-urban migration remains a global concern, as pointed out by the United Nations 2030 Agenda, affecting the continuity of rural communities and the sustainability of family farms. The lack of successors represents a critical challenge to the future viability of family farming (Foguesatto et al., 2020).

Thus, it is believed that a circular business model that adds value to agricultural residues can contribute to income generation and sustainable development in these regions. For instance, Moreira-Dantas et al. (2023) note that although Brazil is a major agro-exporting power, this economic growth does not equitably extend to areas predominantly inhabited by family farmers, who face shortages of inputs, limited market access, and stagnant productivity.

Thus, supporting family farmers through public policies and financial incentives can be a key factor to ensure the success of initiatives based on the circular economy.



In Brazil, the National Program for Strengthening Family Farming (Pronaf) represents the main public policy aimed at providing microcredit and encouraging sustainable production (Pronaf, 2019). According to Coelho de Souza et al. (2023), family farming is characterized by the integration between production and social reproduction, which underscores the importance of policies that consider this dynamic.

It is noteworthy that some regional initiatives have already demonstrated the transformative potential of family farming, such as the Agrotourism Association “Acolhida na Colônia,” the Ecovida Agroecology Network, the National Rural Learning Service (SENAR), and the Slow Food movement. All of these initiatives focus on valuing local and sustainable production and can serve as examples for other global regions (Coelho de Souza et al., 2023).

It is worth highlighting that the history of rural development is intrinsically linked to the pursuit of innovative solutions in the face of resource scarcity and persistent environmental and economic challenges. Rural entrepreneurs have adopted innovative approaches to add value to their production and strengthen the local economy (Hossain et al., 2023a). Hossain et al. (2023) further emphasize the role of community enterprises and informal institutions as catalysts for social transformation. The adoption of innovative technologies and approaches has contributed to expanding access to markets, employment, and essential services in rural areas, thereby promoting the achievement of the Sustainable Development Goals (SDGs).

However, Verger and Le Bars (2024) caution that many studies on food systems still fail to address the real needs of smallholder farmers, as they are often conducted without the direct participation of these stakeholders. The promotion of participatory and sustainable projects that incorporate local knowledge is essential to ensure the effectiveness of proposed solutions and to build resilient family farming systems.

To this end, circular economy initiatives should prioritize mechanisms that actively engage farmers in the design, implementation, and monitoring of solutions. Approaches such as co-design workshops, participatory action research, and community-based pilot projects can serve as effective strategies to involve smallholder farmers as co-creators of innovation. These participatory methods enhance the relevance and acceptance of proposed models, promote knowledge exchange, and strengthen social cohesion (Cavicchi et al., 2022).

In this context, the proposed circular business model directly addresses the challenges faced by smallholder farmers, creating new economic opportunities through the valorization of agricultural residues. By converting banana pseudostems into commercially viable textile fibers, the model reduces dependence on external inputs and enhances land-use efficiency by leveraging already cultivated banana plantations, thus avoiding the need for land-use change or deforestation to support new income-generating activities. It also encourages the development of localized value chains and promotes income diversification. Furthermore, it enables cooperative organization and integration into sustainable value chains, potentially improving

access to markets, financial services, and technological resources.

## 4.2 Circular Economy and Valorization of Banana Crop Residues

The textile and food industries stand out as major sectors responsible for environmental impacts on a global scale. The textile industry, in particular, is characterized by intensive use of natural resources such as water and energy, in addition to requiring large volumes of chemicals used in processes such as dyeing, washing, and fabric finishing. This combination renders textile production one of the most polluting industrial activities today. Furthermore, the improper disposal of textile waste, especially that derived from synthetic fibers, significantly contributes to the release of microplastics into the environment, negatively affecting aquatic and terrestrial ecosystems (Provin et al., 2024; Xu et al., 2020).

Simultaneously, the food industry, especially the tropical fruit agro-industry, generates substantial quantities of organic waste which, if not managed appropriately, constitute significant sources of greenhouse gas emissions and can lead to serious environmental problems such as soil and water contamination, in addition to the loss of biomass with high valorization potential (Provin et al., 2024).

Di Fraia et al. (2024) indicate that global food waste may reach 2.2 billion tons by 2025, highlighting the urgent need to implement sustainable solutions for the valorization of such residues and the promotion of efficient resource use. In this context, the circular economy emerges as a strategic approach to mitigate the environmental impacts of these sectors.

Based on the principles of reduction, reuse, and recycling, the circular economy advocates the creation of regenerative production systems that keep resources in use for the longest possible time and eliminate waste generation whenever feasible. The valorization of residues from banana cultivation represents a promising example of the practical application of these principles, integrating agro-industrial waste into new sustainable production chains. Global banana production, in addition to being significant in volume, also generates substantial amounts of waste. For every ton of harvested bananas, approximately four tons of residues are estimated to be produced, including peels, leaves, roots, and primarily the plant's pseudostem (Abdullah et al., 2023).

Traditionally discarded after harvest, the pseudostem holds significant potential for utilization, particularly for the extraction of natural fibers with textile applications. This reuse represents an opportunity to transform an environmental liability into a productive asset while simultaneously contributing to the reduction of demand for conventional and fossil-based raw materials. Fibers extracted from the banana pseudostem have attracted attention from researchers and industry due to their mechanical and structural properties, which make them suitable for use in sustainable textile products. Numerous studies indicate that these fibers exhibit tensile strength, flexibility, and absorption capacity comparable to or exceeding those of oth-

er commonly used natural fibers such as hemp, flax, and sisal (Pan et al., 2020; Daou et al., 2020).

Moreover, unlike synthetic fibers, banana fibers are biodegradable and renewable, underscoring their suitability for circular production models. The incorporation of these fibers into the textile sector can play a pivotal role in replacing non-biodegradable synthetic fibers such as polyester and nylon, whose production relies on fossil resources and is associated with high carbon emissions. The use of natural banana fibers enables a reduction in the environmental footprint of textile products, as well as a decreased dependence on non-renewable inputs. Additionally, these fibers require less water and energy during processing compared to conventional fibers such as cotton, whose production chain is also associated with significant environmental impacts (Subash & Perumalsamy, 2023).

From a socioeconomic perspective, the valorization of banana cultivation residues for textile purposes can promote the inclusion of small producers and rural communities in sustainable value chains. In banana-producing countries such as Brazil, India, the Philippines, and Ecuador, the establishment of micro and small industries focused on the processing of natural fibers may stimulate regional development by generating employment and income in rural areas. Thus, beyond the direct environmental benefits, this strategy can contribute to the strengthening of local economies and the promotion of more equitable and resilient business models (Shirvanimoghaddam et al., 2020; Pan et al., 2020).

It is worth highlighting that banana plant residues also hold potential for various other industrial applications, such as the production of bioplastics, bioethanol, paper, biodegradable packaging, and other bioproducts. These possibilities broaden the positive impact of valorizing these residues, contributing to economic diversification and the transition toward a circular bioeconomy based on the efficient use of biological resources (Sawarkar et al., 2022).

Despite the significant environmental and socioeconomic potential, the valorization of banana fiber still faces major barriers to scalability. Among the main challenges are the absence of standardized extraction processes, the scarcity of specific machinery for fiber processing, and the lack of structured value chains that effectively integrate these materials into the conventional textile market. Additionally, logistical issues related to the collection, transportation, and storage of biomass are particularly pressing in regions with limited rural infrastructure (Sarangi et al., 2023).

Overcoming these obstacles requires targeted investments in research and development (R&D) focused on improving extraction techniques, enhancing fiber quality, and reducing production costs. The establishment of pilot units and public-private partnerships can significantly contribute to testing technical feasibility and attracting commercial interest. Case studies reveal varying experiences regarding the implementation of such solutions (Sarangi et al., 2023).

In the Philippines, for instance, the company Bananatex® developed a line of fabrics made from banana pseudostem fibers by engaging local cooperatives and promot-

ing high-value-added exports. The material was created by the Swiss bag brand QWSTION, in collaboration with a spinning expert and a weaver, both based in Taiwan. The collaboration among these three actors aimed to generate a positive impact on the planet's future, resulting in a next-generation fabric that is biodegradable in both industrial and marine environments (in compliance with EN 13432 and ISO 14851) and developed according to Cradle to Cradle principles (Bananatex®, 2025).

In contrast, experiences in Latin America, such as in Colombia, face consolidation difficulties due to the lack of continued technical support. According to Montoya Berrio et al. (2024), approximately 70% of banana cultivation output is discarded as waste after harvest, largely due to poor management and underutilization of materials such as the pseudostem, which holds significant potential for fiber extraction. In addition, technical challenges persist in the production and treatment of these fibers, including the definition of appropriate drying parameters (temperature and methods), which are essential to preserve or enhance their mechanical and chemical properties and ensure their viability as a reinforcing material in composites, textiles, and other products.

These variations also underscore the importance of adequate political and institutional frameworks for the success of such initiatives. Public policies play a decisive role in creating a favorable environment for the development of a circular bioeconomy. In Brazil, although there are programs focused on family farming and technological innovation, such as the National Bioeconomy Program (PNB), its implementation still lacks integration with the textile sector and circular economy policies (Brazil, 2024a). Colombia, despite having strategies for both the Circular Economy and the Bioeconomy since 2020, still faces several challenges, as observed in the studies by Montoya Berrio et al. (2024).

Conversely, India and the Philippines have adopted more integrated approaches, featuring tax incentives, targeted financing mechanisms, and technical assistance tailored to the valorization of agricultural residues. Examples include India's National Policy for Management of Crop Residues (NPMCR) and the Philippines' Action Plan for Sustainable Consumption and Production, alongside the National Innovation Agenda. According to Sarangi et al. (2023), well-designed public policies can play a strategic role in enabling the large-scale adoption of circular and bioeconomic solutions. Analyzing these regional disparities helps clarify how political and institutional contexts shape the viability of circular business models based on agro-industrial residues.

#### **4.3 Circular Business Models for the Rural Base of the Pyramid**

The transition to Circular Business Models (CBMs) has emerged as a promising strategy to promote sustainable agriculture practices, particularly within rural communities and among small-scale producers. Traditionally, agricultural residues were incinerated or disposed of in landfills, resulting in air and soil pollution. However, there has been

growing recognition of the potential of these residues as raw materials for high-value-added products such as textile fibers, biofertilizers, biomaterials, and energy sources (Haque et al., 2023; Nesterov et al., 2024).

In this context, CBMs present tangible opportunities for income diversification and social entrepreneurship. In the case of banana cultivation, the conversion of residues into textile fibers represents an innovative alternative that integrates sustainability with value creation in the rural economy (Straub et al., 2023). By fostering the establishment of cooperatives and decentralized production networks, these models enable greater economic independence and resilience for smallholder farmers in the face of market instabilities (Fedele & Formisano, 2023).

The literature further evidences that agroindustrial cooperatives play a significant role in structuring these more sustainable models. They enhance efficiency within the agri-food supply chain, strengthen access to technologies, and encourage collaborative practices and industrial symbiosis, particularly through the sharing of residues among producers and companies aimed at their transformation into new resources (Barros, de Jesus, et al., 2023). This synergy contributes to reinforcing environmental and social sustainability in rural areas.

However, Schiavon et al. (2021) caution that, although most studies and innovations focus on agribusiness and the food industry, initiatives targeting family farming and small rural entrepreneurs remain scarce. In this context, agroecology emerges as a strategic approach, promoting practices that integrate various factors of the agri-food system and seek to overcome the negative impacts of conventional agriculture. The rise of methods such as organic farming, permaculture, and agroforestry reinforces the development of self-sufficient agricultural ecosystems that are more resilient to market transformations.

To support the implementation of circular business models, various tools and frameworks have been proposed, such as Ecocanvas, which incorporates environmental, social, and governance aspects into the business model structure (Daou et al., 2020). Additionally, the integration of Industry 4.0 and innovative technologies can enhance process efficiency, reduce waste, and support the creation of competitive bio-based products. Factors such as logistics, cooperation, geographic proximity, institutional support, and social acceptance are equally critical for the success of these models (Donner et al., 2021).

According to Cavicchi et al. (2022), practical examples such as the use of a high-tech hydroponic system that recovers water and utilizes CO<sub>2</sub> generated by a biogas cogeneration system illustrate how the Circular Economy can be effectively applied. Specifically at the base of the pyramid, notable cases include the Indian company Boond, which provides clean energy and essential services to low-income communities, and Mitticool, a manufacturer of clay refrigerators that operate without electricity, both demonstrating how circular business models can integrate innovation, affordability, and sustainability in rural contexts. Another example is Jayaashree, which develops low-cost biodegradable sanitary pads aimed at women in rural areas, promoting menstrual health, income generation, and

waste reutilization. It is emphasized that these models are considered frugal innovations and demonstrate the viability of inclusive circular solutions at the base of the pyramid (Hossain et al., 2023b; (Sarkar & Mateus, 2022) ; (McPhee et al., 2018).

In terms of metrics, measuring circularity remains a challenge. Although there is no globally accepted standard, evaluation initiatives are based on frameworks encompassing categories such as design, production, use, and end-of-life. Three levels of circularity can be identified: within the rural property, among neighboring properties, and through integration with the agroindustrial cooperative. This approach enables economic gains such as energy consumption reduction and resource reutilization (Barros, de Jesus, et al., 2023).

Silva and Morais (2022) conducted a study with companies in the textile and fashion industry in developing countries that have been adopting different circular business models, classified as Adopters and Holders. The authors observed that while Adopters operate based on linear structures and gradually implement circular strategies, prioritizing low-risk solutions with higher financial returns, Holders are inherently guided by circular economy principles, adopting innovative practices such as upcycling and textile banks. The business models of Holders demonstrate greater integration of economic, social, and environmental criteria, reflecting stronger commitments to circularity. Furthermore, they differ in management profiles: Adopters tend to outsource competencies, whereas Holders invest in internal capacity building and maintain their own infrastructure to support sustainable operations.

Beyond environmental and productive benefits, circular economy practices in agriculture also stand out for their social impact. Food waste reduction, which currently accounts for approximately one-third of total global production, is a strategic priority with the potential to mitigate hunger and significantly reduce greenhouse gas emissions (Scarano et al., 2022). Initiatives that transform waste into new products, such as biogas and textile fibers, also provide employment opportunities for youth and foster the development of green markets (Çaloğlu & Binay, 2023; Koul et al., 2022).

Despite its potential, many small producers and SMEs still face challenges related to access to financing and the necessary technological infrastructure. Cavicchi et al. (2022) emphasize the importance of establishing collaborative networks among companies, public institutions, and investors, aiming to strengthen the economic and technical viability of the circular transition.

Finally, progressing towards an agricultural system based on circularity requires, as a first step, the selection of appropriate approaches for waste conversion, the use of specific machinery or the reutilization of existing compatible equipment, the understanding of end-use applications, and the detailed characterization of raw materials. In this regard, an alignment of technology, knowledge, and cooperation is observed, whereby circular business models become a powerful tool to transform the environmental and social challenges of agriculture into sustainable and innovative opportunities for the sector's future (Haque et al., 2023).



#### 4.4 Benefits and Challenges of Model Implementation

The adoption of agro-industrial residues for sustainable textile production represents a promising opportunity to mitigate the negative impacts of these industries. Ali et al. (2024) highlight the conversion of organic waste into bioplastics as an environmentally viable solution aligned with the principles of the circular bioeconomy. Recent studies indicate that banana fiber may be a viable alternative to reduce dependence on petroleum-derived synthetic fibers, contributing to a more sustainable production system and aligned with circular economy principles (Provin et al., 2024).

Regarding the use of banana cultivation residues for textile production, this approach faces certain technical and commercial challenges. The feasibility and quality of the resulting textile products are affected by the availability, purity, and composition of banana residues, which can vary considerably. To overcome these challenges, comprehensive research is required to address various issues related to this process (Kee et al., 2021).

Chaves et al. (2024) emphasize that the valorization of these residues can drive new sustainable business models and strengthen local economies, particularly in farming communities that rely on the diversification of their income sources. Khan et al. (2024) demonstrate that the processing of banana pseudostems can enable the production of high-quality yarns and fabrics, contributing to the development of a sustainable supply chain. Venkatesh and Kumar (2024) explore the physical properties of fabrics made from banana fiber, highlighting their viability for innovative applications in the textile sector.

However, the production of fibers derived from banana cultivation still faces challenges related to process efficiency and industrial scalability. As noted by Akatwijuka et al. (2022), the techniques currently employed for fiber extraction are relatively costly and may cause negative environmental impacts if not properly managed. Therefore, it is necessary to develop and invest in the adoption of more efficient and environmentally sustainable technologies and machinery. Furthermore, the demand for banana fibers remains limited when compared to other widely used natural fibers, which poses a barrier to their economic viability in large-scale production contexts.

Beyond financial and technical challenges, cultural and market acceptance of products derived from the circular economy represents a critical factor for the success of this approach. It is important to raise awareness among consumers and businesses regarding the environmental and social benefits of adopting sustainable textiles, promoting the value of these products through certifications and awareness campaigns (Korsunova et al., 2022b).

According to Subash and Perumalsamy (2023), banana fibers are durable, biodegradable, and exhibit high tensile strength. Their properties—such as spinnability and structural resilience—make them suitable for fabric production. When properly processed and treated, these fibers can also serve as substitutes for non-biodegradable synthetic

fibers, thereby contributing significantly to the reduction of environmental impact.

However, despite the existence of established concepts, models, and ongoing research, there are still considerable challenges to be addressed. Overcoming regulatory barriers and public policy constraints that hinder the expansion of Circular Business Models (CBMs) requires a logic of scaling. In particular, the deep scaling logic, which aims to transform cultural values and beliefs, is essential for shifting from a traditional, linear, and fast fashion model toward an industry grounded in circular business practices. Despite growing acceptance of circular strategies, challenges such as uncertain market demand, limited knowledge of circularity, and a lack of trust in new collaborative partners continue to impede progress toward greater circularity in the fashion sector (Sandberg & Hultberg, 2021).

In some developing countries, agricultural cooperatives have improved the performance of smallholder farms by facilitating access to new technologies, sustainable practices, and agricultural product marketing. The emphasis on collaboration, knowledge sharing, and inter-cooperation highlights the potential of industrial symbiosis in transforming agricultural waste into valuable resources for various industries. A strong commitment to sustainability, including environmental protection and social development, is a defining characteristic of these cooperatives, promoting responsible business practices and offering solutions to both economic and environmental challenges in rural areas (Barros, Salvador, et al., 2023).

Basu et al. (2021) emphasize that the Base of the Pyramid (BoP) market encompasses billions of low-income consumers in developing countries, who possess limited purchasing power and are often overlooked by companies. Both social and commercial organizations can address this demand not only as a business opportunity but also as a means to contribute to the improvement of these consumers' living conditions. However, engagement in this market must occur responsibly and sustainably, taking into account its cultural, economic, and social specificities.

Within this context, family farming faces challenges in adopting sustainable and circular practices. Among these, the need to develop basic elements to strengthen the domestic market stands out, along with tackling the economic, social, and environmental complexities involved. A holistic model may facilitate a better understanding of the strategic structure and organizational value of sustainable family farming. This model enables the visualization of interactions among various dimensions, such as globalization, technology, and changes in market demand, thereby supporting the coordination of marketing strategies and necessary organizational adaptations (Schiavon et al., 2021).

Cavicchi et al. (2022) underscore the importance of the circular economy for small and medium-sized enterprises (SMEs) in the agricultural sector, particularly concerning the implementation of circular business models. However, the financial feasibility of clean production practices and sustainable agricultural technologies requires economic incentives. Examples such as hydroponic systems that reuse water and utilize CO<sub>2</sub> generated from biogas cogen-

eration illustrate how the circular economy can be efficiently applied. Nevertheless, a lack of financial and technical resources limits many SMEs. Therefore, the establishment of collaborative networks among companies, public institutions, and investors is recommended to strengthen financial and technical capacity and facilitate the adoption of circular innovations.

Finally, despite the challenges in implementing circular practices, such as greenwashing or deceptive marketing strategies claiming sustainability, there are also significant opportunities. The fashion industry, for example, can benefit by adopting a circular approach, enhancing its sustainability and responding to increasing demands for more responsible practices (Tsironis & Tsagarakis, 2023). Hellström and Olsson (2024) point out that while digital technologies may enable innovation, they are not the true drivers of transformation. Rather, consumer centrality is identified as the primary catalyst for transitioning toward circularity, requiring a profound cultural and strategic shift within organizations.

#### 4.5 Bioeconomy, Circularity, and International Regulations

The transition to a more sustainable economic model has become a global priority, and the intersection between the bioeconomy and the circular economy has emerged as a strategic pathway to reduce waste and environmental impact across various sectors, including the textile industry. In this context, both international and national documents have established guidelines to support this transition by promoting the efficient use of renewable resources and encouraging sustainable practices across different productive contexts, including family farming and its integration into more sustainable value chains.

The European Union has developed structured policies to integrate the bioeconomy with the circular economy. The document *A Sustainable Bioeconomy for Europe: Strengthening the Connection between Economy, Society, and the Environment* proposes a holistic approach, promoting the sustainable use of biomass, the development of markets for bio-based products, and sustainable agricultural practices. These actions are directly related to circularity, as they involve converting organic waste into valuable resources and optimizing material flows within closed-loop systems. Public education and participatory governance are also emphasized, recognizing the essential role of stakeholders in shaping sustainable policy frameworks (European Commission, 2018; Dace et al., 2024; WBCSD, 2020).

The Circular Economy Action Plan: *For a Cleaner and More Competitive Europe* complements these initiatives by proposing guidelines for sectors with high environmental impact, such as textiles. It encourages ecodesign, the use of recycled materials, the reduction of hazardous substances, and the extension of product life cycles (European Commission, 2020). The EU Strategy for Sustainable and Circular Textiles reinforces this commitment by establishing concrete targets for 2030, such as increasing the use of recycled fibers, eliminating hazardous substances, and making the separate collection of textiles mandatory

starting in 2025. Mechanisms such as Extended Producer Responsibility (EPR) and fee modulation are intended to promote more circular design models (UN, 2023; Voukkali et al., 2024).

At the national level, European countries have also implemented specific plans. In Portugal, the Action Plan for the Circular Economy (PAEC) identifies the textile sector as a priority, focusing on ecodesign, the valorization of agricultural waste, and the promotion of natural fibers to reduce the environmental impact of the production cycle. The Action Plan for a Sustainable Bioeconomy (PABS) presents ambitious goals, such as replacing fossil-based raw materials with local and renewable alternatives, increasing water and energy use efficiency, and enhancing the value of biological residues through industrial symbiosis (DGAE, 2023; Portugal, 2018).

In Italy, the document BIT II – Bioeconomy in Italy and the report *Economic Instruments for the Circular Economy* reinforce the integration of the bioeconomy into industrial sectors, with particular emphasis on textiles. The focus lies on transforming agricultural waste into higher value-added products, such as fibers and fabrics, and on converting industrial areas into biorefineries. The country is investing in innovation hubs, tax incentives, and public policies to promote circularity and reduce the use of non-renewable resources (Italy, 2019, 2023).

In Brazil, recent developments include the publication of the National Strategies for Bioeconomy and Circular Economy. Decree No. 12.082/2024, dated June 27, 2024, established the National Circular Economy Strategy, aimed at promoting the transition from a linear production model to a circular economy by encouraging the efficient use of natural resources and the adoption of sustainable practices throughout the production chain (Brazil, 2024b). In addition, the country has consolidated its regulatory framework on the circular economy with the adoption of the Brazilian Association of Technical Standards (ABNT) circularity standards approved in 2024, namely: a) ABNT NBR ISO 59004, which establishes vocabulary, principles, and guidelines for implementing the circular economy, offering a common reference for companies and institutions (Abnt, 2024b); b) ABNT NBR ISO 59010, which guides the transition of business models and value networks, facilitating the adoption of circularity across various productive sectors (Abnt, 2024a); and c) ABNT NBR ISO 59020, which defines criteria for measuring and assessing circularity performance, enabling the monitoring and continuous improvement of circular practices.

The implementation of integrated policies demonstrates significant progress toward global sustainability. Initiatives such as Trash-2-Cash and the use of biomaterials like Piñatex® highlight the transformative potential of the circular bioeconomy in the fashion industry. However, the transition still faces challenges, from regulatory barriers to infrastructure needs and technical capacity building, especially in countries with lower levels of industrialization. In this scenario, integrating the circular bioeconomy into family farming represents a strategic opportunity. The use of banana crop residues, such as the pseudostem, for textile fiber production exemplifies the articulation between social

innovation, environmental sustainability, and productive inclusion. The proposed circular business model for smallholder farmers aims to convert environmental liabilities into economic resources, adding value to agro-industrial waste and connecting these producers to sustainable value chains, in alignment with both international and national regulatory frameworks (Subash & Perumalsamy, 2024).

## CONCLUSIONS

This study proposed a Circular Business Model (CBM) focused on the value of banana farming residues, particularly the pseudostem, for sustainable textile production, offering an inclusive strategy to promote circularity in rural contexts. Through an integrative literature review, it identified not only the environmental benefits of reducing agro-industrial waste and synthetic fiber use, but also the socioeconomic potential to diversify income, strengthen family farming, and foster rural development.

The proposed model addresses key challenges at the rural base of the pyramid, including low resilience, lack of access to value chains, and economic marginalization of smallholder farmers. It demonstrates how agricultural residues can become strategic resources within regenerative systems, advancing climate goals and aligning with global and national policy frameworks on the circular bioeconomy.

However, despite its theoretical robustness and alignment with sustainability agendas, the implementation of this model faces significant barriers. Technological challenges include the absence of standardized and scalable fiber extraction methods, high operational costs, and limited availability of processing infrastructure, especially in regions with poor logistics and limited industrial capacity. Economically, market demand for banana fibers remains low, and smallholders often lack the financial instruments and technical support to engage in value-added activities. Culturally, there are still gaps in consumer awareness and acceptance of circular textiles, which may hinder the commercial viability of such initiatives.

In addition, this study is limited by its conceptual nature and reliance on secondary data. While literature offers substantial theoretical insight, empirical validation is necessary to assess the feasibility of the model under real conditions. Regional heterogeneity, in terms of infrastructure, governance, social capital, and institutional support, demands localized, participatory, and adaptive approaches. The transferability of the model to different contexts should not assume uniform conditions or capacities. Instead, future research must address place-based configurations, involving stakeholders through co-creation and experimentation in pilot projects.

Further studies are also needed to investigate mechanisms of cooperation between farmers, cooperatives, textile companies, and public institutions, as well as governance models that ensure fair distribution of value and environmental responsibility. The inclusion of metrics to assess circularity performance, traceability, and socioeconomic impact will be essential to evaluate outcomes and guide scaling strategies. In this sense, innovations that combine technological solutions with social design, such as frugal innovations and community-based business

models, can play a key role.

Ultimately, transitioning from linear to circular production systems requires more than technical solutions. It demands a shift in cultural paradigms, consumer behavior, and institutional logic. The adoption of CBMs in banana farming is not merely a matter of technological feasibility, but of political will, stakeholder alignment, and a commitment to systemic change. By advancing in these directions, the circular valorization of agro-industrial residues can serve as a replicable model for sustainable development, social equity, and environmental regeneration.

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# TRUCK TYRE CHARACTERISATION AND KINETIC MECHANISM STUDY FOR VALUABLE CHEMICALS PRODUCTION

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## ABSTRACT

Waste tyre pyrolysis is a promising strategy for converting end-of-life tyres into valuable chemical feedstocks. This study investigates the thermal degradation behaviour of truck tyre (TT) crumbs and evaluates the selective production of high-value compounds, particularly limonene and indene, under varying pyrolysis conditions. A combined approach employing thermogravimetric analysis, kinetic modelling (both model-free and model-fitting methods), and analytical pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC/MS) was used to elucidate the relationship between temperature, heating rate, and product selectivity. Activation energy estimates ranged from 122 to 145 kJ.mol<sup>-1</sup> across different kinetic models, indicating a multi-step degradation mechanism. The highest limonene selectivity (64.2%) was achieved at 400°C, but this declined to 28.5% at 700°C due to secondary cracking and aromatisation reactions. Additionally, faster heating rates enhanced limonene yield, with selectivity increasing from 30.8% at 20°C/min to 42.7% at 100°C/min. These results highlight the importance of optimising thermal parameters to favour the formation of target chemicals and provide essential kinetic and chemical data for the design of tyre pyrolysis systems focussed on selective product recovery.

## 1. INTRODUCTION

The depletion of natural resources and the need to minimise solid waste in metropolitan areas have necessitated the incorporation of used materials, especially waste tyres (WT), into manufacturing processes to valorise this form of garbage while reducing natural resources. As a result, techniques and recycling methods have been established to use tyres as feedstock for marketable products due to their high calorific value and a significant amount of carbon black. Among several techniques, pyrolysis has emerged as the most appealing for treating WTs (Mwelwa et al., 2023).

Pyrolysis is a feasible method for recovering valuable materials from waste tyre; however, commercial viability remains a challenge (Quek & Balasubramanian, 2012). In response, researchers have extensively studied its kinetics and mechanisms, predominantly using thermogravimetric analysis (TGA) to develop mathematical models that describe the thermal decomposition process. For instance, Williams and Besler (1995) correlated TGA profiles of different tyres with those of three rubber compounds (NR, BR, and SBR), enabling the extraction of kinetic parameters us-

ing Arrhenius-based models. Similarly, Seidelt et al. (2006) identified the main tyre constituents and superposed their DTG curves onto experimental tyre data to validate component-specific kinetics. While these approaches offered valuable insights into thermal degradation, they lacked the resolution to fully capture the chemical complexity of the pyrolysis vapour phase.

Han et al. (2018) used a thermogravimetric analyser in conjunction with a mass spectrometer to further understand the mechanism of WT pyrolysis. They discovered that WT pyrolysis DTG curves featured a bimodal peak between 250 and 500°C, and a modest peak between 600 and 800°C. In addition, the development of gaseous products detected using a mass spectrometer and the functional groups on the surface of the residue char detected with a Fourier-transform infrared (FTIR) spectrometer indicated that tyre pyrolysis could be partitioned into four different stages. The first stage occurred when the temperature was below 320°C, and at this stage, only minor mass was lost due to water vaporisation and plasticiser. The second stage is associated with the weight loss in the temperature range of 320 and 400°C and was attributed to the decom-

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position of natural rubber. The third stage took place when the temperature was between 400 and 520°C and was attributed to the decomposition of synthetic rubber, while the fourth stage started when the temperature was above 520°C and was associated with little weight loss. Using the Master Plots method, Aslan et al. (2017) probed the most appropriate reaction model for waste tyre pyrolysis. Isoconversional methods were used to determine the averaged activation energy of  $162.8 \pm 23.2 \text{ kJ.mol}^{-1}$  throughout a mass fraction conversion interval of 0.20 to 0.80. The reaction order of three was found to describe the pyrolytic decomposition better.

These earlier studies primarily emphasised devolatilisation, with limited focus on the formation of specific compounds. As a result, they offer minimal insight into how operational parameters such as temperature and heating rate influence the yields of target chemicals like limonene or indene, an aspect critical for optimising tyre pyrolysis for chemical and economic viability.

Recent efforts have shifted toward optimising pyrolysis parameters and modelling product-specific kinetics. Ngxangxa (2016) employed the qualitative and quantitative gas chromatography-mass spectrometric (GC-MS) and comprehensive two-dimensional gas chromatography (GC×GC) approaches to identify market-value compounds in tyre-derived oils (TDOs), including dl-limonene, p-cymene, benzothiazole, ethylbenzene, toluene, p-xylene, 3-ethyl toluene and  $\alpha$ -terpinolene. Mkhize et al. (2019) further demonstrated that increasing heating rates influenced the synthesis of isoprene and dl-limonene, with higher rates favouring limonene production. Using the Kissinger method, they estimated activation energies of 133 and 115  $\text{kJ.mol}^{-1}$  for isoprene and dl-limonene, respectively.

More recently, Menares et al. (2020) published a paper on fast WT pyrolysis using quasi-isothermal thermogravimetric analysis, kinetic modelling and an analytical pyrolyser with gas chromatography/mass spectrometry (Py-GC/MS). They found that devolatilisation/condensation and depropagation processes characterise WTs pyrolysis up to 482°C, while cyclisation and aromatisation of primary products create predominantly monoaromatics at higher temperatures. Isoprene (20.5%) and limonene (51%) were the most common chemicals found at temperatures below 500°C. Monoaromatics and gases were formed more readily at higher temperatures (over 600°C), with the equilibrated Diels-Alder reaction governing limonene and isoprene composition. Furthermore, the model-based and isoconversional approaches yielded kinetic parameters in high agreement (101-176  $\text{kJ.mol}^{-1}$ ). These studies highlight the importance of tracking chemical selectivity rather than just mass loss.

Despite the various studies on the thermochemical treatment of WT, data on the tracking of chemical formation remain scarce. Available literature still lacks comprehensive kinetic and mechanistic studies that integrate TGA-based models with Py-GCMS to simultaneously capture thermal and chemical evolution. Particularly scarce are studies that analyse the effect of both temperature and heating rate on the selectivity of key pyrolysis products by simultaneously applying both model-free/model-fitting ki-

netic analysis with chemical-specific Py-GC/MS tracking, as is done in this work.

The present study systematically investigates the pyrolysis behaviour of truck tyre (TT) with the goal of enhancing the selective recovery of valuable chemical compounds, notably limonene and indene. Unlike traditional approaches that primarily monitor devolatilisation behaviour through mass loss data, this study integrates advanced thermogravimetric modelling with dual-mode analytical pyrolysis-gas chromatography/mass spectrometry under both single-shot and EGA modes to assess how temperature and heating rate directly affect the selectivity of the target products. The combined use of model-free and model-fitting kinetic analyses addresses the complexity and multi-step nature of waste tyre pyrolysis. Model-free methods, such as Friedman and Starink, offer conversion-dependent activation energy estimates without the need to assume a specific reaction mechanism, making them robust for heterogeneous reactions. Meanwhile, model-fitting approaches like the Coats-Redfern method facilitate mechanistic interpretation by aligning experimental data with theoretical kinetic models. When coupled with compound-specific Py-GC/MS analysis, which enables precise identification and quantification of key pyrolysis products, this approach provides both thermal and molecular-level insights into reaction pathways. This integrated methodology offers a powerful framework for evaluating the influence of temperature and heating rate on product selectivity, ultimately contributing to improved process optimisation and the potential design of efficient tyre pyrolysis systems geared toward chemical valorisation.

## 2. MATERIALS AND METHODS

### 2.1 Feedstock compositional analysis

Truck Tyre (TT) crumbs samples of particle size less than 1 mm (maximum particle size), obtained from a local tyre recycler and stored in airtight plastic bags, were used for all experiments conducted in this study. The proximate analysis was carried out using a thermogravimetric analyser (TA 60WS, Shimadzu, Japan) and computations using a slightly modified ASTM E 1131-08 (2008). The maximum temperature was set to 800°C to determine the mass loss as temperature increases and nitrogen was used as an inert medium to purge hot volatiles at a low heating rate (10°C/min) before switching to oxygen, the combusting/oxidising medium. The ultimate analysis was conducted using the Leco analyser (SC632, Leco, United States) to evaluate the C, H, N, and S quantities in the analytical TT. For CO<sub>2</sub> and SO<sub>2</sub> formation, a sample of 0.5 mm was combusted into pure O<sub>2</sub>, followed by detection and quantification by infrared detection. The higher heating value of the sample (HHV) was calculated using the Boiés correlation (Han et al., 2017) for polymeric materials and biomass. Finally, the organic compounds in TT crumbs were investigated using a Fourier transformed infra-red (FT-IR) spectrometer (Prestige-21, Shimadzu, Japan) integrated with a platinum attenuated total reflection (ATR) single-reflection module. The samples' spectra were aggregated from 32 scans with a

resolution of 4 cm<sup>-1</sup> in the 400-4000 cm<sup>-1</sup> range, and data were analysed using LabSolutions IR software.

## 2.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was applied to investigate the thermal degradation behaviour of the TT. A tyre crumbs sample of (10±1) mg was used in all tests, with a single repetition. A thermobalance (TA 60WS, Shimadzu, Japan) was used to record weight loss as a function of temperature from 30 to 800°C. Experiments were conducted in triplicate under identical operating conditions, at several heating rates (10, 20, 30, 40 and 50°C/min) and making use of the same carrier gas N<sub>2</sub> (99.99% pure) at the rate of 100 mL/min. The resulting thermogravimetric (TG) and derivative thermogravimetric (DTG) curves from the three runs exhibited similar thermal degradation trends.

## 2.3 Kinetic analysis

The linear mathematical analysis methods allow the estimation of the kinetic parameters such as the activation energy and the pre-exponential factor by establishing linear relationships between the kinetic parameters, using mass loss information collected at multiple devolatilisation rates.

The rate of a solid-state reaction in its most general form is depicted by the following equation:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (1)$$

where  $k$  represents the reaction rate constant,  $f(\alpha)$  the reaction model, and  $\alpha$  the conversion fraction.

The conversion percent at any particular time in isothermal thermogravimetric analysis, given by:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (2)$$

with  $m_0$  the initial sample weight,  $m_t$  the sample weight at time  $t$ , and  $m_\infty$  the final sample weight.

In non-isothermal thermogravimetric analysis, the conversion fraction at a given temperature is:

$$\alpha = \frac{m_0 - m_T}{m_0 - m_\infty} \quad (3)$$

where:  $m_T$  represents the weight of the sample at temperature  $T$ .

The integral rate law is obtained by integrating the above equation Equation (1),

$$g(\alpha) = kt \quad (4)$$

where:  $g(\alpha)$  is the integral model of degradation.

The temperature dependence of the rate constant is described by the following Arrhenius equation,

$$k = Ae^{-E_a/RT} \quad (5)$$

where:  $A$  represents the pre-exponential factor,  $E_a$  the activation energy,  $T$  the absolute temperature, and  $R$  the gas constant.

The substitution of Equation (5) into rate law equations gives,

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT} f(\alpha) \quad (6)$$

And,

$$g(\alpha) = Ae^{-E_a/RT} t \quad (7)$$

The following equation can be used to convert Equations (6) and (7) into non-isothermal rate equations that express reaction rates as a function of temperature at a fixed heating rate:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \cdot \frac{dt}{dT} \quad (8)$$

where:  $da/dT$  is the non-isothermal reaction rate,  $da/dt$  the isothermal reaction rate, and  $dT/dt$  the heating rate ( $\beta$ ).

The differential formulation of the non-isothermal rate law is obtained by substituting Equation (6) into the preceding equation.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E_a/RT} f(\alpha) \quad (9)$$

Upon integration, Equation (9) gives,

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-E_a/RT} dT \quad (10)$$

This study employed both model-free and model-fitting kinetic approaches to rigorously investigate the thermal decomposition behaviour of TT pyrolysis. The adoption of this hybrid methodology lies in the inherent complexity and heterogeneity of waste tyre materials, which undergo multi-phase and multistep decomposition processes involving overlapping primary and secondary reactions. Model-free methods (Friedman, Kissinger, and Starink) were selected for their capability to estimate the apparent activation energy ( $E_a$ ) as a function of conversion ( $\alpha$ ) without requiring a predefined reaction mechanism. This feature makes them particularly well-suited for analysing systems where the reaction pathway is not singular or where multiple overlapping mechanisms occur, as is characteristic of polymeric solid waste pyrolysis.

In contrast, model-fitting methods such as Coats-Redfern and the Differential method require the assumption of a specific reaction model but offer insights into the likely reaction mechanism when the best-fitting model function is identified through statistical criteria (e.g.,  $R^2$ ). The Coats-Redfern method, in particular, is widely used due to its mathematical simplicity and effectiveness in evaluating single-step approximations of complex reactions. The application of the differential method further allows for fine-resolution analysis at discrete temperature intervals, adding robustness to the kinetic interpretation.

Combining these two methodological paradigms ensures a comprehensive kinetic assessment: model-free methods offer mechanistic neutrality and robustness across conversion ranges, while model-fitting approaches facilitate mechanistic hypothesis testing and validation. This multi-method strategy enhances the reliability and interpretive depth of the kinetic parameters derived (Seidelt et al., 2006; Starink, 2003; Vyazovkin et al., 2011). Importantly, this integrated approach provides not only activation energies but also mechanistic insights, which are essential for the design and optimisation of pyrolysis processes aimed at selective recovery of valuable compounds such as limonene and indene.

The direct differential technique employs the differential formulation of the non-isothermal rate law. By considering the logarithm form of the non-isothermal rate law, the general expression of this method is given by Equation (11) below. The activation energy ( $E_a$ ) and pre-exponential fac-

tor ( $k_0$ ) are obtained from the slope of  $\ln d\alpha/dT/f(\alpha)$  versus  $1/T$  (Khawam & Flanagan, 2006).

$$\ln \frac{d\alpha/dT}{f(\alpha)} = \ln \frac{k_0}{\beta} - \frac{E_a}{RT} \quad (11)$$

with  $f(\alpha)$  the reaction model,  $\alpha$  the conversion fraction,  $T$  the temperature,  $\Delta\alpha$  and  $\Delta T$  their respective incremental differences,  $d\alpha/dT$  the non-isothermal reaction rate,  $R$  the gas constant and  $\beta$  the heating rate.

The Coats-Redfern method uses the integral form of the non-isothermal rate law and its approximation. The mathematical assumption of this method corresponds to a zero-order reaction, and its general equation is given by Equation (12) below. The  $E_a$  and  $k_0$  are obtained from the slope of  $\ln g(\alpha)/T^2$  versus  $1/T$  (Coats & Redfern, 1965; Khawam & Flanagan, 2006).

$$\ln \frac{g(\alpha)}{T^2} = \ln \left( \frac{k_0 R}{\beta E_a} \left[ 1 - \left( \frac{2RT_{exp}}{E_a} \right) \right] \right) - \frac{E_a}{RT} \quad (12)$$

where  $g(\alpha)$  represents the integral decomposition model,  $\beta$  the heating rate and  $T_{exp}$  the mean experimental temperature.

The Friedman's isoconversional approach is based on a comparison of tests conducted at various linear heating rates. It works with varying conversion degrees by using the logarithm of conversion rate as a function of inverse temperature (Friedman, 1964; Venkatesh et al., 2013). The mathematical form of this method is given by Equation (13). The Kinetic parameters are obtained from the plot of  $\ln (\beta d\alpha/dt)$  against  $1/T$ , with  $d\alpha/dt$  the isothermal reaction rate.

$$\ln \frac{g(\alpha)}{T^2} = \ln \left( \frac{k_0 R}{\beta E_a} \left[ 1 - \left( \frac{2RT_{exp}}{E_a} \right) \right] \right) - \frac{E_a}{RT} \quad (13)$$

The Kissinger method is based on determining the temperature at the highest devolatilisation rate at different heating rates (Kissinger, 1957). The mathematical form of the Kissinger method is given by Equation (14). In this method,  $E_a$  and  $k_0$  are obtained from the slope of  $\ln (\beta/T_m^2)$  versus  $1/T$ ,  $T_m$  is the temperature at which the maximum rate occurs.

$$\ln \left( \frac{\beta}{T_m^2} \right) = \ln \left( \frac{k_0 R}{f(\alpha)} \right) - \frac{E_a}{RT_m} \quad (14)$$

The Starink's method combines the Flynn-Wall-Ozawa (FWO) and Kissinger-Akira-Sunose (KAS) isoconversional methods into a single expression (Starink, 2003) given by Equation (15). In this expression,  $C_s$  is a constant factor that is irrespective of  $\beta$  and  $T$ . The Starink's activation energy and pre-exponential factor are calculated from the slope of  $\ln (\beta/T^{1.8})$  against  $1/T$ .

$$\ln \left( \frac{\beta}{T^{1.8}} \right) = C_s - 1.0037 \left( \frac{E_a}{RT} \right) \quad (15)$$

## 2.4 Pyrolysis coupled with mass spectrometry (Py-GC/MS)

The pyrolysis was performed in a multi-shot pyrolyser (EGA/PY-3030D, Frontier Laboratories Ltd., Japan) based on a proprietary, high-temperature-resistant ceramic heater with low heat capacity. The system consists of the pyrolyser furnace, which also serves as a thermal desorption unit, and a temperature controller. The multi-shot pyrolyser is coupled with the GC/MS equipment, which comprises a gas chromatograph combined with a mass spectrometer

to separate, categorise and measure sophisticated polymeric materials.

This study used a multi-shot pyrolyser EGA/PY-3030D interfaced with a gas chromatograph (GC-2010 Plus, Shimadzu, Japan) with the AOC-201 auto-injector, fitted with a MS detector (QP 2010 Ultra, Shimadzu, Japan). In all the tests, the interface line remained fixed at 250°C, and the volatile compounds were carried out of the pyrolysis reactor using a regular air flow of 54.1 mL/min.  $1 \pm 02$  mg of TT sample were loaded into a sample holder (Frontier Laboratories Eco-cup SF, 50  $\mu$ L) and inserted into the oven using an auto-shot sampler.

The products of pyrolysis (1:50 split ratio) were isolated in a Zebron capillary GC column (ZB-5MS) of 30 m length, 0.25 mm internal diameter and 0.25  $\mu$ m film thickness, and were analysed in a mass spectrometer sensor (70 eV ionisation) in the  $m/z$  range of 30-800. The carrier gas was made up of 99.99% pure helium.

Two separate analytical procedures were applied, namely single-shot and evolved gas analysis (EGA). The single-shot experiments have been conducted to investigate the effect of temperature on the chemical production and, therefore, determine the optimal pyrolysis temperature. Based on data from the thermogravimetric analysis, tests were carried out at various temperatures (400, 500, 600, and 700°C). Chromatograms were analysed regarding the peak area% of two marketable chemicals, i.e., limonene and indene. The EGA experiments, however, have been conducted at various heating rates considered in the kinetics study (10, 20, 30, 40 and 50°C /min) to investigate the effect of heating rate at the optimal temperature. A difference in split ratios (96 for single-shot vs. 50 for EGA) was used to balance signal intensity and resolution. A lower split ratio in EGA mode ensures sufficient detection sensitivity over extended heating rate ranges, while a higher split ratio in single-shot mode prevents detector saturation at higher analyte concentrations during fixed-temperature runs. All analyses were performed in triplicate to confirm the reproducibility of the chemical composition profiles. The chromatographic profiles obtained from the replicate runs displayed consistent retention times and relative peak intensities for major compounds.

Product quantification was carried out on a relative basis from the total ion chromatograms (TIC) obtained by the Py-GC/MS system. Compounds were identified through the National Institute of Standards and Technology (NIST) library matching and confirmed by characteristic retention times.

The data from the Py-GC/MS analysis were analysed using the selectivity to a specific species  $S_i$ , defined as the proportion of an  $i$ th- chromatographic compound's peak ( $PArea_i$ ) to the aggregate of all detected peak areas ( $\Sigma PArea_i$ ) and given by Equation (16). Additionally, the factor  $\xi_{a-b}$  was employed to assess the relative production of relevant compounds, Equation (17) (Menares et al., 2020).

$$S_i = 100 \times \left( PArea_i / \sum_{i=1}^n PArea_i \right) \quad (16)$$

$$\xi_{a-b} = (S_a/S_b) \quad (17)$$



With:

$S_p$ , the selectivity to a specific specie or compound ,  
 $PArea_p$ , the chromatographic peak of an ith compound,  
 $\sum_{i=1}^n PArea_i$  the aggregate of all detected peak areas,  
 $\xi_{a-b}$ , a quantifier of a and b compounds relative formation  
a, b, the produced compounds such as limonene, etc.

### 3. RESULTS AND DISCUSSION

#### 3.1 Compositional characterisation

The process of tyre decomposition and the final composition of the volatile products from tyre pyrolysis are affected by waste tyre properties or composition. These components are identified via proximate and ultimate investigations that allow for the estimation of the pyrolysis opportunities of WTs. Table 1 summarises the proximate and ultimate analysis data.

The reported high content of volatile matter (60.8%) indicates that the studied material is pyrolysable. The results in Table 1 are consistent with many of those previously published on waste tyres, which range from 58 to 66% for the volatile matter, 27.5 to 32% for the fixed carbon and 4.2 to 5.4% for the ash content (Iwarere & Mkhize, 2019; Li et al., 2004; Menares et al., 2020; Roy & Unsworth, 1989; Tsipa et al., 2024). The high carbon content of the investigated material indicates that it is a promising source of energy, whether through direct combustion or as a raw material for the generation of liquid fuels. The estimated higher heating value (HHV) matched that reported by previous research (Li et al., 2004; Menares et al., 2020).

The FTIR spectrum of the sample (Figure 1) presented two characteristic bands at 2915 and 2846  $\text{cm}^{-1}$ , which are commonly linked to -CH- asymmetric stretching vibrations of -CH<sub>3</sub> and -CH<sub>2</sub>- chemical groups and, to the -C-H symmetric stretching vibrations of the same chemical groups. Nunes et al. (2008) associated the two bands to be characteristic of the spectrum of natural rubber. Besides the two bands, three other characteristic vibrational signals were observed at around 1537, 1438 and 1373  $\text{cm}^{-1}$ . These

**TABLE 1:** Waste truck tyre compositional analysis.

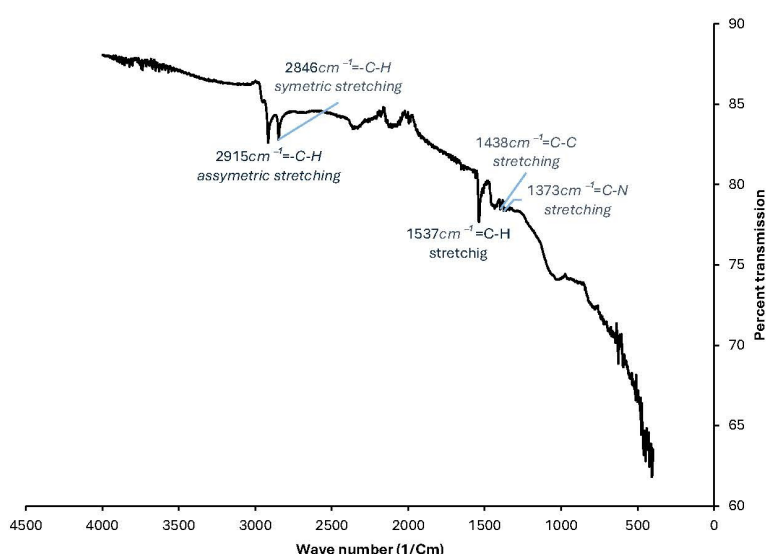
| Proximate analysis (wt.%) |       | Standard deviation ( $\sigma$ ) |
|---------------------------|-------|---------------------------------|
| Moisture                  | 3,4   | 0.17                            |
| Volatile Matter           | 60,8  | 3.04                            |
| Fixed Carbon              | 31,8  | 1.59                            |
| Ash                       | 5,3   | 0.27                            |
| HHV (MJ/kg)               | 34,12 | 1.71                            |
| Ultimate Analysis (wt.%)  |       | Standard deviation ( $\sigma$ ) |
| C                         | 77,9  | 3.90                            |
| H                         | 6,6   | 0.33                            |
| N                         | 0,5   | 0.03                            |
| S                         | 2,8   | 0.14                            |
| O                         | 6,8   | 0.34                            |

absorbance peaks respectively showed the stretching of C-H, C-C and C-N functional groups, related to the Synthetic rubber (SBR and BR) (Khan et al., 2017, Nunes et al., 2018).

#### 3.2 Thermogravimetric analysis (TGA)

The profiles of the thermogravimetric analysis based on the pyrolysis temperature at five heating rates are illustrated in Figure 2.a. It is observed from Figure 2.a that although the mass loss of TT appears to begin at about 200°C, the rate of mass loss stays modest until 300°C, when the tyre devolatilisation becomes considerably more rapid until the final temperatures are reached. The final or terminal temperature is illustrated by graphs appearing to reach a plateau at various heating rates and estimated at 500-600°C for the experimental tyre.

The thermogravimetric profiles reveal that irrespective of the heating rate, the shapes converge to the same solid residual value at the end of pyrolysis. The stated char values are the aggregate of the fixed carbon and ash contents observed during proximate analysis and are based on an



**FIGURE 1:** Truck tyre FTIR spectrum.

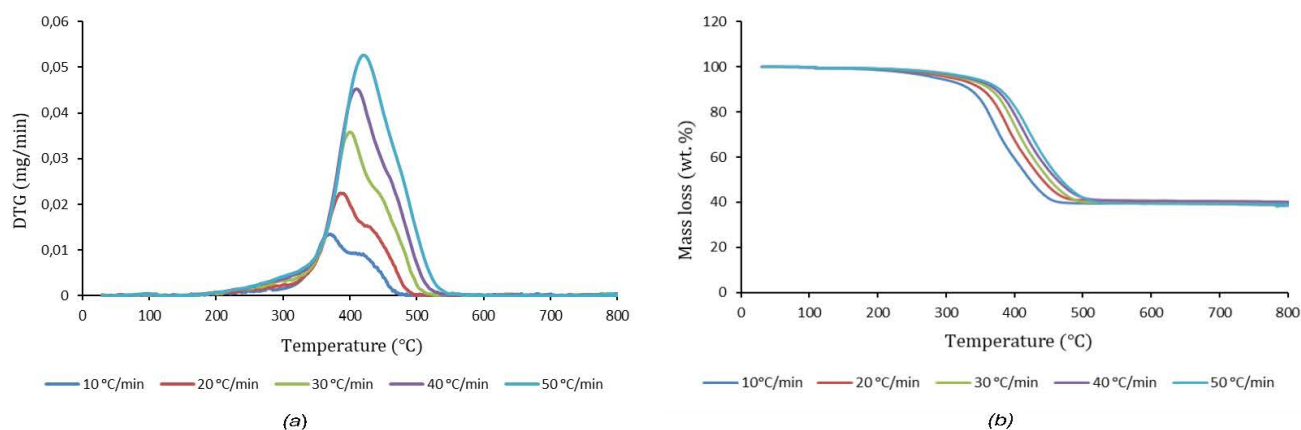


FIGURE 2: a. TGA and b. DTG curves derived from the thermogravimetric analysis of TT.

average of all the heating rates (10 to 50°C/min). The observed char residual, 38.7 wt.%, is comparable to the previously reported work (Menaes et al., 2020).

The DTG profile at heating rate  $\beta=20^\circ\text{C/min}$  illustrated in Figure 2.b, presents a prominent devolatilisation peak around 378,9°C associated with the thermal breakdown of NR via  $\beta$ -scission, and a shoulder at 433,7°C associated with SBR decomposition and styrene evolution; which are comparable to those reported in previous work at the similar heating rate (Menaes et al., 2020). These two peaks have long been thought to be characteristic of polyisoprene rubbers (Danon & Görgens, 2015). When the heating rate increases, the prominent peak increases while the shoulder disappears. This phenomenon has been linked to the reduction of second reactions at higher heating rates with a promotion of the rubbers' devolatilisation (Danon et al., 2015). Devolatilisation/condensation reactions at moderate temperatures are more likely to produce condensation compounds, which then fragment and reorganise to produce pyrolysis products, according to several studies (Mkhize et al., 2016; Xu et al., 2018). Furthermore, at lower temperatures, the primary devolatilisation peak has been

linked to the decomposition of polyisoprene and, to less extent, styrene-butadiene rubber. Hence, some alkenes such as limonene are abundant in the pyrolysis of hot volatiles at these lower temperatures (363.35°C at 10°C/min to 424.6°C at 50°C/min) (Danon et al., 2015; Mkhize et al., 2016).

The relationship between the heating rate and the devolatilisation reaction progress is depicted in Figure 3. The influence of the heating rate on the devolatilisation peak temperature is evidenced by a rise of temperature linked with the maximum devolatilisation rate as the heating rate rises.

### 3.3 Kinetic analysis

#### 3.3.1 Model-free methods

The Friedman, Kissinger and Starink's methods were the model-free methods used to calculate the activation energy and pre-exponential factor. Linear regression graphs for these methods are plotted using Equations (13), (14) and (15), and their linear graphs are shown in Figures 4.a., c. and d., respectively.

The Friedman linear plots, represented in Figure 4, have an identical gradient, therefore the estimated activation en-

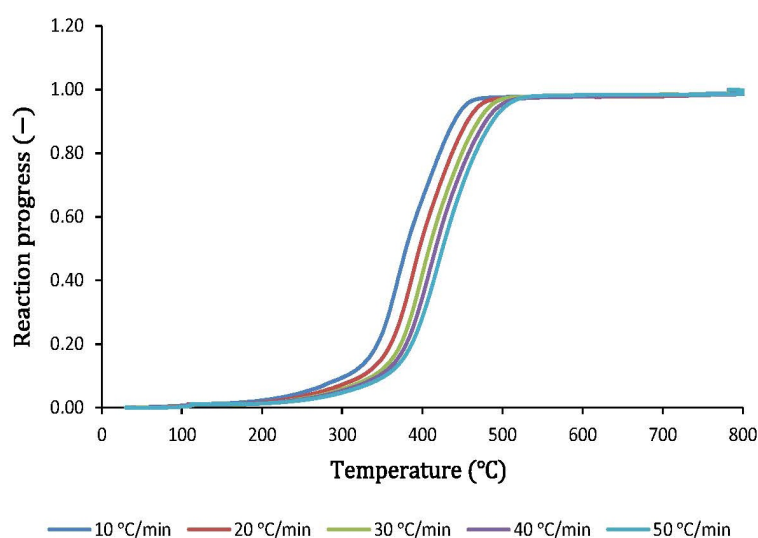


FIGURE 3: Reaction progress of the waste truck tyre.

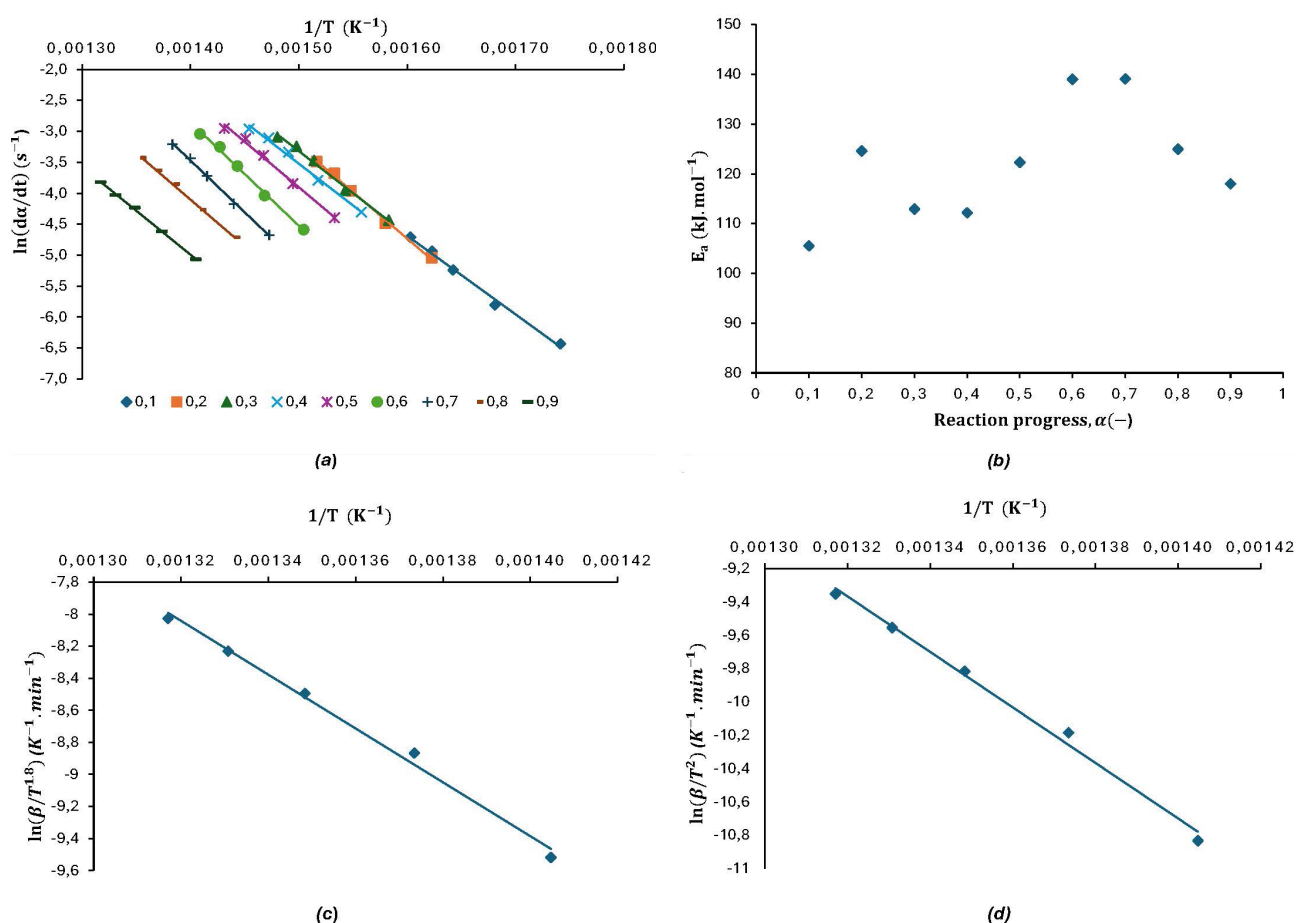
ergy is irrespective of the reaction progress. Figure 5 presents the activation energies at various conversion rates, calculated from the gradient of different plots. Two sets of linear plots have been identified for the experimental TT, i.e., the first set from reaction progress of 0.1 to 0.4 with a maximum peak at reaction progress of 0.2 and the second set from reaction progress of 0.4 to 0.9 with the maximum peak at reaction progress of 0.7. As a result, the activation energy ( $E_a$ ) as a measure of the reaction progress ( $\alpha$ ) reaches a maximum value of  $139.04 \text{ kJ.mol}^{-1}$  at reaction progress of 0.7. Iwarere and Mkhize (2019) also reported a maximum peak at reaction progress of 0.7 for truck tyres, with a similar estimation approach. Values of  $E_a$  obtained in the present study by the isoconversional Friedman method ranged from  $105.5$  to  $139.04 \text{ kJ.mol}^{-1}$  with an average estimated at  $122.0 \text{ kJ.mol}^{-1}$ . The pre-exponential factor ( $k_0$ ) also presents a similar trend with an average  $k_0$  estimated at  $2\text{E}+08 \text{ s}^{-1}$ .

The two peaks identified on the  $E_a$  vs  $\alpha$  profile are associated to two pyrolysis process regions. The first region, between  $343^\circ\text{C}$  and  $386^\circ\text{C}$  is associated with the devolatilisation/condensation of NR and SBR. The allylic poly-isoprene molecules undergo depropagation and intramolecular cyclisation-scission in this zone, generating isoprene and limonene as hinted by Mkhize et al. (2016). The second region, between  $392$  and  $437^\circ\text{C}$ , could be linked to the scis-

sion and dehydrogenation of the SBR, which results in the synthesis of styrene and butadiene monomers. Menares et al. (2020) also reported the presence of two significant regions at  $358\text{--}382^\circ\text{C}$  and  $387\text{--}433^\circ\text{C}$  respectively.

The Kissinger method uses an integrated approach to determine activation energy ( $E_a$ ) and pre-exponential factor ( $k_0$ ). The  $E_a$  estimated using the Kissinger plots was  $138.5 \text{ kJ.mol}^{-1}$  with a pre-exponential factor of  $3\text{E}+05 \text{ s}^{-1}$ . A difference between the  $E_a$  calculated from the Friedman method (average), and the Kissinger method is around  $16.5 \text{ kJ.mol}^{-1}$ . However, the value of  $E_a$  obtained with the present method is comparable to the maximum value of  $E_a$  estimated with the Friedman method at around  $0.5$  units of difference. The appearance of the shoulder on the profiles of the first derivative, which disappears as the heating rate rises, could explain the disparity in activation energy values. The absorption of the shoulder to the prominent peak affects the estimation of the  $E_a$ . In addition, the pre-exponential coefficient in the Friedman approach was shown to be greater than in the Kissinger approach.

Similar to the Kissinger method, Starink's method integrates into a single equation two iso-conversional techniques, i.e., the FWO and the KAS techniques. The estimated values of  $E_a$  and  $k_0$  using this method, were  $139.7 \text{ kJ.mol}^{-1}$  and  $1\text{E}+06 \text{ s}^{-1}$ , respectively. The obtained  $E_a$  value falls in the range of those obtained by Menares et al. (2020)



**FIGURE 4:** Model-free methods: a. Friedman method linear plots, b. Friedman activation energy vs reaction, c. Kissinger method linear plot, and d. Starink's method linear plot.



using a similar method. They reported values of  $E_a$  ranging from  $101.5 \pm 2$  to  $176.7 \pm 2$  kJ.mol<sup>-1</sup>. The maximum values of  $E_a$  estimated with the model-free methods have slight differences, with the highest value obtained with Starink's approach. The same technique presented the highest pre-exponential factor.

### 3.3.2 Model-based methods

Two conventional methods, namely the direct differential and the Coats-Redfern methods, were used for five distinct heating rates (10, 20, 30, 40 and 50°C/min). For  $E_a$  and  $k_0$  estimation, we fitted ten models in the two calculation methods. The used models were the first order (F1), the second-order (F2), the first diffusion (D1), the second diffusion (D2), the power law (P2), the power law (P3), the Avrami-Erofyev (A2) and (A3), the Prout-Tompkins (B1) and the contracting area (R2) models. For each method, the best-fitting model used to evaluate the kinetic parameters has a greater coefficient of determination  $R^2$ . The linear plots of the considered models for the two methods at 20°C/min are presented in Figures 5.a and b.

The  $E_a$  and  $K_0$  were estimated for each considered model, and among all the considered models, the second-order and first diffusion models were considered the best fitting for respectively the Coats-Redfern (C&R) and differential method (Diff.), based on the higher coefficient determination  $R^2$  of 0.98 and 0.99, respectively. While the D2 and F2 models showed the best statistical fit based on  $R^2$  values, we acknowledge that pyrolysis is a multi-step and heterogeneous process involving overlapping reactions such as depolymerisation, cyclisation, and aromatisation. Therefore, the identified models should be viewed as approximations capturing dominant mechanisms under the tested conditions, not comprehensive descriptors of the entire process.

Using the differential method,  $E_a$  was estimated at 144.4 kJ.mol<sup>-1</sup> while 128.3 kJ.mol<sup>-1</sup> was found for Coats-Redfern approach. The respective pre-exponential factors  $k_0$  were  $1.6E+10$  s<sup>-1</sup> and  $2.8E+03$  s<sup>-1</sup>.

A comparison of different activation energies estimated at various heating rates reveals an increase in activation energy as the heating rate rises. A similar trend was observed for the pre-exponential factor  $k_0$  that tended to

increase with the increase in the heating rate. These results are in good correlation with those reported by Leung and Wang (1998) while conducting a kinetic analysis of WT pyrolysis. The average  $E_a$  has been estimated respectively at 144.41 kJ.mol<sup>-1</sup> and 130.60 kJ.mol<sup>-1</sup> for the Differential method and the Coats-Redfern method. The respective obtained pre-exponential factor is  $1.9E+10$  s<sup>-1</sup> and  $3.7E+03$  s<sup>-1</sup>.

To assess the robustness and reliability of the derived kinetic parameters, each kinetic model applied in this study was subjected to linear regression analysis. The linear plots used to estimate activation energy from  $\ln(g(\alpha)/T^2)$  versus  $1/T$  (Coats-Redfern), or  $\ln(\beta/T^2)$  versus  $1/T$  (Kissinger, Starink), demonstrated excellent linearity, with correlation coefficients ( $R^2$ ) consistently exceeding 0.95. These high  $R^2$  values indicate a strong statistical fit between the experimental data and the kinetic model assumptions, validating the appropriateness of the chosen models for describing the pyrolysis of TT. In addition to  $R^2$  evaluation, the standard deviations of the calculated activation energies were estimated from the slope errors of the linear regressions. This provided a quantitative measure of variability and uncertainty associated with the  $E_a$  values obtained. These deviations ranged from  $\pm 3.2$  to  $\pm 6.7$  kJ.mol<sup>-1</sup>, depending on the method used and the temperature interval considered. The relatively narrow error bands confirm that the reported activation energies are statistically significant and reproducible within the experimental design.

The different activation energies and pre-exponential factors estimated with the five considered approaches are summarised in Table 2.

The differential method provided the highest activation energy with a difference of about five units within the two model-free approaches of Kissinger and Starink. Friedman's and Coats-Redfern methods present the lower activation energy values with a significant difference of about 22 and 16 with the differential method. The estimated values of  $E_a$  derived from this study range between 122 and 145 kJ.mol<sup>-1</sup>, depending on the kinetic method applied. These values are in strong agreement with those reported in the literature for waste tyre pyrolysis. For instance, Menares et al. (2020) reported  $E_a$  values between 101 and 176 kJ.mol<sup>-1</sup> for fast pyrolysis of ground waste tyres, while Seidelt et al. (2006) Danon et al. (2015) report-

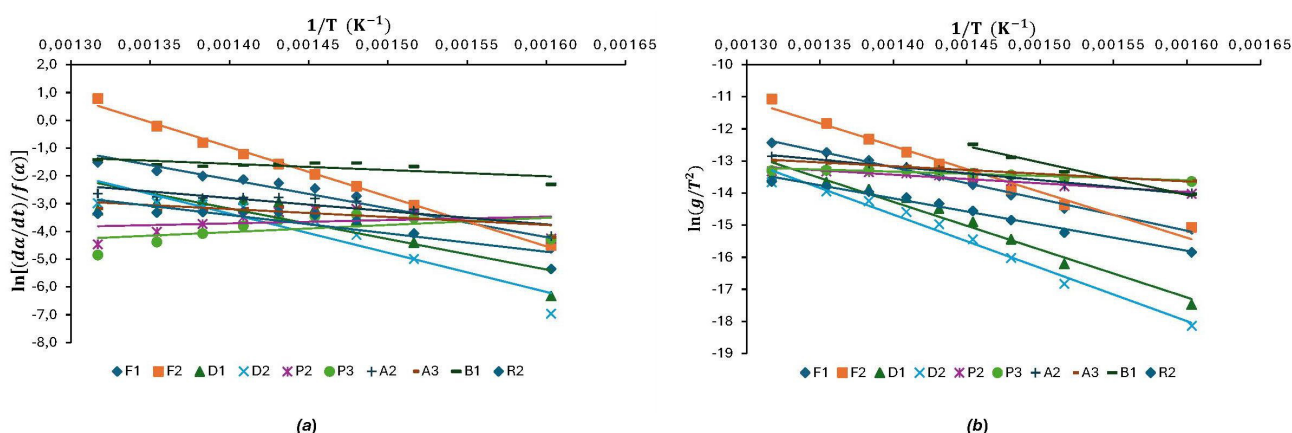


FIGURE 5: Model-based methods: a. Differential method linear plots and b. Coats-Redfern method linear plots.

**TABLE 2:** Kinetic parameters obtained with different methods.

| Methods       | E <sub>a</sub> (kJ.mol <sup>-1</sup> ) | k <sub>0</sub> (s <sup>-1</sup> ) |
|---------------|----------------------------------------|-----------------------------------|
| Friedman      | 122.00                                 | 1.9E+08                           |
| Kissinger     | 138.46                                 | 3.0E+05                           |
| Starink       | 139.68                                 | 1.4E+06                           |
| Differential  | 144.41                                 | 1.9E+10                           |
| Coats-Redfern | 130.60                                 | 3.7E+03                           |

ed ranges of 143 to 254 kJ.mol<sup>-1</sup> and 80 to 434 kJ.mol<sup>-1</sup> respectively, depending on the heating rate and analytical technique. This consistency underscores the reliability and reproducibility of the kinetic data generated in this study, despite variations in experimental conditions and analytical models.

Notably, the highest E<sub>a</sub> value obtained from the differential method (144 kJ.mol<sup>-1</sup>), consistent with its sensitivity to early-stage decomposition, closely aligns with the maximum activation energies calculated via the model-free methods, particularly Kissinger and Starink, thereby demonstrating methodological convergence and internal robustness. The slight deviations observed among different methods are expected due to their inherent mathematical formulations and assumptions. Model-free methods estimate apparent activation energies across the full range of conversion without assuming a reaction model, while model-fitting techniques interpret data based on specific mechanistic functions.

Additionally, the variation in E<sub>a</sub> values is also influenced by the complex composition of the feedstock. Truck tyres, like most commercial tyres, consist of a heterogeneous mixture of NR, SBR, carbon black, plasticisers, sulphur, and metallic additives. Each of these components decomposes over distinct temperature ranges and via different mechanisms, leading to overlapping thermal processes. This multicomponent nature results in broader activation energy distributions and can shift the average E<sub>a</sub> evaluation depending on whether devolatilisation is dominated by NR, SBR, or secondary crosslink breakdown. These lower activation energies obtained in this study indicate that the process requires less energy and, therefore, does not necessarily require a catalyst for its completion.

### 3.4 Py-GC/MS

To match the TGA data and kinetic observations with the potential reaction pathways occurring in truck tyre pyrolysis, various Py-GC/MS tests were conducted. WTs pyrolysis is a technique with unique characteristics in terms of products distribution. Some variables, such as the heating rate and, most significantly, the reaction temperature, are critical in determining transport restrictions and reaction kinetics. To improve the selectivity of specific marketable chemicals, a detailed evaluation of WT pyrolysis variables is necessary.

#### 3.4.1 Compound identification

The most abundant compounds identified among several chemicals from the TT pyrolysis are gases (alkanes, alkenes, CO<sub>x</sub> and H<sub>2</sub>), cyclic hydrocarbons (Cyclo-butene,

cyclo-propane, limonene, isoprene and indene) and aromatics (xylene, benzene, and styrene). Aromatics are generated after a significant conversion cyclic compounds through aromatisation and hydrogenation, as observed by Ding et al. (2016).

From all the experiments conducted at different temperatures (400-700°C), two peaks were identified and are associated with isoprene and limonene. These two chemicals have a cumulative peak-based selectivity of about 40% below 600°C, which declines at temperatures of 600°C and above. The significant cumulative selectivity below 600°C indicates that only minor cyclisation and aromatisation reactions occur in condensed molecules. The increase in temperature to 500°C and above led to the peak-based selectivity of benzene, toluene, xylene, styrene, and indene to increase from about 6% to 12% at 700°C. According to the findings, temperature emerges as the most important factor in the pyrolysis of truck tyres and dictates the kinetics and product distribution.

#### 3.4.2 Temperature influence on chemical production

As observed in previous research, temperature is a major operating parameter in WT pyrolysis (Ding et al., 2015; Menares et al., 2020; Xu et al., 2018). This research examines two chemicals derived from TT during Py-GC/MS experiments and involves tests conducted at various temperatures. Figure 6 presents the temperature effect on the selectivity of significant chemicals.

The selectivity to limonene (S) appeared to continuously decay with the increase in temperature up to a minimum selectivity of 28.5% at 700°C. In contrast, the selectivity to indene (tends to be constant at 500 and 600°C (Table 3). The latter has been only detected at temperatures of 500 and 600°C, and the temperature has no major influence on the productivity of this compound in the considered range of temperatures. These results on indene productivity agree with those obtained by Li et al. (2004), who observed an increase in indene productivity at around 500°C before it tends to decrease at higher temperatures. However, the transition of limonene to alkenes under 600°C and the conversion of a fraction of limonene into monocyclic aromatics such as benzene, toluene and xylene can justify the drop in the selectivity to limonene. Isoprene, one of the significant compounds detected, shows a maximum at around 500°C. Therefore, 500°C emerged as optimal temperature. To better characterise the product distribution, a semi-quantitative analysis of the key compounds using normalised peak area integration of the Py-GC/MS chromatogram obtained at 500 , showed that limonene was the dominant compound, representing 49.9% of the total detected peak areas. Isoprene (37.6%) was the second most abundant. Indene (0.2%), toluene (3.0%), and styrene (4.2%) were also detected in smaller proportions, indicating secondary cracking and aromatisation reactions.

Several researchers have evidenced that isoprene and limonene are synthesised from natural rubber, via a sequence of β-scission and depropagation processes of NR and intramolecular cyclisation and scission of monomeric isoprene, respectively. Limonene is also synthesised from isoprene at higher temperatures through Diels-Alder re-

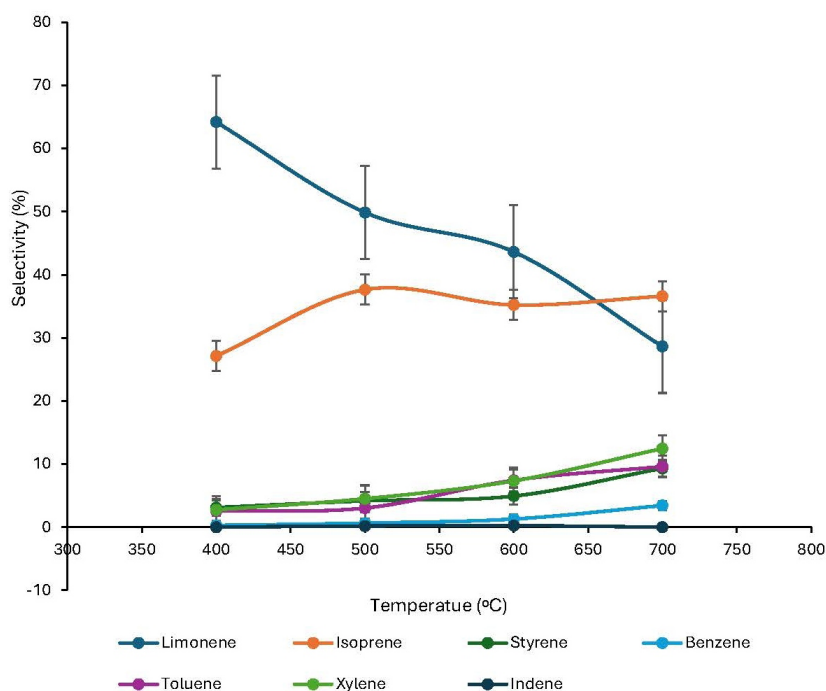


FIGURE 6: Selectivity to important compounds.

actions (Mkhize et al., 2016; Xu et al., 2018). On the other side, Doddipatla et al. (2021) proved that indene is formed via a bimolecular reaction involving the simplest organic radical methylidyne (CH) and styrene (C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>H<sub>5</sub>) through the hitherto elusive methylidyne addition, cyclisation and aromatisation.

The relative formation of limonene to isoprene ( $\xi_{i-i}$  or  $S_i/S_s$ ) and indene to styrene ( $\xi_{i-s}$  or  $S_i/S_s$ ) have been estimated and tend to be constant and graphically present a plateau between 500 and 600°C with respective values of (0.4-0.5) and (1.3-1.2), as shown in Figure 7. Although full peak deconvolution was constrained by instrumental sensitivity and spectral overlap, compound identification was achieved using a combination of retention time matching, Kovats retention indices, and spectral correlation with a mass spectral library. This approach, while semi-quantitative, allowed identification of the dominant pyro-products and enabled selectivity trend analysis across the tested temperature range.

The formation of limonene, a key target compound due to its industrial relevance as a monoterpene solvent and fuel additive, is mechanically attributed to the intramolecular cyclisation of isoprene radicals. These radicals are derived from the depolymerisation and  $\beta$ -scission of polyisoprene chains in NR, particularly under moderate heating conditions (400-500°C). This pathway is supported by a previous study by Mkhize et al. (2016) and is consistent with the prevalence of limonene observed at lower pyrolysis temperatures. However, at higher temperatures (>600°C), a significant decline in limonene selectivity ratio to isoprene (up to 0.7 at 70°C) was noted. This behaviour is attributed to secondary thermal transformations, including Diels-Alder rearrangements, dehydrogenation, and cracking reactions, which convert limonene into monoaromatic hydrocarbons such as toluene, xylene, and styrene. Xu et al. (2018) and Menares et al. (2020) have reported similar findings, demonstrating that limonene acts as a thermally labile intermediate whose ring structure opens or rearrang-

TABLE 3: Peak areas and selectivity of main compounds.

| Compounds  | Peak areas (%) |       |       |       | Selectivity (%) |      |      |      |
|------------|----------------|-------|-------|-------|-----------------|------|------|------|
| Temp. (°C) | 400            | 500   | 600   | 700   | 400             | 500  | 600  | 700  |
| Isoprene   | 10.21          | 16.81 | 13.52 | 11.67 | 27.1            | 37.6 | 35.2 | 36.6 |
| Limonene   | 24.17          | 22.28 | 16.75 | 9.13  | 64.2            | 49.9 | 43.6 | 28.6 |
| Styrene    | 1.17           | 1.86  | 1.89  | 2.97  | 3.1             | 4.2  | 4.9  | 9.3  |
| Benzene    | 0.1            | 0.28  | 0.49  | 1.09  | 0.3             | 0.6  | 1.3  | 3.4  |
| Toluene    | 0.97           | 1.35  | 2.85  | 3.06  | 2.6             | 3.0  | 7.4  | 9.6  |
| Xylene     | 1.03           | 2.01  | 2.81  | 3.97  | 2.7             | 4.5  | 7.3  | 12.4 |
| Indene     |                | 0.08  | 0.09  |       | 0.0             | 0.2  | 0.2  | 0.0  |
| Total      | 37.65          | 44.67 | 38.4  | 31.89 | 100             | 100  | 100  | 100  |



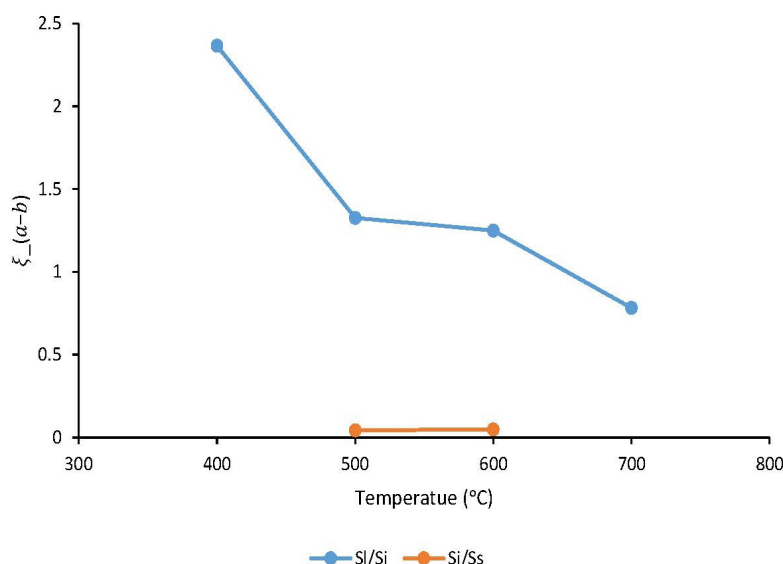


FIGURE 7: Relative formation of important compounds.

es under severe thermal steps, favouring aromatisation pathways.

Furthermore, the enhanced presence of monoaromatics and light hydrocarbons in the high-temperature chromatograms provides strong evidence of secondary degradation reactions, including the cracking of heavier terpenes and recombination of smaller radicals. These reactions shift the product spectrum from oxygenated or cyclic compounds to thermodynamically favoured aromatics and gases, aligning with the thermochemical principles of pyrolysis under kinetic versus thermodynamic control.

### 3.4.3 Heating rate influence on chemical influence

In a series of Evolved Gas Analysis experiments, the heating rate was varied from 20 to 50°C/min and 100°C/min at the obtained optimal temperature of 500°C.

The heating rate was found to have an influence on WT's pyrolysis kinetic parameters by increasing the activation energy and pre-exponential coefficient with an increase in the heating rate (Leung & Wang, 1998). Moreover, Mkhize et al. (2019) evidenced the effect of heating rate on isoprene and dl-limonene production. They reported that the reaction progress at peak dl-limonene increased as the heating rate was raised to higher values, up to 100°C/min. In this study, the heating rate has been increased and varied from 20 to 50°C/min, then 100°C/min for trend verification and confirmation. Figure 8 presents the selectivity to limonene formation at various heating rates.

The selectivity to limonene increases with the rise of heating rate, from around 30.8% at 20°C/min to 37.8% at 50°C/min. To confirm the observed trend, an experiment at a greater heating rate, i.e., 100°C/min, has been conducted and the selectivity to limonene continues to rise with the rise of heating rate values. Therefore, the heating rate plays a major role in the WT's pyrolysis for the formation of valuable products. From the above observations, limonene formation is favoured by high heating rates, as stated by Mkhize et al. (2019). The enhancement of limonene selectivity

at higher heating rates can be attributed to two synergistic effects. First, rapid heating limits the residence time of primary volatile species in the hot zone, thereby suppressing secondary cracking and aromatisation reactions that typically degrade monoterpenes such as limonene into smaller or more stable aromatic compounds. Second, high heating rates accelerate the fragmentation of polyisoprene chains in natural rubber, increasing the formation of isoprene radicals. These radicals undergo intramolecular cyclisation to form Limonene through a gas-phase mechanism, a process favoured kinetically under rapid thermal ramping conditions.

When benchmarked against recent studies, the limonene selectivity of 49.9% (peak-area) achieved in this work at 500°C is among the highest reported for thermal pyrolysis without added catalysts, while the 0.2% indene selectivity reflects its lower abundance but confirmed presence in the vapour-phase product spectrum. Menares et al. (2020) reported a comparable limonene peak area of ~51% at < 500°C using quasi-isothermal Py-GC/MS, though indene was not quantified. In fixed-bed pyrolysis, Mkhize et al. (2016) obtained a maximum limonene yield of 7.62 wt% of the oil fraction at 475°C, significantly lower than the present peak-area percentage, while their subsequent kinetic study quantified activation energies for limonene and isoprene but not indene. At pilot scale, Li et al., (2004) reported about 5.4 wt% limonene in the liquid fraction at 500°C, demonstrating the challenges of maintaining high selectivity during scale-up. These comparisons underscore the advantage of the hybrid TGA-Ty-GC/MS methodology in this work, which integrates kinetic analysis with compound-specific detection to achieve both low apparent activation energies (122-145 kJ.mol<sup>-1</sup>) and high limonene selectivity under optimized conditions.

While the formation of limonene and indene is found to be favoured under specific pyrolysis conditions (500°C and 100°C/min), the commercial viability of their recovery also depends on the ease of downstream separation. Limonene, being a relatively volatile and thermally stable

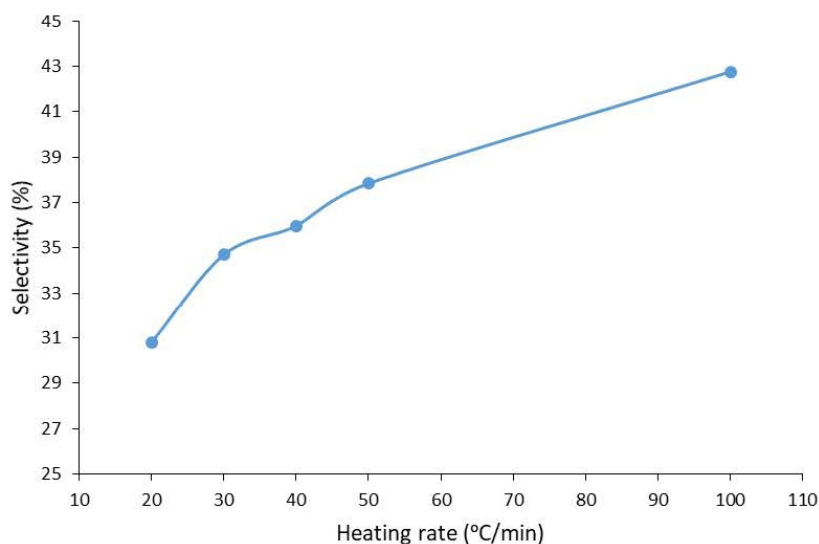


FIGURE 8: Selectivity to limonene formation.

monoterpene, can be efficiently separated via fractional condensation or distillation due to its distinct boiling point ( $\sim 176^{\circ}\text{C}$ ) and low affinity for co-condensed char. Indene (boiling point  $\sim 181^{\circ}\text{C}$ ), though more prone to secondary polymerization, may also be recovered via low-temperature condensation or vacuum distillation techniques. A central difficulty arises from the close boiling points of limonene and indene, which can lead to co-elution in distillation and limit achievable purities without advanced separation measures. Furthermore, tyre pyrolysis oil contains a complex matrix of other mono- and polycyclic aromatics, some of which share similar volatility and molecular weight, complicating isolation. Multi-stage fractional distillation with high-efficiency packing can improve separation sharpness but increases capital and operational costs. Adsorption-based process using tailored sorbents such as modified zeolites or silica-alumina offers a means of selectively retaining aromatic compounds, enabling partial enrichment of limonene in the raffinate phase. Membrane-assisted pervaporation has also been explored for hydrocarbon mixtures, providing a potentially lower energy alternative that exploits molecular size and polarity differences (Smitha et al., 2004).

From a scale-up perspective, integration of these techniques into continuous pyrolysis systems must also consider fouling behaviour, regeneration of adsorbents or membranes, and the trade-off between purity and recovery efficiency. While high-purity limonene and indene markets could offer attractive revenue streams, the economic feasibility will depend on developing hybrid separation trains that combine condensation, adsorption, and membrane processes to achieve the necessary selectivity at a competitive cost. This underscores the need for further research into optimised separation pathways specifically tailored to tyre pyrolysis oils, incorporating not only thermodynamic and kinetic considerations but also material compatibility and process economics. Such studies would be instrumental in bridging the gap between laboratory-scale chemical yield optimisation and viable industrial-scale production.

## 4. CONCLUSIONS

This study investigated the pyrolysis behaviour of TT crumbs using integrated thermogravimetric analysis, kinetic modelling, and Py-GC/MS to understand the formation and selectivity of valuable compounds, notably limonene and indene. Model-free and model-fitting approaches revealed activation energy values ranging from 122 and 145  $\text{kJ}\cdot\text{mol}^{-1}$  and identified key reaction zones associated with NR and SBR degradation. The process was best described by D2 and F2 kinetic models, indicating multi-step decomposition behaviour.

Product analysis showed that limonene formation peaked at moderate temperatures, with selectivity decreasing from 64.2% at  $400^{\circ}\text{C}$  to 28.6% at  $700^{\circ}\text{C}$  due to secondary reactions. Conversely, increasing the heating rate significantly enhanced limonene selectivity, rising from 30.8% at  $20^{\circ}\text{C}/\text{min}$  to 42.7% at  $100^{\circ}\text{C}/\text{min}$ . Based on these findings, optimal operating conditions for limonene production are identified as  $500^{\circ}\text{C}$  and  $100^{\circ}\text{C}/\text{min}$ , offering a practical benchmark for process optimisation.

The findings from this study offer important theoretical contributions by identifying reaction zones linked to the production of limonene and indene and providing activation energy profiles across conversion extents. Practically, the kinetic and selectivity data can inform the development of optimised pyrolysis protocols. High limonene yield at moderate temperature and fast heating rates suggests opportunities for targeted reactor control strategies to enhance the economic viability of tyre-derived oil recovery. Although this study does not include a process simulation or scale-up assessment, the kinetic parameters and product selectivity profiles generated herein provide a robust foundation for future modelling and design of industrial units targeting specific chemical yields. For instance, the identification of  $500^{\circ}\text{C}$  and  $100^{\circ}\text{C}/\text{min}$  as optimal conditions for limonene production can guide reactor temperature and residence time settings.

Limitations of this study include the use of tyre feedstock from a single source and the absence of a catalyst

or continuous reactor validation. Despite these constraints, the findings have direct implications for industrial scale-up and contribute to the development of tailored pyrolysis strategies aimed at chemical valorisation from end-of-life tyres.

Future research should explore the use of catalytic systems to enhance selectivity toward targeted chemicals like limonene and indene. The incorporation of zeolite-based catalysts, for instance, may provide shape-selective advantages and suppress unwanted side reactions. Additionally, transitioning to continuous pyrolysis systems with integrated vapour recovery and purification units would be essential for industrial implementation. Investigating solvent-assisted or membrane-based separation methods could also offer energy-efficient alternatives for post-processing.

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# UNLOCKING COPPER FROM ELECTRONIC WASTE: OPTIMIZED LEACHING STRATEGIES AND RAPID ANALYTICAL CHEMISTRY EVALUATION

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## ABSTRACT

This study presents a novel method for evaluating copper (Cu) extraction efficiency by combining chemometric approaches with non-invasive analytical techniques, including Energy-Dispersive X-Ray Fluorescence (ED-XRF) and Laser-Induced Breakdown Spectroscopy (LIBS). Aligned with Process Intensification (PI) principles, our methodology utilizes the Design of Experiments (DoE) approach to streamline decision-making in metal recovery processes. While the in-situ generation of Cu ions in the liquid medium yielded suboptimal results, this approach warrants further investigation to optimize its potential. On the other hand, our findings demonstrate that LIBS and XRF are highly effective in differentiating leachates based on Cu signals, offering advantages such as higher analytical frequency and lower operational costs compared to traditional methods like Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES). These non-invasive techniques enhance process understanding, enabling more efficient and informed decision-making. By integrating PI with DoE, this study advances Cu recycling strategies from Waste Electrical and Electronic Equipment (WEEE), paving the way for more sustainable and cost-effective recovery processes. This approach holds significant promise for addressing the growing challenges of e-waste management and resource recovery.

## 1. INTRODUCTION

Electronic waste (e-waste) represents one of the fastest-growing and most pressing environmental challenges globally. Despite its severity, adequate collection and recycling initiatives remain limited in Brazil, other Latin American nations, and Nigeria. The associated logistics and treatment processes are highly complex, requiring substantial human resources and incurring considerable costs for selective collection, secure transportation, and waste processing. These constraints significantly hinder the feasibility of large-scale implementation (Lundgren, 2012).

Any electrical and electronic equipment (EEE) discarded by its owner with no intention of reuse is considered e-waste, also known as waste electrical and electronic equipment (WEEE). In 2022, approximately 62.0 million tons (Mt) of e-waste were generated worldwide. Of this amount, 14.0 Mt (around 23%) were produced in the Amer-

icas, with the United States leading at 7.2 Mt, followed by Brazil with 2.4 Mt (Baldé et al., 2024).

Why has e-waste generation increased annually? This can be attributed to rapid technological advancements, which introduce new devices with enhanced functionalities and a wider variety of options. As a result, the lifecycle of existing equipment has shortened significantly, often to just 1-2 years or even less (Lundgren, 2012; Andrade et al., 2019; Baldé et al., 2024). For instance, a smartphone is typically used for less than two years before being replaced by a more advanced model that offers new attributes. These technological advancements meet global demands, including the need for real-time connectivity, fast access to information, and app-based services provided by these devices (Lundgren, 2012; Baldé et al., 2024).

The primary issue with e-waste is its proper disposal and management. Its complex chemical composition varies based on the device's type, model, manufacturer, and

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production date (Abdelbasir et al., 2018). Improper disposal can cause severe harm to the environment and human health due to the presence of hazardous elements such as Pb in solder, glass panels, batteries, and printed circuit boards (PCBs); Cd in semiconductor chips; Hg in thermostats; and flame retardants in PCBs (Kiddee et al., 2013; Dey et al., 2023).

On the other hand, e-waste recycling offers significant opportunities. Beyond hazardous and toxic components, e-waste contains base metals (Al, Cu, Fe), precious metals (Au, Ag, Pd) from telecommunications and IT equipment, as well as critical elements (In) and rare earth elements (REEs) (Abdelbasir et al., 2018; Baldé et al., 2024). In this context, reverse logistics systems are crucial for promoting the proper management of these materials.

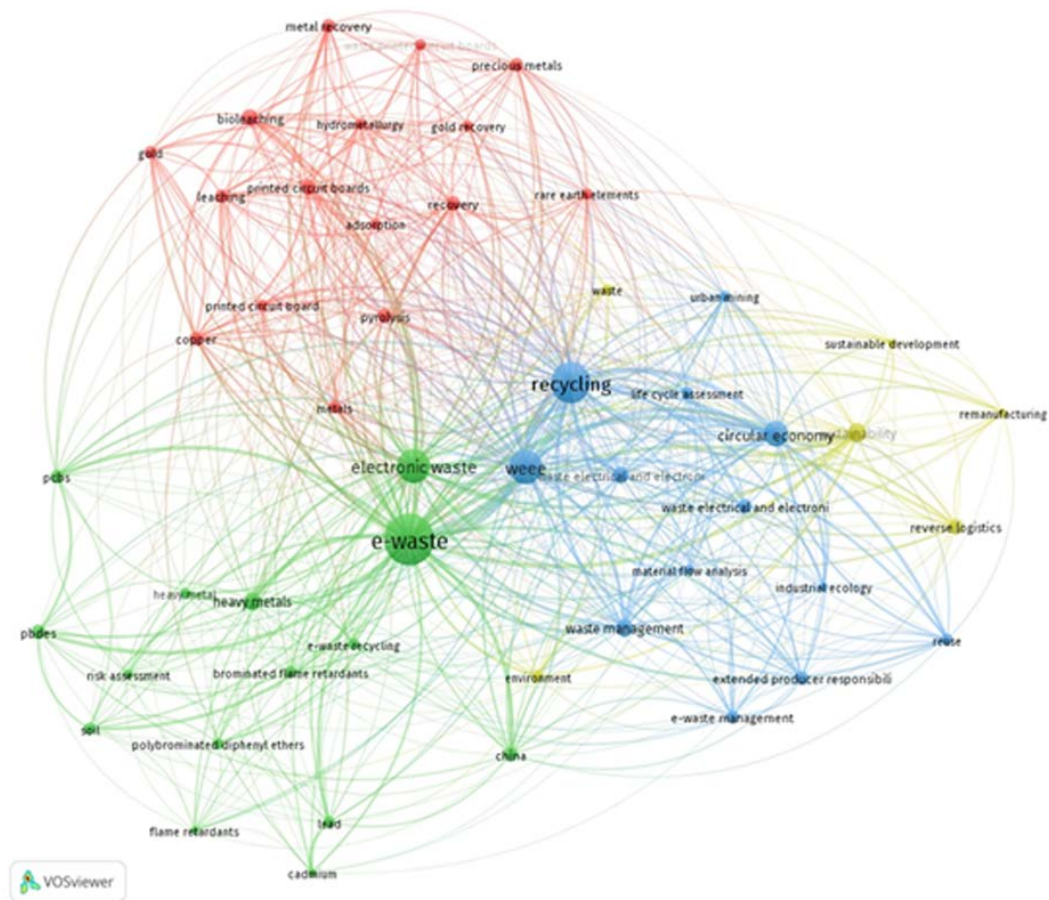
The bibliometric map shown in Figure 1 illustrates the relationships among the 50 most frequently occurring keywords across the 9,175 publications analyzed from 2003 to 2025. The node size is proportional to the number of publications, the line thickness corresponds to the strength of the connection between keywords, and the color of each cluster indicates a grouping of keywords with stronger relationships in the publications (Andrade et al., 2019).

The red cluster encompasses studies on recovering valuable or higher-value-added metals, such as Au and Cu. The green cluster highlights publications addressing the

risks to humans and the environment posed by certain substances found in e-waste, such as polychlorinated biphenyls, flame retardants (PBDEs), Cd, Pb, and other potentially toxic metals. The blue cluster encompasses studies on e-waste management and the reuse of recycled and recovered materials. Finally, the yellow cluster includes studies on reverse logistics, sustainability, and the environment.

In developed countries, legislation is more effective and restrictive, with e-waste collected by companies responsible for waste management or government entities and processed through recycling. In contrast, less developed countries often lack adequate infrastructure and legislation, and most waste ends up in open dumps or sanitary landfills, or is incinerated, with little to no separation. In Brazil, projects dedicated to this type of collection are still in their infancy, failing to meet current demand or cover all regional areas of the country (Baldé et al., 2024).

The sectoral agreement requires manufacturers, importers, and distributors to meet collection and disposal targets for EEE sold in the consumer market. Additionally, cities with over 80,000 inhabitants must establish voluntary collection points in easily accessible consumer locations, such as retail stores, educational institutions, and public squares. The federal decree reinforces these targets and emphasizes the implementation of a reverse logistics system for household electronic products, with responsi-



**FIGURE 1:** Bibliometric map generated using the 50 most frequently occurring keywords from 9,175 publications analyzed between 2003 and 2025.

bilities shared among manufacturers, distributors, importers, and retailers (Kiddee et al., 2013; Souza, 2020).

Brazil still faces challenges in collecting these materials. EEE collected properly by licensed companies undergoes a screening process to determine if any items are still usable. Usable items are donated to educational institutions or charities, while non-usable items are classified as waste, dismantled, and separated for value recovery. Specialized companies further process these materials, separating polymers and metals such as Al and Cu. These materials are then sent to other companies to be used as raw materials for manufacturing new products (Souza, 2020).

Although some companies segregate waste, recycling processes capable of transforming waste into new products with high purity levels remain largely inaccessible. As a result, interest in research on this niche continues to grow worldwide (Li et al., 2022).

Our investigation aims to develop a method for evaluating the efficiency of Cu extraction using chemometrics and non-invasive techniques, such as Energy-Dispersive X-Ray Fluorescence (ED-XRF) (Jenkins, 1999) and Laser-Induced Breakdown Spectroscopy (LIBS) (Pereira-Filho et al., 2025). This goal aligns with the principles of Process Intensification (PI), as outlined by Muscetta (2024), which highlights the application of Design of Experiments (DoE) to accelerate decision-making processes in metal recovery. Both analytical techniques can directly analyze solid samples with minimum sample preparation, allowing for the obtaining of complementary results. ED-XRF is capable of determining elements with atomic numbers (Z) greater than 11. Using LIBS, it is possible to obtain analytical signals even for light elements, such as Li, C, and Al (Jenkins, 1999; Pereira-Filho et al., 2025).

## 2. MATERIALS AND METHODS

### 2.1 Sampling and sample preparation

End-of-Life (EoL) computers, laptops, smartphones, and tablets were collected, totaling 12 kg of e-waste. The

year of manufacturing varied from 2002 to 2019. These materials were manually disassembled and separated into five parts: polymers, electronic components, cables, metal parts, and PCBs. The PCBs were the primary target samples of this study, which were weighed and processed in a Tecnal TE-650 knife mill (Piracicaba, Brazil). After grinding, the material was sieved until it reached a particle size of less than 212  $\mu\text{m}$ , which was used in the study. At the end of the material preparation process, from collection to obtaining the PCB powder, 1.2 kg of powdered samples were obtained, and destined for the subsequent leaching stages. Table 1 illustrates the 11 experiments performed for each extractor:  $\text{HNO}_3$ , water, and  $\text{HNO}_3$  combined with NaCl, totaling 33 experiments. In each experiment, a sample mass of around 1.6 g was used. The experiments from 9 to 11 (Table 1) are replicates, and the results obtained were used to compare the analytical techniques.

### 2.2 Chemicals

All solutions were prepared using ultrapure water produced by Milli-Q Plus equipment (Millipore Corp., Bedford, MA, USA). Before use, all glassware and polypropylene bottles were decontaminated with detergent, immersed for 24 hours in a 10% v v<sup>-1</sup> nitric acid ( $\text{HNO}_3$ ) solution (Synth, Diadema, Brazil), and then rinsed with ultrapure water. The reagents used in the leaching processes were analytical grade (P.A.)  $\text{HNO}_3$  and NaCl (Synth, Diadema, Brazil). Additionally, the concentrated  $\text{HNO}_3$  was previously distilled using Distillacid BSB-939-IR equipment (Berghof, Eningen, Germany) to ensure the required purity for analysis.

A certified stock standard solution of Cu (1000 mg L<sup>-1</sup>, Specsol, São Paulo, Brazil) was used for the preparation of calibration standards. The detailed procedure for the preparation of the calibration curve is described in Section 2.6.

### 2.3 Leaching procedure

This study conducted metal leaching experiments using three different extractors: (1) 10 mL of 3 mol L<sup>-1</sup>  $\text{HNO}_3$ ,

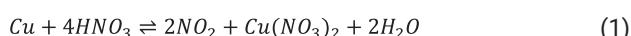
**TABLE 1:** An experimental design matrix (DoE) with 2<sup>3</sup> experiments, including a central point (more 3 experiments, 9-11), was used to optimize Cu leaching conditions, and this process was repeated for all three extractors (a total of 33 experiments). The conditions consisted of 10 mL of 3 mol L<sup>-1</sup>  $\text{HNO}_3$ , 10 mL of water, and 1 mL of 3 mol L<sup>-1</sup>  $\text{HNO}_3$  combined with 9 mL of 3 mol L<sup>-1</sup> NaCl.

| Experiments | Temperature (V1) |       | Mixing time every 15 minutes (V2) |       | Extraction time (V3) |       |
|-------------|------------------|-------|-----------------------------------|-------|----------------------|-------|
|             | Real (°C)        | Coded | Real (min)                        | Coded | Real (h)             | Coded |
| 1           | 25               | -1    | 1                                 | -1    | 1                    | -1    |
| 2           | 70               | 1     | 1                                 | -1    | 1                    | -1    |
| 3           | 25               | -1    | 2                                 | 1     | 1                    | -1    |
| 4           | 70               | 1     | 2                                 | 1     | 1                    | -1    |
| 5           | 25               | -1    | 1                                 | -1    | 2                    | 1     |
| 6           | 70               | 1     | 1                                 | -1    | 2                    | 1     |
| 7           | 25               | -1    | 2                                 | 1     | 2                    | 1     |
| 8           | 70               | 1     | 2                                 | 1     | 2                    | 1     |
| 9           | 47.5             | 0     | 1.5                               | 0     | 1.5                  | 0     |
| 10          | 47.5             | 0     | 1.5                               | 0     | 1.5                  | 0     |
| 11          | 47.5             | 0     | 1.5                               | 0     | 1.5                  | 0     |

(2) 10 mL of water, and (3) 1 mL of 3 mol L<sup>-1</sup> HNO<sub>3</sub> combined with 9 mL of 3 mol L<sup>-1</sup> NaCl. Three full factorial designs (Table 1) with a central point (experiments 9 – 11) were developed for each extractor, considering the variables temperature of extraction (V1), mixing time (V2, every 15 minutes), and extraction time (V3), as shown in Table 1. A total of 33 experiments were performed.

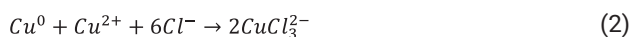
For Cu leaching using the extractors described earlier, 33 conical tubes (50 mL) were used, and approximately 1.6 g of PCB was weighed into each one. Heating was performed by placing the 33 conical tubes in a block rack set on top of a magnetic stirrer with a heater (model 752A, Fisatom, São Paulo, Brazil), as specified in the experimental design (Table 1). This setup ensured uniform and stable heat transfer to all tubes simultaneously.

In the case of HNO<sub>3</sub> 3 mol L<sup>-1</sup>, 10 mL was added to tubes 1 through 11. The Cu leaching is performed according to Equation 1:



According to the factorial design, the mixture was agitated at 15-minute intervals. This agitation involved manually vortexing each tube for the specified duration (1, 1.5, or 2 minutes) to ensure complete resuspension of the solid particles. This procedure was based on the conditions evaluated by Dutta et al. (Dutta et al., 2018). After leaching, the solid (inert material) and liquid phases (rich Cu phase) were separated using quantitative filter paper (Unifil, black tape, 125 mm Ø, Germany).

The second leaching was conducted using only water (tubes from 12 to 22). In this case, no leaching process occurs, and the objective was to determine whether the analytical techniques (discussed in detail in the following sections) can effectively distinguish between effective and ineffective extractors. For Cu leaching using HNO<sub>3</sub> combined with NaCl, 9 mL of the 3 mol L<sup>-1</sup> HNO<sub>3</sub> solution and 9 mL of the 3 mol L<sup>-1</sup> NaCl solution were added to tubes numbered 23 to 33. The procedure followed the same experimental conditions as leaching with HNO<sub>3</sub>, which were based on the parameters studied by Yazici and Deveci (Yazici & Deveci, 2013; Yazici & Deveci, 2015). The study proposed by Yazici and Deveci utilizes Cu ions (Cu<sup>2+</sup>) in combination with Cl<sup>-</sup> to form a Cu complex (CuCl<sub>3</sub><sup>2-</sup>), as described by Equation 2:



After each leaching, the samples were filtered, and the resulting solid residue was dried in an oven at 40°C until a constant mass was achieved. The liquid phase was separated for further Cu determination using a reference analytical technique described in section 2.6. The following section details the experimental conditions for each leaching strategy evaluated.

## 2.4 LIBS data analysis

After leaching, the obtained solid residues were dried to a constant mass in an oven at 40°C and then manually homogenized. Then, 500 mg of each sample was weighed and pressed in an SSP-10 hydraulic press (Shimadzu, São Paulo, SP, Brazil) with a force of 60 kN for 1

minute, forming pellets with a diameter of 12 mm and a thickness of 2 mm to optimize the instrument's data acquisition. Then, the pellets were directly analyzed using a LIBS system.

LIBS emission spectra were acquired using the LIBS J200 instrument (Applied Spectra, Fremont, CA, USA), which was controlled by the Axiom 2.5 software (Applied Spectra) to configure the operating parameters. The system is equipped with an Nd: YAG laser (Quantel Ultra, Bozeman, MT, USA) with a wavelength of 1064 nm, a pulse duration of 5 ns, and a maximum laser pulse energy of 100 mJ, as well as a 6-channel CCD spectrometer, which records spectral information in the 186 to 1042 nm range. The operating parameters used in this study were a laser pulse fluence of 1,000 J cm<sup>-2</sup>, a spot size of 100 µm, a delay time of 1 µs, and a laser pulse energy of 80 mJ, following previously optimized conditions (Ferreira et al, 2023). The spectra were acquired in a 12 × 12 matrix arrangement, with two pulses applied per point. The spectral data obtained resulted in a 288 × 12,288 matrix, where 288 represents the total number of pulses recorded in the sample, and 12,288 corresponds to the number of emission lines detected within the instrument spectral range (from 186 to 1042 nm).

## 2.5 ED-XRF data analysis

ED-XRF technique was also used to analyze the same solid samples as LIBS. In this case, a benchtop Energy-Dispersive X-Ray Fluorescence (ED-XRF) spectrometer, Rigaku NEX QC<sup>+</sup> (Austin, TX, USA), was used to acquire ED-XRF spectra. This instrument features an X-ray tube with an Ag target and a high-performance silicon drift detector, operating at a maximum voltage of 50 kV with an energy resolution of 0.024 keV across 2048 channels. Three distinct instrumental settings were utilized during the analysis: (1) 50 kV and 10 µA, (2) 30 kV and 10 µA, and (3) 6.5 kV and 50 µA, with each measurement conducted over a 30s acquisition time. All spectra were collected under ambient air conditions.

## 2.6 Copper determination to obtain reference values

ICP OES technique was used to obtain the reference concentration values for Cu, utilizing an iCAP 7000 Thermo ICP OES (Thermo Fisher Scientific, Madison, WI, USA). The instrument operated under robust conditions with radial observation, and all measurements were carried out using high-purity argon gas (Ar, 99.999%, White Martins-Praxair). The instrumental conditions employed were: radiofrequency (RF) power of 1.15 kW, plasma flow of 12.0 L min<sup>-1</sup>, auxiliary flow of 0.50 L min<sup>-1</sup>, and nebulizer flow of 0.70 L min<sup>-1</sup>. The integration time varied between 5 and 15 seconds, using a Mira Mist nebulizer and a cyclonic spray chamber. The emission lines monitored for Cu were 324.754 nm, 327.396 nm, and 224.700 nm.

Quantification was performed using an external calibration curve prepared from a certified standard solution of Cu at 1000 mg L<sup>-1</sup> (Specsol, São Paulo, Brazil), as mentioned in Section 2.2. An analytical curve composed of eleven points was constructed by preparing standards at concentrations of 0.5, 1.0, 2.0, 3.0, and up to 10.0 mg L<sup>-1</sup>.



All standards and the calibration blank were prepared in a 1% v/v  $\text{HNO}_3$  matrix to match the matrix of the diluted leachate samples. The calibration curve was accepted for analysis only when the linear correlation coefficient ( $R^2$ ) was  $\geq 0.999$ . The method presented a Cu limit of detection (LoD) of  $0.006 \text{ mg kg}^{-1}$ .

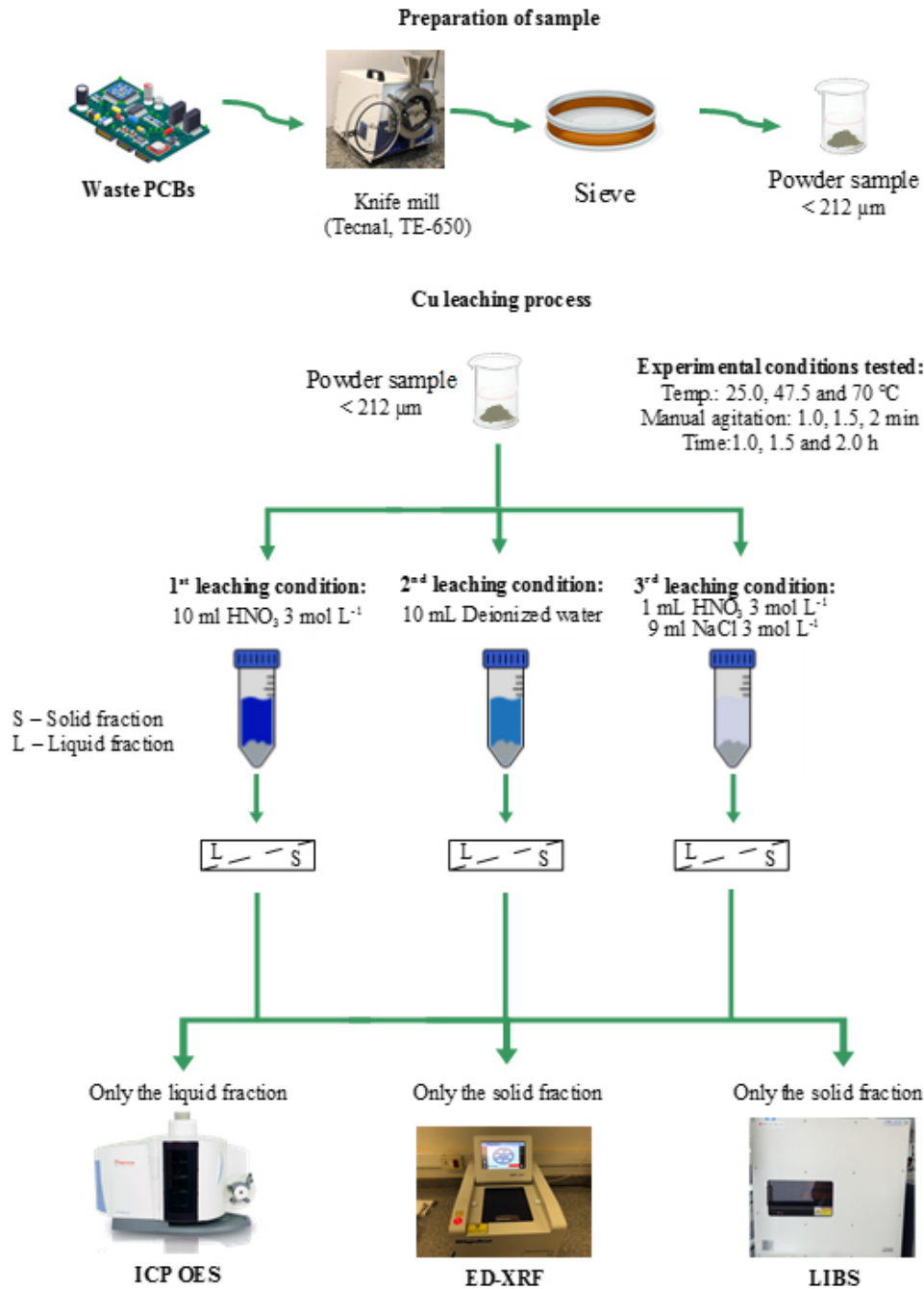
### 2.7 Data evaluation

The obtained data were evaluated using MATLAB® 2022b (MathWorks, Natick, MA, USA), Octave (version 8.4.0), and Microsoft Excel for data evaluation, calculations, and statistical tests. Figure 2 summarizes all the steps described previously: sample preparation, Cu leach-

ing processes, and instrumental Cu determination using ICP OES (reference values), ED-XRF, and LIBS.

### 2.8 Analysis of Method Precision

The precision of the instrument and method was evaluated to demonstrate the repeatability of the measurements. For this purpose, data obtained from the center point replicates ( $n=3$ , Table 1) were used for each of the four scenarios evaluated: (i) leaching with  $\text{HNO}_3$  (experiments 9, 10, 11), (ii) leaching with water (experiments 20, 21, 22), (iii) leaching with  $\text{HNO}_3$  + NaCl (experiments 31, 32, 33), and (iv) the initial sample without leaching. The mean areas (or extraction efficiency), standard deviation (SD),



**FIGURE 2:** Description of the experimental procedure for sample preparation and chemical characterization.

and relative standard deviation ( $RSD = SD/mean \times 100$ ) were calculated for the reference analysis by ICP OES, for the Cu K $\alpha$  signal from ED-XRF, and for the six most relevant Cu emission lines from LIBS.

### 3. RESULTS AND DISCUSSION

#### 3.1 Copper reference concentrations using ICP OES

The analytical metric used to evaluate the leaching extraction was the extraction efficiency (EE, %), which is calculated according to Equation 3:

$$EE (\%) = \frac{[Analyte\ concentration\ in\ the\ liquid\ extract]}{[Initial\ analyte\ concentration\ in\ the\ solid]} \times 100 \quad (3)$$

The initial Cu mass fraction in the sample was 19% w w<sup>-1</sup>, being obtained after sample preparation using aqua regia (Ferreira & Pereira-Filho, 2025). An excellent EE is close to 100%, which means all the analyte was extracted from the solid to the liquid. Table 2 shows the extraction efficiency (EE) in percentage after Cu determination in the liquid leachates. The EE varied from 0% in the experiments with water (as expected) to 94.8% in experiment 6 with HNO<sub>3</sub> 3 mol L<sup>-1</sup>. The experiments with the mixture of HNO<sub>3</sub> and NaCl yielded an EE lower than 1%. As noted and expected, the best performance was obtained for the HNO<sub>3</sub> 3 mol L<sup>-1</sup> solution.

ICP OES determinations are often time-consuming and costly. This raises a critical question to be explored in the following sections: Can Cu EE be accurately described using non-invasive, high-throughput analytical techniques such as XRF and LIBS?

#### 3.2 Results of first-glance ED-XRF measurements

After obtaining the reference and EE values using ICP OES. The solid residues from each leaching experiment (Table 1) were directly analyzed using ED-XRF. A total of 33 experimental tests were conducted to assess the optimization variations for Cu leaching in the PCB sample and determine the most effective method for evaluating it in future EE estimation.

Figure 3a shows the PCA results (matrix X = 33:2048) when considering XRF data. The score values represent

the results for Instrumental Setting 1. The best extractor type was HNO<sub>3</sub>, as indicated by the red symbols over the others. The idea was to provide a scenario with the best leaching conditions for HNO<sub>3</sub> (indicated by the red spheres), the worst for H<sub>2</sub>O (indicated by the blue spheres), and an intermediate scenario involving HNO<sub>3</sub> combined with NaCl (indicated by the pink spheres). The original samples, without extraction (see green spheres), were also used in the calculation to facilitate comparison. The other variables, such as temperature (Figure 3b), mixing time (Figure 3c), and extraction time (Figure 3d), do not influence the clustering of samples, as shown in Figure 3a, because all scores are mixed independently of the experimental condition. The extractor type (Figure 3a) formed two clusters separated by PC1 (94.96%). The negative part of PC1 included samples extracted with HNO<sub>3</sub>, while the positive part included most of the samples extracted with the other extractors.

The ED-XRF spectra effectively detected Cu as the element with the highest variation, as shown in the loadings depicted in Figure 4. These results indicate that Cu leaching occurred, considering that other relevant x-ray fluorescence lines were Cu K $\alpha$  at 8.906 keV and Fe K $\alpha$  and K $\beta$  at 6.400 and 7.058 keV, respectively.

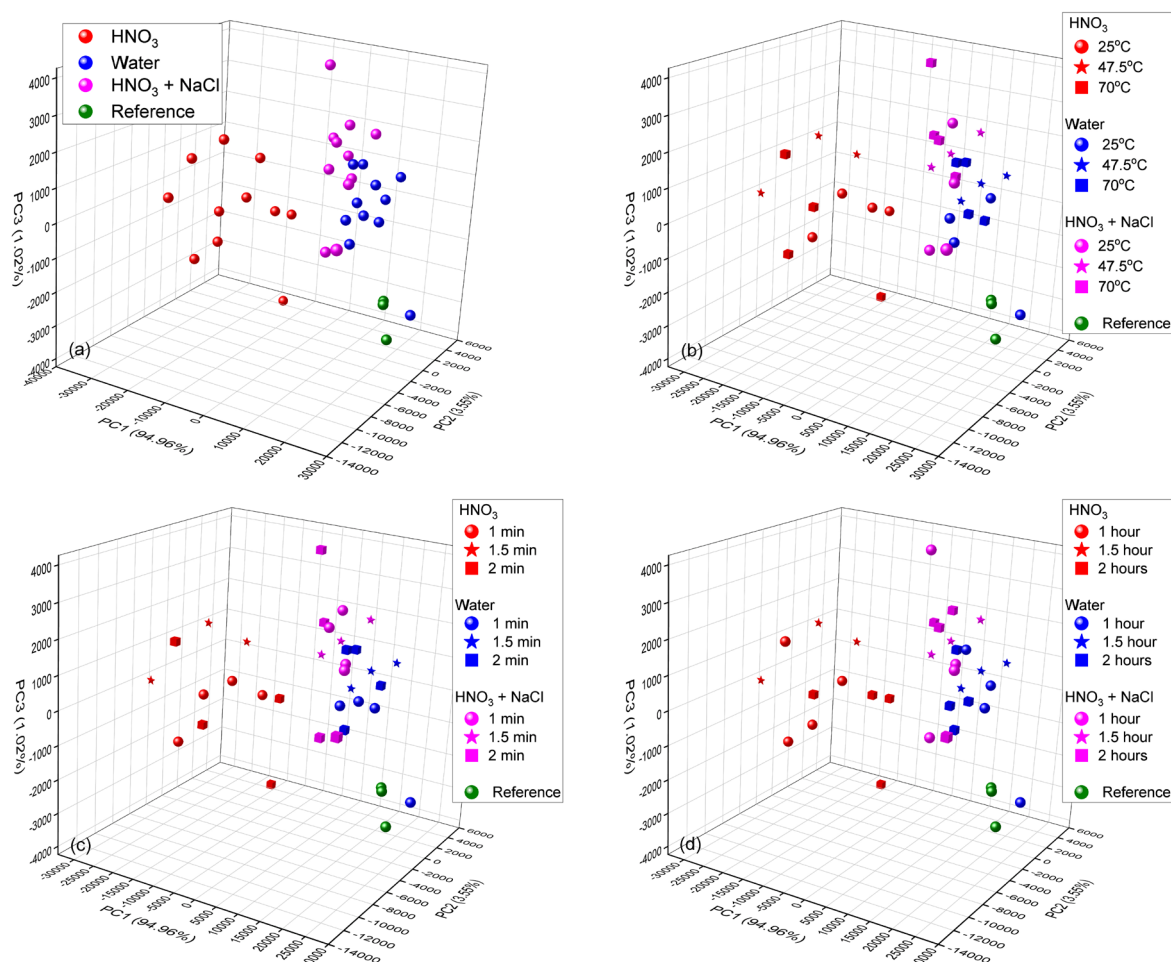
The instrumental setting three yields an interesting result: the scores in Figure 5 cluster according to the Cl, as indicated by the loadings in Figure 6. This clustering aligns with positive PC1, being associated with samples leached with HNO<sub>3</sub> and NaCl.

#### 3.3 Results observed using LIBS

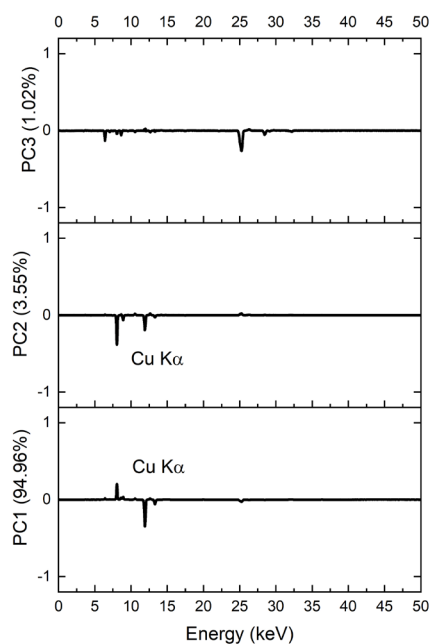
In the case of LIBS, a total of 37 Cu emission lines were previously monitored. Six emission lines were selected: 203.713 nm (ionic emission line denoted as II), 229.384 nm (atomic emission line denoted as I), 282.437 nm (I), 510.554 nm (I), 578.213 nm (I), and 809.263 nm (I); signal areas were then calculated. These emission lines showed the highest correlation (r), with the EE values varying from -0.6637 (for the 578.213 nm line) to -0.6061 (for the 203.713 nm line). As can be observed, the r values are negative, meaning that the higher the EE (i.e., less Cu in the sol-

**TABLE 2:** Extraction efficiency (%) obtained after ICP OES determination for 10 mL of HNO<sub>3</sub> 3 mol L<sup>-1</sup> (experiments from 1 to 11), 10 mL water (from 12 to 22), and 1 mL of HNO<sub>3</sub> 3 mol L<sup>-1</sup> combined with 9 mL of NaCl 3 mol L<sup>-1</sup> (from 23 to 33).

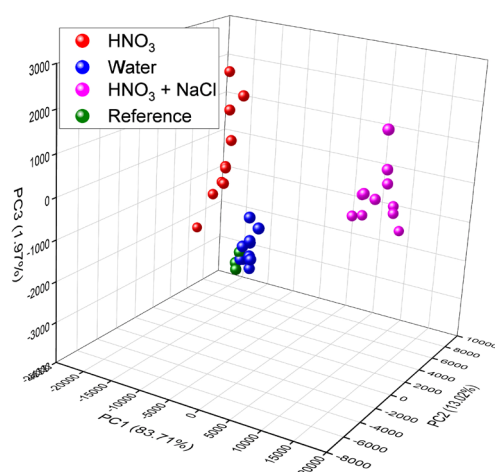
| Experiments                                      | EE (%) | Experiments     | EE (%) | Experiments                                   | EE (%) |
|--------------------------------------------------|--------|-----------------|--------|-----------------------------------------------|--------|
| Leachate: HNO <sub>3</sub> 3 mol L <sup>-1</sup> |        | Leachate: Water |        | Leachate: HNO <sub>3</sub> combined with NaCl |        |
| 1                                                | 82.6   | 12              | 0.0    | 23                                            | 0.0    |
| 2                                                | 67.8   | 13              | 0.0    | 24                                            | 0.2    |
| 3                                                | 79.6   | 14              | 0.0    | 25                                            | 0.4    |
| 4                                                | 71.6   | 15              | 0.0    | 26                                            | 0.5    |
| 5                                                | 63.1   | 16              | 0.0    | 27                                            | 0.2    |
| 6                                                | 94.8   | 17              | 0.0    | 28                                            | 0.0    |
| 7                                                | 84.4   | 18              | 0.0    | 29                                            | 0.2    |
| 8                                                | 71.8   | 19              | 0.0    | 30                                            | 0.6    |
| 9                                                | 68.5   | 20              | 0.0    | 31                                            | 0.4    |
| 10                                               | 62.2   | 21              | 0.0    | 32                                            | 0.3    |
| 11                                               | 59.0   | 22              | 0.0    | 33                                            | 0.4    |



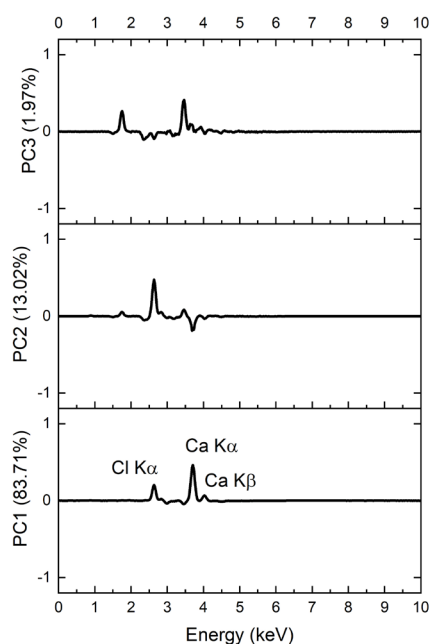
**FIGURE 3:** Score values using instrumental setting one obtained for PCA of ED-XRF: type of extractors (a), temperature (b), mixing time (c), and extraction time (d) for the 11 experiments performed using an experimental design matrix (DoE) with  $2^3$  experiments, including a central point.



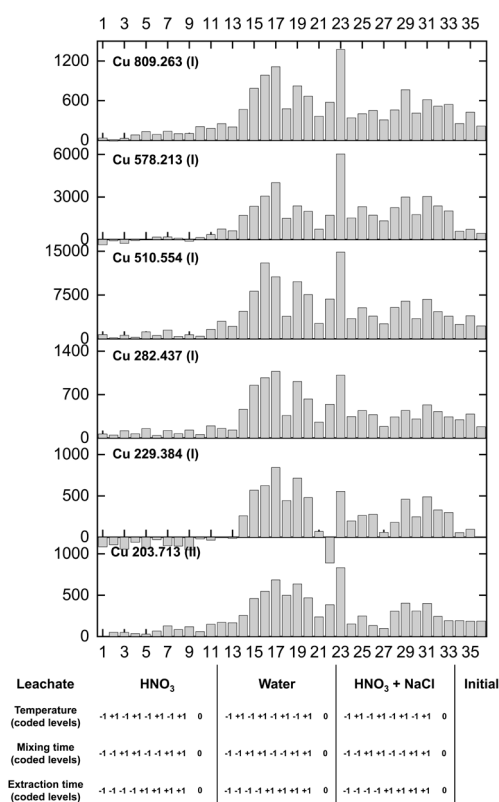
**FIGURE 4:** Loading values for PC1, PC2, and PC3 with Cu K $\alpha$  highlighted.



**FIGURE 5:** Score values using instrumental setting three were obtained for PCA of ED-XRF, considering only the type of extractors from the experimental design matrix (DoE) with  $2^3$  experiments, including a central point.



**FIGURE 6:** Loading values for PC1, PC2, and PC3 highlighted for Cl K $\alpha$ , Ca K $\alpha$ , and Ca K $\beta$ .



**FIGURE 7:** Cu signal areas for the six emission lines selected from LIBS inspection.

id residue), the lower the areas. Figure 7 shows the signal area for the six lines from the 33 experiments and the three initial samples (34, 35, and 36).

As noted, the samples from 1 to 11, extracted using HNO<sub>3</sub>, presented the lowest areas of Cu, showing good

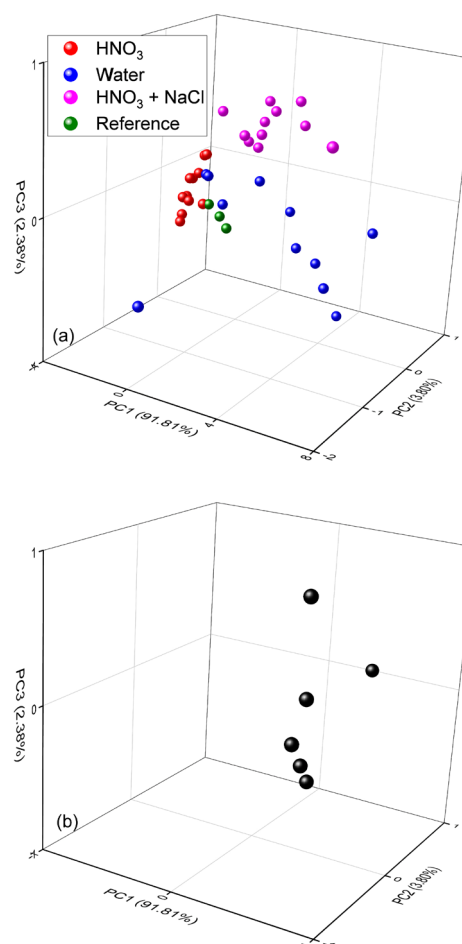
concordance with the EE, which varied from 59.1% (experiment 11) to 94.8% (experiment 6). Similarly, using XRF, it was impossible to detect a difference in the other variables studied in the DoE. The experiments extracted with water (12-22) presented the highest Cu area.

A PCA was also calculated using the entire dataset (matrix **X** 33:6) after autoscaling. Figure 8 shows the results of the scores (Figure 8a) and loadings (Figure 8b). The samples submitted to HNO<sub>3</sub> extraction exhibited different behavior compared to the others. The last evaluation performed was a Tukey test (Christensen, 1996) to confirm differences among the three extractors.

Figure 9 shows the results for the six emission lines described earlier: 203.713 nm (Figure 9a), 229.384 nm (Figure 9b), 282.437 nm (Figure 9c), 510.554 nm (Figure 9d), 578.213 nm (Figure 9e), and 809.263 nm (Figure 9f). A difference was observed between the HNO<sub>3</sub> (represented as b) and the other extractors (represented as a) with a 95% confidence level.

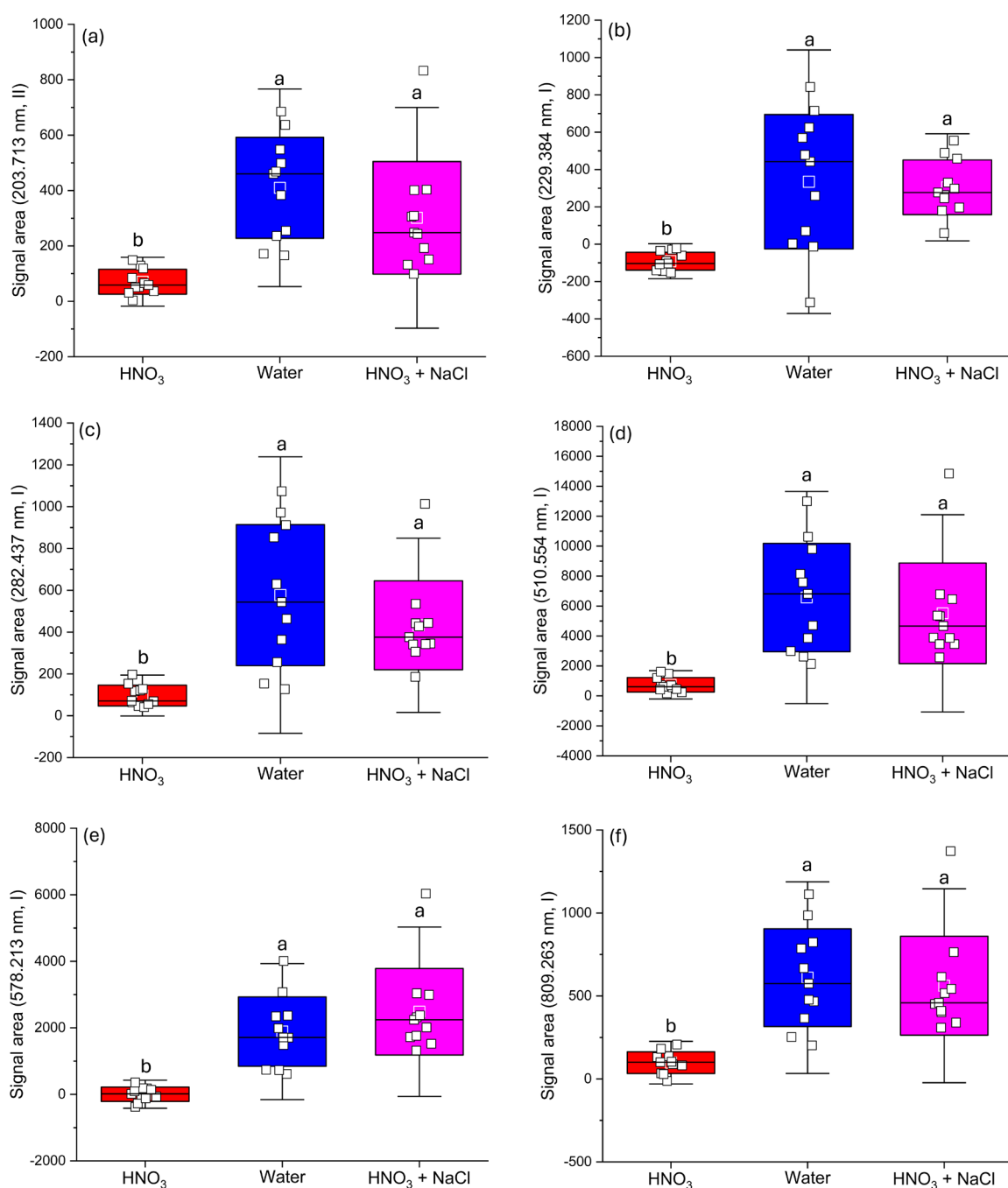
### 3.4 Precision analysis and comparative performance

To evaluate the reliability and practical applicability of the proposed non-invasive techniques, a performance analysis was conducted, focusing on both the precision of



**FIGURE 8:** Score (a) and loading (b) values for the six Cu emission lines selected from LIBS inspection.





**FIGURE 9:** Tukey tests were performed on the six Cu emission lines selected: 203.713 nm (a), 229.384 nm (b), 282.437 nm (c), 510.554 nm (d), 578.213 nm (e), and 809.263 nm (f). The extractors' water and HNO<sub>3</sub> + NaCl are statistically similar (depicted as a) and different from HNO<sub>3</sub> (shown as b).

the measurements and the overall performance in comparison with the reference method (ICP OES).

To assess the reliability of each technique, the precision of the measurements was quantified and compared. Table 3 presents the precision data, calculated from the center point replicates ( $n=3$ ), for the three leaching scenarios (Table 1).

Table 3 provides a basis for comparing the performance of each method. ICP OES, as the reference technique, exhibits excellent precision (4.85), with an RSD of approximately 7.7% for the leaching processes. This value

encompasses the variability of the entire experimental procedure (weighing, reaction, filtration, dilution, and measurement), confirming the high repeatability of the developed leaching protocol.

The direct solid analysis techniques, ED-XRF and LIBS, show, as expected, greater variability. For ED-XRF, the RSD of the Cu K $\alpha$  signal was 37.8% in the low concentration scenario (after leaching with HNO<sub>3</sub>), an expected increase in variability when measurements approach the limit of detection of an instrument. In contrast, in high Cu concentration scenarios (extraction with water and the mixture

**TABLE 3:** Precision data (mean, Standard Deviation - SD, and Relative Standard Deviation - RSD) for the analytical techniques, estimated from the center points (n = 3) of each matrix from the Design of Experiments (DoE).

| Scenario                                                                     | Technique | Analyte/Signal                                     | Mean    | SD      | RSD (%) |
|------------------------------------------------------------------------------|-----------|----------------------------------------------------|---------|---------|---------|
| HNO <sub>3</sub> Leaching<br>(Effective Leaching,<br>pellets 9-11)           | ICP OES   | Extraction Efficiency (%)                          | 63.25   | 4.85    | 7.66    |
|                                                                              | ED-XRF    | Area at Cu K $\alpha$                              | 0.106   | 0.040   | 37.8    |
|                                                                              | LIBS      | Area at 510.554 nm                                 | 923.53  | 609.97  | 66.0    |
|                                                                              | LIBS      | Area at 229.384 nm                                 | -70.05  | 72.57   | -104    |
|                                                                              | LIBS      | Area at 282.437 nm                                 | 126.41  | 70.49   | 55.8    |
|                                                                              | LIBS      | Area at 203.713 nm                                 | 108.55  | 45.87   | 42.3    |
|                                                                              | LIBS      | Area at 578.213 nm                                 | 123.23  | 238.25  | 193     |
|                                                                              | LIBS      | Area at 809.263 nm                                 | 163.85  | 53.89   | 32.9    |
| Water Leaching<br>(Ineffective Leaching,<br>pellets 20-22)                   | ICP OES   | Extraction Efficiency (%)                          | 0       | 0       | N/A     |
|                                                                              | ED-XRF    | Area at Cu K $\alpha$                              | 1.094   | 0.104   | 9.53    |
|                                                                              | LIBS      | Area at 510.554 nm                                 | 5671.31 | 2672.47 | 47.1    |
|                                                                              | LIBS      | Area at 229.384 nm                                 | 78.83   | 395.16  | 501     |
|                                                                              | LIBS      | Area at 282.437 nm                                 | 476.33  | 195.83  | 41.1    |
|                                                                              | LIBS      | Area at 203.713 nm                                 | 362.66  | 117.50  | 32.4    |
|                                                                              | LIBS      | Area at 1475.074 nm                                | 1475.07 | 662.05  | 44.9    |
|                                                                              | LIBS      | Area at 535.6534 nm                                | 535.65  | 154.69  | 28.9    |
| HNO <sub>3</sub> + NaCl Leaching<br>(Ineffective Leaching,<br>pellets 31-33) | ICP OES   | Extraction Efficiency (%)                          | 0.350   | 0.027   | 7.62    |
|                                                                              | ED-XRF    | Area at Cu K $\alpha$                              | 0.896   | 0.179   | 20.0    |
|                                                                              | LIBS      | Area at 510.554 nm                                 | 5106.42 | 1507.29 | 29.5    |
|                                                                              | LIBS      | Area at 229.384 nm                                 | 372.22  | 102.34  | 27.5    |
|                                                                              | LIBS      | Area at 282.437 nm                                 | 434.73  | 96.27   | 22.1    |
|                                                                              | LIBS      | Area at 203.713 nm                                 | 278.77  | 109.22  | 39.2    |
|                                                                              | LIBS      | Area at 578.213 nm                                 | 2473.40 | 519.46  | 21.0    |
|                                                                              | LIBS      | Area at 809.263 nm                                 | 557.44  | 50.53   | 9.06    |
| Initial Sample<br>(No Leaching, pellets<br>34-36)                            | ICP OES   | Initial Cu concentration<br>(% w w <sup>-1</sup> ) | 19.02   | 3.08    | 16.2    |
|                                                                              | ED-XRF    | Area at Cu K $\alpha$                              | 1.77    | 0.156   | 8.78    |
|                                                                              | LIBS      | Area at 510.554 nm                                 | 2878.88 | 940.26  | 32.7    |
|                                                                              | LIBS      | Area at 229.384 nm                                 | 51.22   | 46.56   | 90.9    |
|                                                                              | LIBS      | Area at 282.437 nm                                 | 287.41  | 101.85  | 35.4    |
|                                                                              | LIBS      | Area at 203.713 nm                                 | 187.54  | 3.26    | 1.73    |
|                                                                              | LIBS      | Area at 578.213 nm                                 | 579.63  | 141.53  | 24.4    |
|                                                                              | LIBS      | Area at 809.263 nm                                 | 297.72  | 112.90  | 37.9    |

of HNO<sub>3</sub> + NaCl), precision improves significantly (RSD of 9.5% and 20.0%).

The LIBS, by its nature, shows a variation in precision between different emission lines. The line at 809.263 nm, for example, demonstrated remarkable precision for a plasma analysis technique on solids, with an RSD of only 9.1% in the leaching (HNO<sub>3</sub> + NaCl) scenario. It is important to note that the RSD of the 229.384 nm line (-103.6%) was anomalous for leaching with HNO<sub>3</sub>. This is because the average Cu signal was practically zero, indicating that the extraction was so efficient that the Cu emission on this line reached the background noise of the instrument, a result that, in itself, demonstrates the success of the process.

In general, the precision analysis described each method experimentally. Although ED-XRF and LIBS are less pre-

cise than ICP OES in terms of RSD, the magnitude of the change in average area between the different scenarios is adequate. For example, the average area of the XRF signal drops by 90% (from 1.09 to 0.11) after leaching with HNO<sub>3</sub>. This change, which is much greater than the measurement precision, allows for an adequate evaluation of the process result. Therefore, the data confirm that the repeatability of ED-XRF and LIBS is entirely sufficient for the proposed process monitoring application, offering a fast and low-cost alternative to the reference method.

## 4. CONCLUSIONS

The tested alternative for the in-situ generation of Cu ions in the liquid medium – using an HNO<sub>3</sub> + NaCl extractor – did not produce satisfactory results, indicating the

need for further investigations to optimize this approach. Conversely, the findings demonstrate that the analytical techniques evaluated — LIBS and ED-XRF — are effective in differentiating leachates based on Cu signals. Moreover, these methods provide higher analytical throughput and lower operating costs compared to ICP OES. Consequently, they can enhance process understanding and facilitate improved decision-making, particularly when Process Intensification (PI) is integrated with DoE in the context of Cu recycling from Waste Electrical and Electronic Equipment (WEEE).

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# INFLUENCE OF IMPURITY ELEMENTS ON THE CASTABILITY OF RECYCLED 6XXX SERIES AL ALLOYS

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## ABSTRACT

Hot tearing represents a relevant limitation to castability, particularly in wrought aluminum alloys having a wide solidification range. To assess the alloy's vulnerability to hot tearing, a variety of predictive models and testing methodologies have been developed. This study aims to validate the Kou model through the comparison of experimental data obtained using the Constrained Rod Casting (CRC) test on selected 6XXX series Al alloys. Additionally, the investigations explore the influence of microstructural features and phase constituents on the formation of hot tears. The results indicate that the sensitivity to hot tears is higher in alloys with 0.2 wt% Fe and decreases by increasing iron content. The  $\alpha\text{-Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$  phase appears to promote grain coalescence, facilitating bridging between primary dendrites and, thereby, improving the castability of the alloy. Furthermore, the study suggests that thermodynamic simulation and the application of Kou index can offer valuable insights into the casting of alloys. These findings will contribute to the identification of optimized alloy chemistries suitable for producing near-net-shape components using casting techniques traditionally applied to Al casting.

## 1. INTRODUCTION

The automotive and aerospace industry is increasingly turning to aluminum alloys (Graf, 2021) for their favorable properties, such as high strength-to-weight ratio, good corrosion resistance, easy formability and, theoretically, indefinite recycling capability (Van den Eynde, et al., 2022). This transition aligns with industry goals to reduce greenhouse gas emissions (Raabe, et al., 2022), dependence on critical raw materials (Ferro & Bonollo, 2023) and overall energy consumption (Cui & Roven, 2010).

However, replacing steel with aluminum presents challenges, particularly because casting aluminum alloys often offer lower mechanical performance required for structural applications. This limitation has led to a growing interest in wrought alloys which offer superior mechanical properties and are now being considered for near-net-shape casting applications (Poznak, Freiberg, & Sanders, 2018). However, using wrought alloys in conventional casting processes remains complex.

These alloys typically exhibit narrow compositional tolerances and broad solidification ranges (Phillion, Thompson, Crockcroft, & Wells, 2008) both of which adversely affect castability, i.e. the ability to be successfully cast into complex shapes without defect formation (Eskin, Suytno, & Katgerman, 2004). Among the various solidification-related defects, hot tearing (also known as hot cracking)

represents a relevant limitation to castability, particularly in wrought alloys having a wide solidification range which increases their susceptibility to thermal contraction.

During the solidification process, these alloys can accumulate internal tensile stress and when the semi-solid metal cannot accommodate these tensile strains, interdendritic cracking, or hot tearing, is likely to form (Dhale & StJohn, 1998). This phenomenon is considered to be one of the most critical and complex defect in casting, resulting from the interaction between multiple factors such as mass flow, thermal gradients, and fluid flow (Eskin, Suytno, & Katgerman, 2004), making analysis and prediction challenging.

As described in the pioneering work of Rappaz and Drezet (Rappaz, Drezet, & Gremaud, 1999), hot tears occur especially due to the constrained contraction in the mushy zone, where the lack of liquid feeding can lead to material failure. When the solidification exceeds the dendritic coherence threshold, the primary aluminum phase forms an interconnected solid network, which incorporates liquid pockets within interstitial spaces. As this network solidifies further, the permeability within the solid structure decreases, leading to the so-called interdendritic separation. Furthermore, shrinkage generates porosity, which acts as nucleation sites for hot tears (Uludag, Çetin, Dispinar, & Tiryakioglu, 2018).



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Industrial casting processes typically proceed under non-equilibrium solidification conditions, well described by the Scheil model (Scheil, 1942). Under these non-equilibrium conditions, micro-segregation areas and intermetallic compounds, which have a significant influence on material strength and susceptibility to hot tearing, are more likely to develop. This tendency is particularly pronounced in secondary alloys, which generally contain higher concentrations of alloying elements and impurities.

Consequently, despite the economic and environmental advantages of producing secondary alloys over primary routes, the use of secondary wrought aluminium alloys unfortunately still remains limited due to their high sensitivity to impurity levels introduced through recycling processes.

To assess the vulnerability of an alloy to hot tearing, a variety of predictive models and testing methodologies have been developed. They serve as predictive tools to design casting processes and alloy compositions to minimize defect occurrence. These include both experimental tests, which directly evaluate cracking tendency under controlled conditions and theoretical or semi-empirical models, which are based on thermodynamic and kinetic simulations of alloy solidification behavior.

Due to its simplicity and ease of application, Kou's criterion is one of the most widely used theoretical approach (Kou, 2015): it proposes that hot tearing occurs when the tensile stress exceeds the combined resistance offered by grain growth and liquid feeding. The model introduces a Hot Tearing Susceptibility (HTS) index, defined by the slope of the temperature versus solid fraction curve ( $T$  vs  $f_s$ ), near the final stage of solidification ( $f_s \rightarrow 1$ ):  $HTS = |\Delta T / \Delta(f_s^{1/2})|$ .

In a previous study (Giansante, Timelli & Fabrizi, 2024), the authors applied the Kou criterion to predict how variations in Si, Mg, Fe and Mn concentrations affect hot tearing in 6XXX series aluminum alloys. The current study extends this work by comparing these predictive results with experimental data obtained through the Constrained Rod Casting (CRC) test, a widely used method to qualitatively assess castability and hot tearing tendency in both vertical and horizontal mold configurations.

The CRC test employs gravity casting into a mold with a series of horizontal arms of different lengths but constant diameters. This setup introduces controlled thermal and mechanical constraints that promote the formation of hot tears at specific locations, making it ideal for evaluating alloy performance under realistic conditions.

This study aims to validate the Kou model using CRC experimental results on selected 6XXX series Al alloys and to examine how microstructural features and phase constituents influence hot tearing behavior in functions of different alloy compositions. The findings will support the

identification of alloy chemistries suitable for producing near-net-shape components using casting techniques traditionally applied to Al casting alloys.

Ultimately, this work contributes to a deeper understanding of the hot tearing phenomenon and provides guidance for the development of casting processes that enable the use of high-performance wrought aluminum alloys in advanced structural applications.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Materials

Based on the findings of a previous work (Giansante, Timelli, & Fabrizi, Influence of Chemical Composition on the Hot Tearing Susceptibility of Wrought 6005 Aluminum Alloys, 2024), three experimental 6xxx series aluminum alloys with different concentrations of Si, Mg, and impurity elements (Fe and Mn) were selected for testing.

All three alloys were then produced using commercially pure aluminum as base material. About 5 kg of ingot pieces were charged into a SiC crucible and they were melted in an electrical furnace at  $750 \pm 5^\circ\text{C}$ . After melting, the surface oxide was skimmed and AlFe20, pure Si, pure Mg and AlMn25 master alloys in the form of waffle or wide rod were added to reach the desired chemical composition. After the addition, the molten bath was held in the furnace for 40 minutes to ensure the correct dissolution and the homogeneity. To reduce hydrogen content and improve the quality of the molten bath, the metal was treated with a commercial salt flux. The bath was stirred prior to flux addition, after which the flux was allowed to react for 20 minutes at the processing temperature. Additionally, a degassing treatment was carried out by purging Argon gas through the melt for 20 minutes. The molten bath was then skimmed and stirred before checking the chemical compositions by optical emission spectrometer (Oxford Instruments - Foundry Master Pro). The average concentrations of the chemical elements for the 3 alloys are listed in Table 1. For each alloy, 2 ingots of 1.5 kg each were then cast and subsequently used in the CRC tests.

### 2.2 Evaluation of Hot Tearing Susceptibility

#### 2.2.1 Kou criterion

The HTS index for each alloy was initially evaluated using Kou's predictive criterion on the solidification curves,  $T$  vs  $f_s$ , generated through ThermoCalc™ (Andersson, Helander, Höglund, Shi, & Sundman, 2002), a commercial thermodynamic simulation software. The solidification paths were computed using Scheil's non-equilibrium model based on data from the TCAL 7.1 aluminum database (TCAL7 Technical Information, 2020). Each simulation started at the temperature of  $750^\circ\text{C}$  with a computing step of  $1^\circ\text{C}$ .

**TABLE 1:** Chemical composition of the experimental alloys (values in wt. %).

| Alloy | Si   | Fe   | Mn   | Mg   | Others | Al   |
|-------|------|------|------|------|--------|------|
| 1     | 1.35 | 0.24 | 0.00 | 0.83 | (0.2)  | Bal. |
| 2     | 1.28 | 0.22 | 0.00 | 1.12 | (0.2)  | Bal. |
| 3     | 0.60 | 0.86 | 0.63 | 0.39 | (0.2)  | Bal. |

In the present investigation, the  $\Delta T/\Delta(f_s^{1/2})$  approximation index within the solid fraction range of  $0.87 < f_s < 0.94$  was used to calculate the HTS values, as this interval was reported to correlate well with experimental observations in aluminum alloys (Kou, 2015).

### 2.2.2 CRC test

To experimentally assess hot tearing susceptibility of the three alloys, the Constrained Rod Casting (CRC) mold in Figure 1 was used. The mold design was adapted from various models reported in the literature; Rajagukgug et al. (Rajagukgug, et al., 2024) highlighted the differences between horizontal and vertical CRC molds. A similar approach was used by Liang et al. (Liang, et al., 2024) in their investigation of the influence of chemical composition and grain refiners on aluminum alloys. Furthermore, Cao & Kou (Cao & Kou, 2006) conducted the CRC test on Mg-Al binary alloys while Uludag et al. (Uludag, Çetin, Dispınar, & Tiryakioglu, 2018) chose this approach to assess the correlation between the hot tearing and melt quality. The CRC mold consists of four rods with a diameter of 9.5 mm and variable lengths. Each rod terminates in a ball end, which serves to prevent free contraction due to shrinkage during solidification. The mold design used in this study includes a pouring basin to minimize turbulence during casting, as well as a thermocouple positioned at the intersection point between the sprue axis and the bottom rod axis, allowing for accurate monitoring of mold temperature. The mold was coated with a graphite-based solution. Prior to casting tests, the previously prepared ingots were melted in a crucible at a furnace temperature of  $760 \pm 5^\circ\text{C}$ . After approximately 60 minutes, the melt was poured into the CRC mold preheated at  $220 \pm 5^\circ\text{C}$  and the final castings were removed from the mold after 5 minutes. At least three castings were carried out for each alloy, following the same procedure.

Hot tears in the castings were inspected by eye and the HTS index according to the CRC test was calculated using

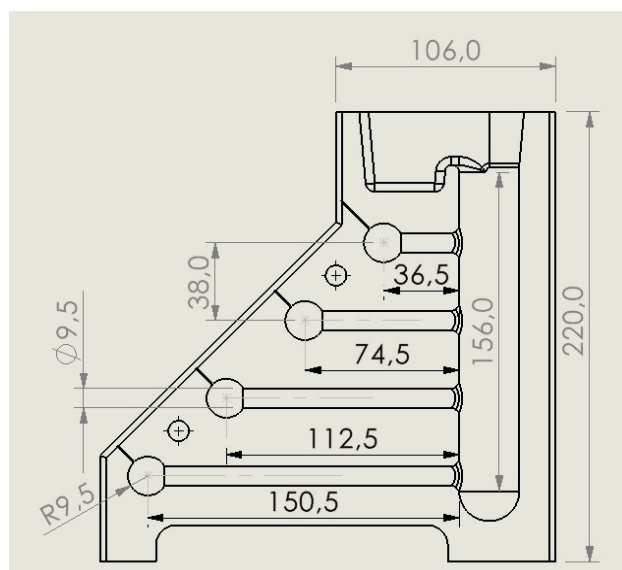


FIGURE 1: Design and dimensions of the CRC mold.

the following equation (Liang, et al., 2024):

$$HTS = \sum_i (w_i * f_i * L_i) \quad (1)$$

where  $w_i$ ,  $f_i$  and  $L_i$  are factors for crack severity, crack location and rod length, respectively. More in details,  $w_i$  represents the so-called weighted index, i.e., a severity index for cracks ranging from 1 for hairline cracks to 4 in cases of complete separation of the involved parts,  $f_i$  denotes the crack location index and can assume values of 1, 1.5, or 2, depending on whether the crack appears near the sprue, on the ball end, or in the middle of the rod, respectively. Lastly,  $L_i$  accounts for the rod length index, which takes the value of 1 for the longest branch and increases up to 4 for the shortest one.

These indices are designed to reflect the susceptibility of a specific rod or areas to crack formation.

The index values are weighted based on the analysis of temperature variations and the resulting thermal strains across different regions of the mold, which show the higher probability of crack formation in the longer branches.

### 2.3 Microstructural analysis

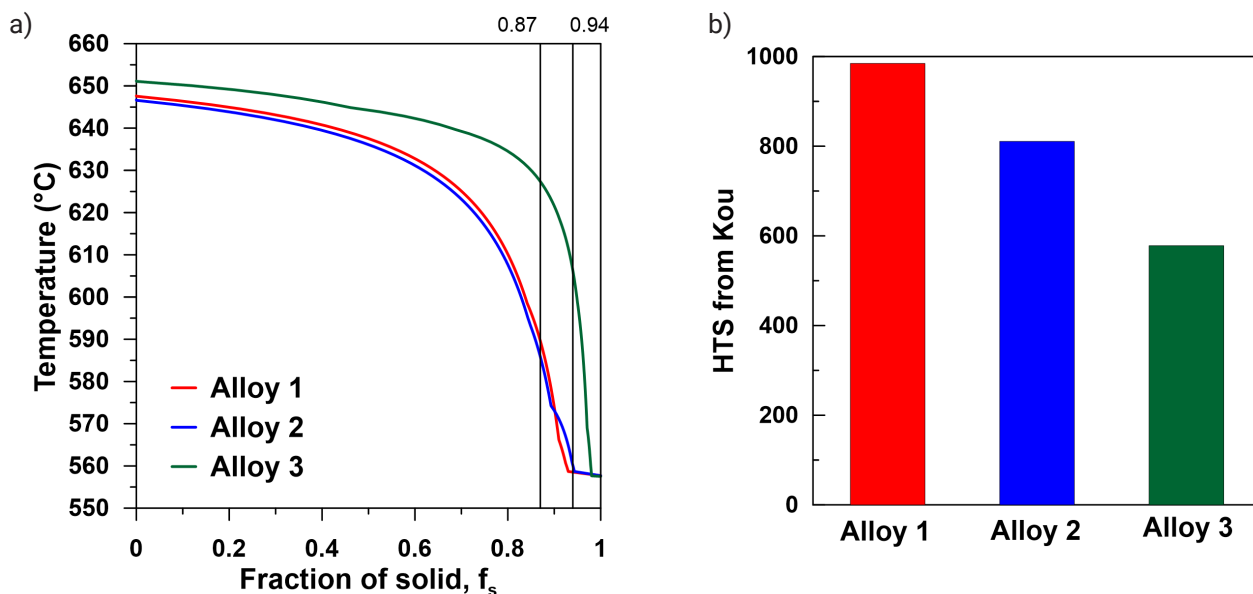
Microstructural investigations were conducted on specimens drawn from the cross-section of the longest rod of the castings. The specimens were embedded in acrylic resin at room temperature and prepared following standard metallographic procedures, which included grinding with SiC abrasive papers and polishing with a 6  $\mu\text{m}$  diamond paste, followed by final polishing using a colloidal silica suspension.

For grain size evaluation, samples were electrochemically etched using Barker's reagent, and the resulting microstructures were examined using an Optical Microscope (OM) with polarized light; grain sizes were then determined by the linear intercept method. Additionally, the polished samples were examined by Scanning Electron Microscope (SEM) equipped with Energy-Dispersive X-ray Spectroscopy (EDS) to characterize the morphology and chemical composition of intermetallic phases.

## 3. RESULTS AND DISCUSSION

Figure 2a illustrates the simulated solidification curves for the three investigated alloys. The curves corresponding to Alloy 1 and Alloy 2 are nearly identical, whereas Alloy 3 exhibits a distinct solidification path. This difference can be attributed to the lower Si and Mg contents and significantly higher Fe and Mn concentrations in Alloy 3 compared to the other two alloys, which are chemically similar. All curves display variations in slope, marked by knee points, particularly near the final stages of solidification. The presence of such knee points indicates the precipitation of secondary phases in addition to the primary  $\alpha\text{-Al}$  phase.

HTS indices were calculated from the solidification curves using Kou's model and the resulting values are presented in the histogram in Figure 2b. Among the three materials, Alloy 1 exhibits the highest vulnerability to the hot tearing. To validate the predictive HTS indices, at least three experimental tests were carried out with the CRC mold and the representing castings of the experimental



**FIGURE 2:** a) T vs.  $f_s$  solidification paths calculated by Scheil's model; b) hot tearing susceptibility as predicted by Kou's model.

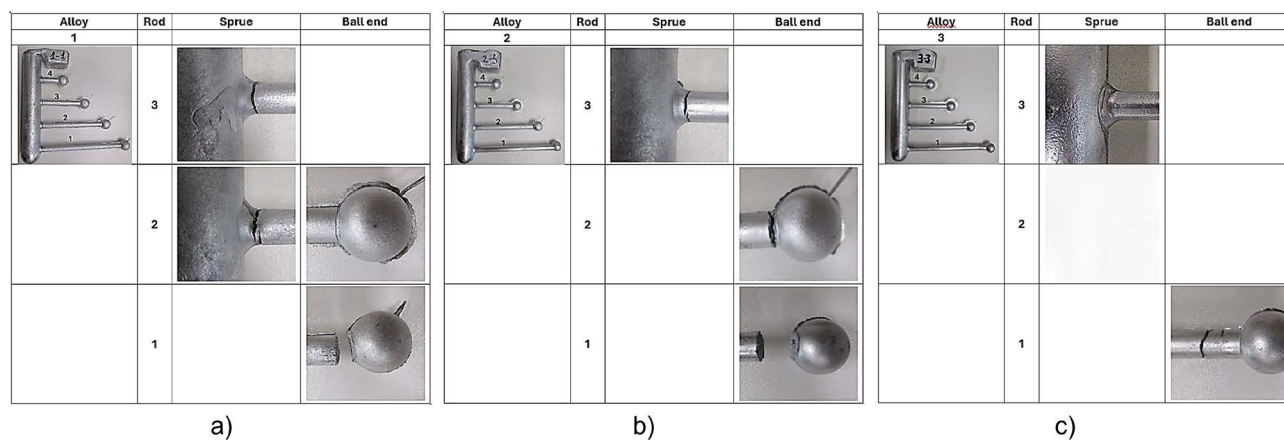
alloys are shown in Figure 3. From the visual inspection, it resulted that cracks tend to form across multiple branches for all the experimental alloys. In particular, for Alloy 1, all tests showed a complete ball separation in rod 1. As shown in the magnified views in Figure 3a, hairline cracks frequently appear at the ball end of rod 2, as well as the occurrence of severe cracks at the sprue area. In addition, light cracks were also detected at the sprue of rod 3. In Alloy 2 (Figure 3b), which registers a higher magnesium content, a slight improvement in crack resistance was observed. In all the castings from Alloy 2, a complete separation was noted near the ball end in rod 1 while severe crack occurred at the sphere of rod 2, while the sprue was always intact. Branch 3 also exhibited light cracking similar to that observed in the casting from Alloy 1. The best results were achieved with the castings produced using Alloy 3 (Figure 3c). In this case, cracks appeared primarily in the middle of branch 1, and light cracks observed at the sprue area of rod 2. Moreover, hairline cracks were found on the sprue of

branch 3. No cracking was observed in rod 4, regardless of the alloy used.

The HTS values calculated in accordance with equation (1) are reported in the Figure 4 and analytically confirm the trends observed during visual inspection.

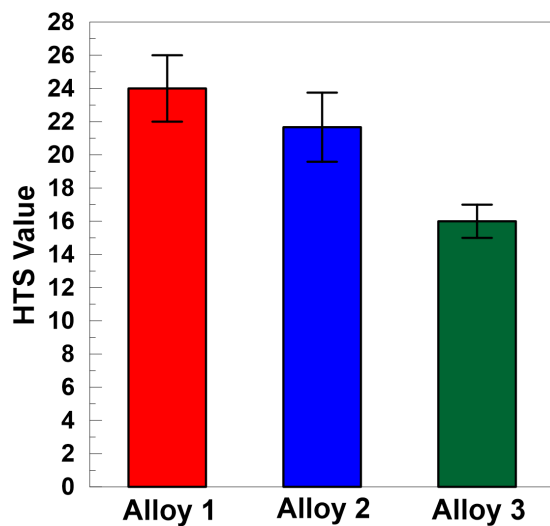
A comparative analysis of the histograms in Figure 2b and Figure 4 highlights a close match between the HTS values predicted using Kou's criterion and those experimentally determined from the CRC tests. This strong correlation validates the applicability of Kou's model as a reliable method for predicting the hot tearing susceptibility in aluminum alloys.

To further investigate the different behavior of the three alloys, microstructural analyses were conducted. Representative micrographs of the three alloys are reported in Figure 5. In all cases, the microstructures exhibit equiaxed dendritic grains with average grain sizes ranging from approximately 110 to 155  $\mu\text{m}$ , as summarized in Table 2.



**FIGURE 3:** Castings from the CRC mold: a) Alloy 1; b) Alloy 2 and c) Alloy 3; in the inset, the close-up views of the tears near the sprue and ball-end of the rod.





**FIGURE 4:** HTS values from the experimental CRC tests.

Nevertheless, no significant correlation was identified between grain size within this dimensional range and HTS values, suggesting that grain size is not a critical parameter in controlling hot tearing behavior. Consequently, more in-depth microstructural investigations were carried out.

Figure 6 presents SEM micrographs acquired in Z-contrast mode. EDS analyses (not shown) revealed the presence of  $\beta\text{-Al}_5\text{FeSi}$  as needle-like or plate-like brighter phases, and  $\text{Mg}_2\text{Si}$ , appearing as darker phases in Alloys 1 and 2 (Figure 6a and Figure 6b), both containing high levels of Si and Mg.

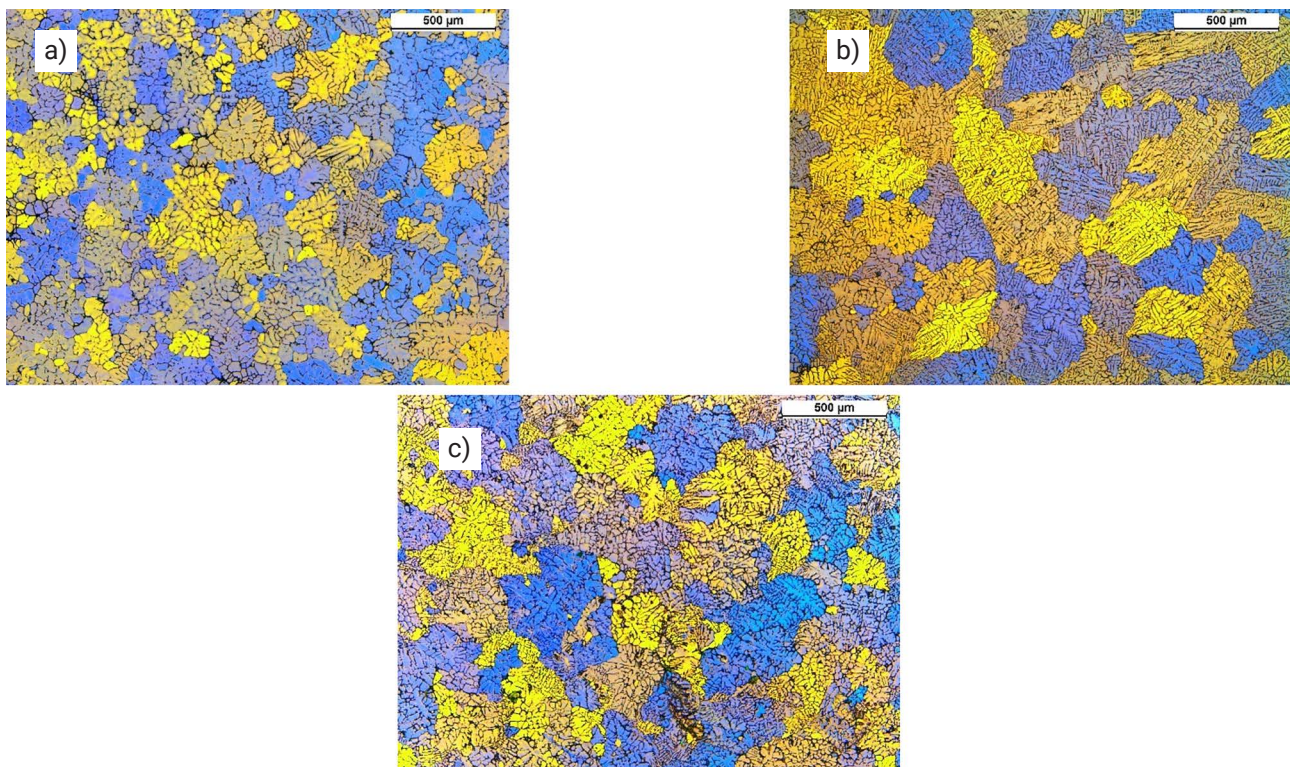
**TABLE 2:** Average grain size.

| Alloy | Grain size ( $\mu\text{m}$ ) |
|-------|------------------------------|
| 1     | $111 \pm 7$                  |
| 2     | $154 \pm 11$                 |
| 3     | $136 \pm 10$                 |

It is worth noting that Alloy 2, with a slightly higher Mg concentration than Alloy 1, exhibited a greater density of these intermetallic compounds with a finer distribution. Additionally, Alloy 2 displayed a visibly smaller secondary dendrite arm spacing (SDAS) compared to Alloy 1.

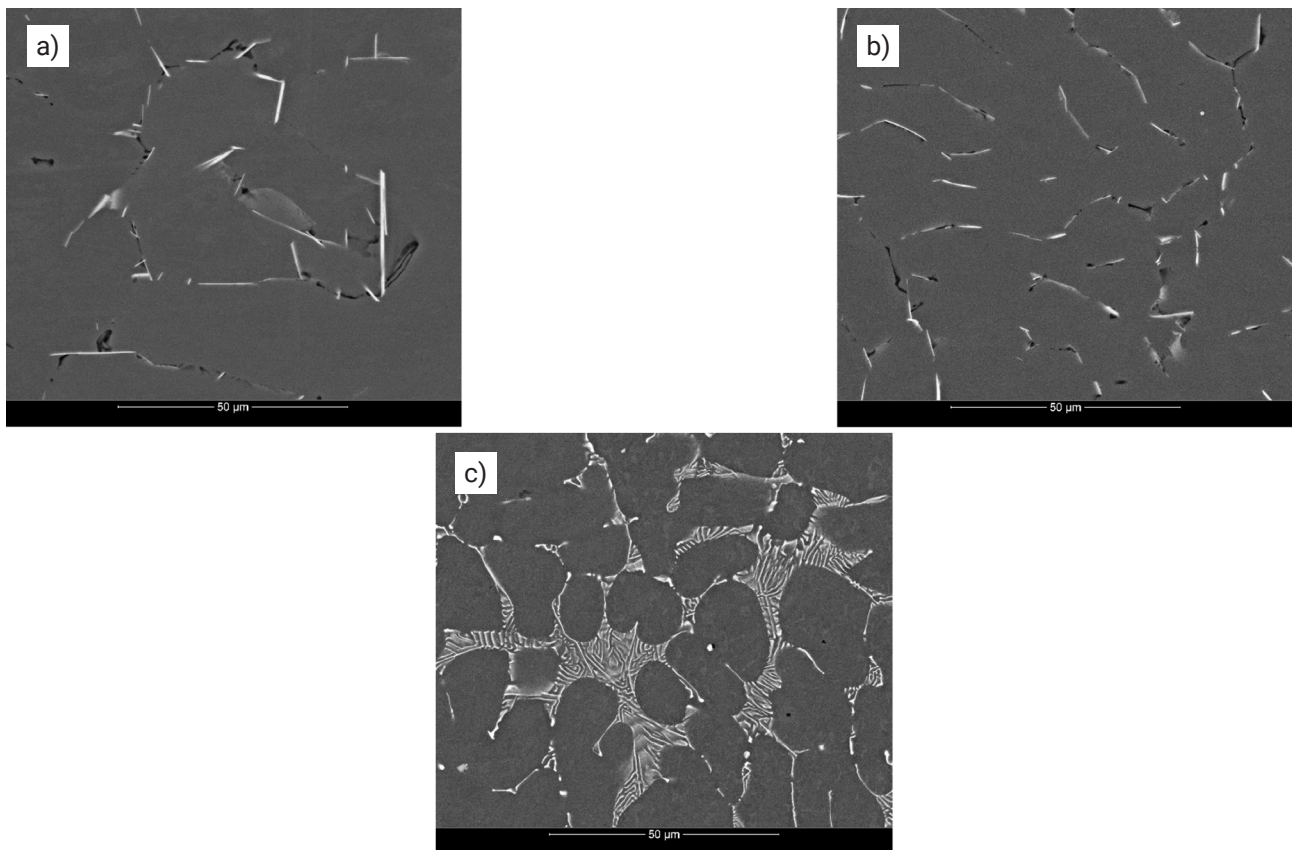
Alloy 3, characterized by a high content of Fe and Mn and significantly lower concentrations of Si and Mg compared to the other two alloys, showed a high density of Chinese-script  $\alpha\text{-Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$  intermetallic compounds (Figure 6c), with no evidence of other phases. The addition of Mn in this alloy has induced a morphological transformation of the acicular  $\beta\text{-Al}_5\text{FeSi}$  phases, previously observed in the Mn-free alloys, into the more branched and interconnected  $\alpha\text{-Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$  structures. Moreover, Alloy 3 appears to exhibit even lower SDAS values than Alloy 2, further suggesting a refined solidification structure that may contribute to its lower hot tearing susceptibility.

Based on the SEM observations, it can be concluded that the reduction in hot tearing susceptibility may also be attributed to the size, morphology and solidification sequence of Fe-based intermetallic and eutectic phases. In particular, the  $\alpha\text{-Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$  phase seems to promote grain coalescence, facilitating bridging between primary dendrites and enhancing the structural integrity during



**FIGURE 5:** Optical micrographs showing the grain structure of a) Alloy 1, b) Alloy 2 and c) Alloy 3.





**FIGURE 6:** SEM micrographs of a) Alloy 1, b) Alloy 2 and c) Alloy 3.

solidification and, finally, improving the castability of the alloy.

#### 4. CONCLUSIONS

The castability of the 6XXX series alloys depends on their chemical composition. CRC testing has shown that the sensitivity to hot tears is higher in alloys with 0.2 wt% Fe and decreases with increased iron content. Improvements in hot tearing resistance are also associated with the presence of manganese, which changes the shape of iron rich intermetallic compounds promoting the formation of the  $\alpha\text{-Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$  phase. This phase acts as a reinforcement for the aluminum matrix and can enhance the bridging between grains.

Furthermore, the study suggests that thermodynamic simulation and the use of the Kou index can provide valuable insights into the casting of alloys. Experimental testing clearly matches the preliminary simulation results and shows the power of the proposed predictive model.

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only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

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# ECO-FRIENDLY DEMETALLISATION OF METALLISED ACRYLONITRILE-BUTADIENE-STYRENE (ABS) BY USING BIOGENIC LIXIVIANTS

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## ABSTRACT

A novel environmental process for the demetallisation of metal coated (Cu, Ni and Cr) acrylonitrile-butadiene-styrene (ABS) was developed. Different biogenic lixiviants were generated and combined to carry out the indirect bioleaching tests on different formats of metallised ABS waste. The best bioleaching conditions were obtained for a high metal dissolution (Cu and Ni), the effective separation of metallic Cr and the obtention of unaltered ABS, suitable to be reused. The lixiviant solution can be reused several times to concentrate Cu and Ni. The process also includes the use of spent pickling acids for pH adjustment, which offered similar results compared to tests done with acids. That settles the circular economy approach in the Valencian sector to recover hazardous wastes.

## 1. INTRODUCTION

The metallisation process of non-conductive materials has been employed for decades. Initially, metallised objects were used exclusively for decorative applications due to the poor adhesion of the metal to the substrate. However, in the 1960s, technological advances in chemistry enabled the commercial metallisation of plastics. Currently, metallised plastics are widely used in the automotive industry, plumbing components, machinery, and electronic devices (Mallory & Hajdu, 1990).

Polypropylene was one of the first plastics used for these processes. Today, in addition to this material, others such as acrylonitrile-butadiene-styrene (ABS), polysulfone, polyethersulfone, polyetherimide, polytetrafluoroethylene (PTFE or Teflon), polyarylether, polycarbonate, polyacetal, and urea-formaldehyde, among others, are employed. The growing application of plastic metallisation is due to several advantages, including low cost, elimination of secondary operations, design flexibility, and weight reduction. Among all these materials, ABS is the most widely used in the metallisation industry. Its thermoplastic structure allows

for the selective removal of butadiene, generating micropores that facilitate metal coating adhesion in the subsequent chemical deposition stage.

Metallization of ABS plastic typically involves electroless deposition of copper or nickel, followed by electrolytic plating of nickel and chromium. After surface activation, a uniform layer of Ni<sup>0</sup> is chemically deposited, serving as a conductive base. Electroplating then builds up additional Cu<sup>0</sup>, then one or more layers on Ni<sup>0</sup> and a final Cr<sup>0</sup> layer for durability and aesthetics. All metals remain in their elemental state on the ABS surface, forming a continuous, adherent coating (Melentiev et al., 2022; Olivera et al., 2016; Suchentrunk, 1993; Uraz et al., 2019).

Metallised ABS pieces rejected by poor quality (10% to 30% of the production) represent a type of toxic waste whose management is particularly complex due to its composition (ABS plastic, Ni, Cu, Cr) (Walls et al., 2023). However, these residues constitute a potential secondary source of materials and have sparked growing interest in the research field known as urban mining (Van Eygen et al., 2015; Van Eygen et al., 2016).

The main industrial sectors that generate and utilize metallised components include the automotive and household appliances. Currently, there is no established commercial process for the recycling or recovery of these components. The predominant management approach involves exporting these wastes to other countries, where they undergo pyro-metallurgical processes or, in many cases, end up in landfills (Walls et al., 2023). No official national figures are available regarding the generation of these residues; however, in the Valencian Community, an estimated production of approximately 200 tons per year has been reported by a specialized company managing over 90% of these wastes (ACTECO, 2020).

Metallic coating on ABS (typically Cu, Ni and Cr) presents a high variability in metal proportions, but an approximation can be found elsewhere: 13.9 wt.% Ni, 7.9 wt.% Cu, 0.2 wt.% Cr, and 78.0 wt.% ABS (Walls et al., 2023). These metals can be dissolved in concentrated acids (sulfuric, nitric, hydrochloric), a process that also degrades ABS and hinders their reuse. Recent studies have shown that leaching with amine complexes under specific conditions ( $\text{NH}_3$  5.0 M,  $\text{NH}_4\text{OH}/(\text{NH}_4)_2\text{CO}_3$  ratio of 4:1, pulp density of 200 g/L, stirring at 400 rpm, temperature of 20°C, and a duration of 120 min) enables efficient extraction of >99% Cu and Ni. The use of  $(\text{NH}_4)_2\text{CO}_3$  as a buffering medium provided the highest recovery efficiency compared to other leaching agents such as  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{Cl}$ , whose yields were below 80% and 60%, respectively. The subsequent separation of Cu and Ni from the leach liquor was achieved through solvent extraction using LIX-84-I (Kim et al., 2018).

Regarding bioleaching, studies have been conducted using *Acidithiobacillus ferrooxidans* as the leaching agent, successfully removing Cu, Ni, and Cr from the polymeric matrix (Markovski et al., 2016). This process was carried out in specialized fermenters with 9K nutrient salt medium at a maximum temperature of 35°C. After 48 hours of agitation with aeration, the plastic particles were completely free of metallic coatings. The dissolved metals were separated by decantation and copper cementation, yielding a solid with ~98% Cu purity. Subsequently, the plastic residues were reprocessed through injection-moulding for new applications.

Despite the potential value of these residues, the number of specialized treatment facilities remains scarce globally. Available processes are primarily based on pyrometallurgical technologies, characterized by their high environmental impact and energy consumption. The complexity of these residues presents a significant technological challenge, with no single efficient treatment process developed to date. The SPAs (Spent Pickling Acids) represent another complex waste without current valorisation alternative. SPAs are acidic wastes, mainly generated in the galvanic industry, with high iron and chloride content resulting from surface treatment industries wastes. The pickling process with HCl, used to remove oxides and impurities from steel, generates ferrous chloride solutions. These high acidic solutions, with a high Fe content, could be utilized as leaching agents for the recovery of metals from metallised ABS.

Bio-hydrometallurgy, based on the use of microorganisms such as bacteria and fungi, is emerging as a sustainable strategy for metal extraction and recovery (John & Gurumurthy, 2025). These microorganisms utilize inorganic compounds as an energy source to produce selective biogenic leachates (Habibi et al., 2020; Tezyapar Kara et al. 2022). Other environmentally friendly alternatives have been sought through electrochemical treatments, which involve the use of electricity to cause specific reactions (Calvo, 2019; Grima-Carmena et al. 2023; Song & Zhao, 2018), however, the need to have the ABS surface unaltered for its reuse, makes the electrochemical approach unlikely suitable.

In the present study, the combination of SPAs and microorganisms, by performing an indirect bioleaching (from now on bioleaching), will be evaluated to optimize the valorisation of ABS. The proposed methodology, based on circular economy principles, offers a low environmental impact alternative to recover the metals contained in metallised ABS waste through the combination of two biogenic liquors and the valorisation of SPAs.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Iron (III) chloride ( $\text{FeCl}_3$ , Comsa, 40%), iron (III) sulfate hydrate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ , LabChem, test > 20%) and sulfuric acid ( $\text{H}_2\text{SO}_4$ , PanReac, ACS 96% reagent), Ferrozine/thioglycolate tablets, Lovibond water testing (IRON LR and IRON II LR).

Culture media: 0K solution (1 L  $\text{H}_2\text{O}$ , 3 g  $(\text{NH}_4)_2\text{SO}_4$  Scharlau ExpertQ® ACS Reag; 0.1g KCl Merck GR for analysis; 0.5 g  $\text{K}_2\text{HPO}_4$  Panreac ACS; 0.5 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  Merk ACS; 0.01 g  $\text{Ca}(\text{NO}_3)_2$  Sigma-Aldrich BioXtra >99.0%; 9K solution (700 ml 0K solution + 300 mL  $\text{Fe}^{2+}$  solution (44.2 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  Scharlau ExpertQ®); elemental sulfur powder (Scharlau flower Pharmapur®). All reagents were used as received and stored at room temperature (RT).

The bacteria used for the generation of the leaching agent ( $\text{Fe}^{3+}$ ) and the acidic medium ( $\text{H}_2\text{SO}_4$ ) were *Acidithiobacillus ferrooxidans* (DSM 14882) and *Acidithiobacillus thiooxidans* (DSM 504), respectively. The provided strains were reactivated in the culture medium recommended by the supplier.

The concentration of metals was determined by Inductively Coupled Plasma Optical Emission spectrometry (ICP-OES) using a 160-900 nm spectral range (PerkinElmer OPTIMA 2000™ with dual-view optics spectrometer).

Materials used for the preparation of biogenic liquors: XS pH meter, XS ORP electrode, temperature sensor, orbital shaker, Jenway UV-Visible Spectrophotometer (iron measurements), jacketed glass bioreactor and lid, stirrer, aeration and recirculation pump (peristaltic), glass bubbler, water bath and recirculation pump, settling tank, vacuum filtration equipment, 45 µm filter.

SPA sample was provided by a local galvanizing company. The whole pieces of waste ABS were provided by a local surface treatment company (W-ABS). The shredded waste ABS (S-ABS) was provided by a local waste management company.



## 2.2 Generation of the biological lixiviant

### 2.2.1 Preparation of leaching liquor generated by *A. ferrooxidans* (F3)

For the culture media, a 9K medium was prepared mixing 2 different solutions. 0K solution reagents are mixed in water and then sterilised in autoclave at 121°C for 20 minutes (Brock, T.D. et al., 2018). Next, Fe solutions were prepared with a concentration of 8.84 g Fe<sup>2+</sup>/L. The pH was adjusted, and the solution was sterilised in autoclave at 121°C for 12 min. The mixed solution is, finally, proven to be at pH 1.8-2.

Measurements for Fe concentrations are determined by spectrophotometry (562 nm). Specific tablets Ferro-zine/thioglycolate were used to calculate Fe<sup>3+</sup> by total Fe and Fe<sup>2+</sup>determination.

The Fe-stream was inoculated with *A. ferrooxidans* (5-10%, v/v) in a jacketed bioreactor with mechanical stirring (150 rpm) and aeration, allowing recirculation of the leaching agent and very short incubation times. As a result, the leachant is obtained in less than a week. In this first stage, the bacteria were fed with the 9K culture medium with a defined concentration of Fe<sup>2+</sup> for 33 days at 27°C. The system was controlled and monitored by pH and ORP, with characteristic rising curves for both parameters (pH peak between 2-3 days and subsequent stabilisation of ORP). The liquid was decanted to purge, and the supernatant was collected. Finally, it was vacuum-filtered to remove micro-organisms (Rawlings, D.E., 2005).

For *A. ferrooxidans* stream, three consecutive cycles were performed, resulting in redox values close to 600 mV and leaching agents at very high Fe<sup>3+</sup> concentrations (11 g/L). The optimum initial pH was found to be 1.8 to achieve the characteristic curves (Figure 1 a) and b)). Fe<sup>2+</sup> depletion was found to occur at a maximum of 2 days after feeding.

### 2.2.2 Preparation of leaching liquor generated by *A. thiooxidans* (T0)

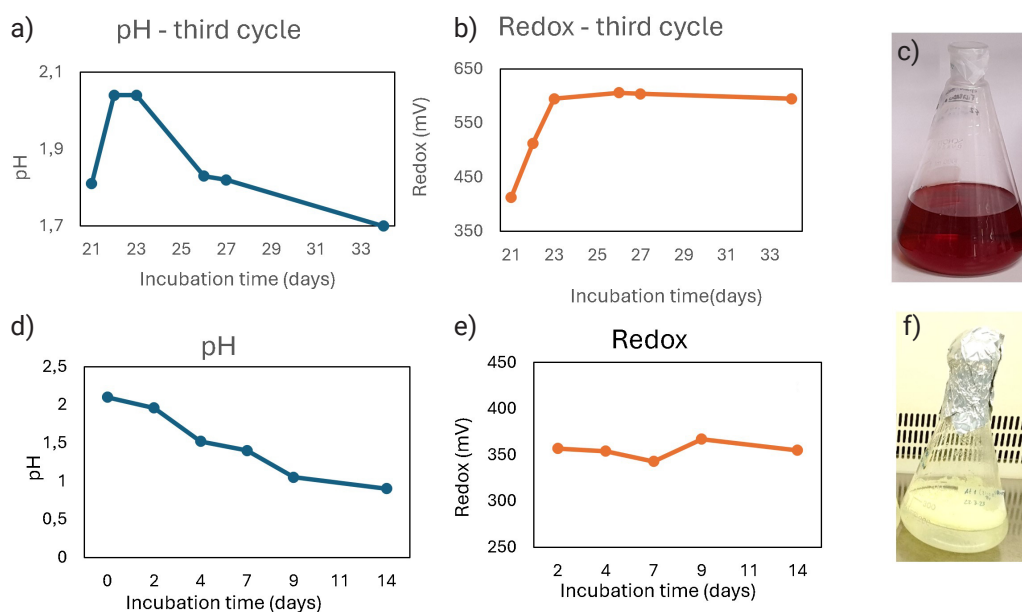
For the culture media, a 0K medium was prepared and the pH was adjusted to 4.2. Then, the solution was sterilised in an autoclave at 121°C for 20 minutes (Brock, T.D. et al., 2018). For the sterilisation of the elemental sulfur powder, the corresponding amount was placed in glass bottles, moistened with a few drops of water and heated for 3 hours at 90-100°C in a bath for 3 consecutive days. Before use, the sulfur was aseptically placed on the surface of the sterilised liquid basal medium.

The equipment used for monitoring bacterial growth is through pH measurements, since for *A. thiooxidans* a decrease in pH means that the bacteria are metabolising sulfur.

The preparation of the liquor was carried out in 500 mL Erlenmeyer flasks, where a volume of 200 mL of 0K medium and 2g of elemental sulfur was added. Then, an amount of inoculum equivalent to a volume of 5-10% (v/v) of the medium was added. Subsequently, each inoculated medium was incubated for 14 days at 27°C under agitation at 100 rpm until the optimum pH was reached. At the end of the test, the sulfur was decanted into the same flask and filtered to remove the remaining elemental sulfur powder from the medium and facilitate sterilisation of the liquid obtained. After sterilisation, it was vacuum-filtered (pore of 45 µm). Finally, a liquor was obtained with a pH < 1 (Rawlings, D.E., 2005).

After 14 days of incubation, a decrease in pH below 1 was observed, resulting in the formation of this acidic leaching liquor. This indicates that the bacteria fully metabolized the elemental sulfur (S<sup>0</sup>). Regarding the redox values, only slight variations were noted, leading to values closely resembling the initial ones (Figure 1 d) and e)).

The resulting product was filtered through a 45 µm filter to remove the bacteria from the medium, yielding a liquid



**FIGURE 1:** Variation during 33 days of (a) pH and (b) redox potential of the third cycle liquor obtained with *A. ferrooxidans*, and (c) aspect of leaching solution (F3) obtained with *A. ferrooxidans*; variation during 14 days of (d) pH and (e) redox potential of the acidic liquor obtained with *A. thiooxidans*., and (f) aspect of leaching solution (T0) obtained with *A. thiooxidans*.

with a pH of 1 (T0). Subsequently, this solution was used as a leaching liquor to perform the biological leaching for the demetallisation of ABS.

### 2.3 Leaching tests

Leaching tests were carried out in glass beakers at RT except for the tests done at 80°C. All tests included a lid to minimize the evaporation and magnetic stirring at 300 rpm. During the tests, samples of 0.5 mL were taken at each defined time, then they were diluted 100-fold and analysed for metal concentrations via ICP-OES. Samples were stored in a refrigerator until their analysis. The calculation of the leaching yield for each metal was the following:

$$\text{Yield (\%}_{\text{metal}}) = g_{\text{metal}} / g_{\text{initial}} \cdot 100 (\%) \quad (1)$$

$$g_{\text{metal}} = \text{ICP}_{\text{metal}} (\text{g/L}) \cdot \text{Dilution} \cdot \text{Vol}_{\text{liquid}} (\text{L}) \quad (2)$$

Where  $g_{\text{initial}}$  is the mass of different types of ABS weighted at the start of each test,  $g_{\text{metal}}$  are the grams of metals in the leaching solution, calculated as the concentration obtained in the ICP (g/L, considering the dilution) and the volume of the liquid solution (L) in each test.

### 2.4 Spent Pickling Acids (SPAs)

Spent Pickling Acids (SPAs) are generated by surface treatment industries. These wastes are considered a highly polluting effluent since they are composed of ferrous/ferric chloride in hydrochloric acid. The amount of acid and iron depends on the process of each company, which may extend the life of the baths by adding more acid or extending the pickling immersion time when the iron content is high. Currently, no effective valorisation technologies exist

for this waste. In this study, a potential valorisation in ABS recycling is proposed. A sample of SPA was provided by a local company. It was used in this study in demetallisation for the pH adjustment (see section 3.3.3). The characterization gave the following main results: pH < 0, 216 g/L Cl<sup>-</sup>, 107.2 g/L Fe, 1.4 g/L Zn; metals such as Ni, Cr, Cu and Al in the range of ppm.

### 2.5 Characterization and pretreatment of ABS wastes

ABS waste was received both in the form of whole pieces (W-ABS) and shredded form (S-ABS) (Figure 3 a) and b), respectively). The whole pieces were obtained from the defective line of a local automotive coating company, while the shredded form was obtained from a local waste management company.

In order to effectively leach the W-ABS, the whole pieces were manually fragmented in smaller pieces that could fit in the beakers for the leaching tests. Regarding the S-ABS, since the metallic layer of ABS consists largely of Ni, magnetic, a physical pretreatment using magnetic separation can be performed (Figure 3 c)). This process yields to a 70% (% weight) of a fraction with a small amount of metal, i.e. almost clean shredded plastic (CS-ABS, Figure 3 e)) and about a 30% (% weight) of mostly metallic shredded ABS (MS-ABS, Figure 3 d)). Due to the high variability of these wastes, an elemental analysis was conducted in triplicate to establish a reference composition. The characterization of the pretreated ABS using aqua regia, after 3 repetitions, yielded the values shown in Figure 3.

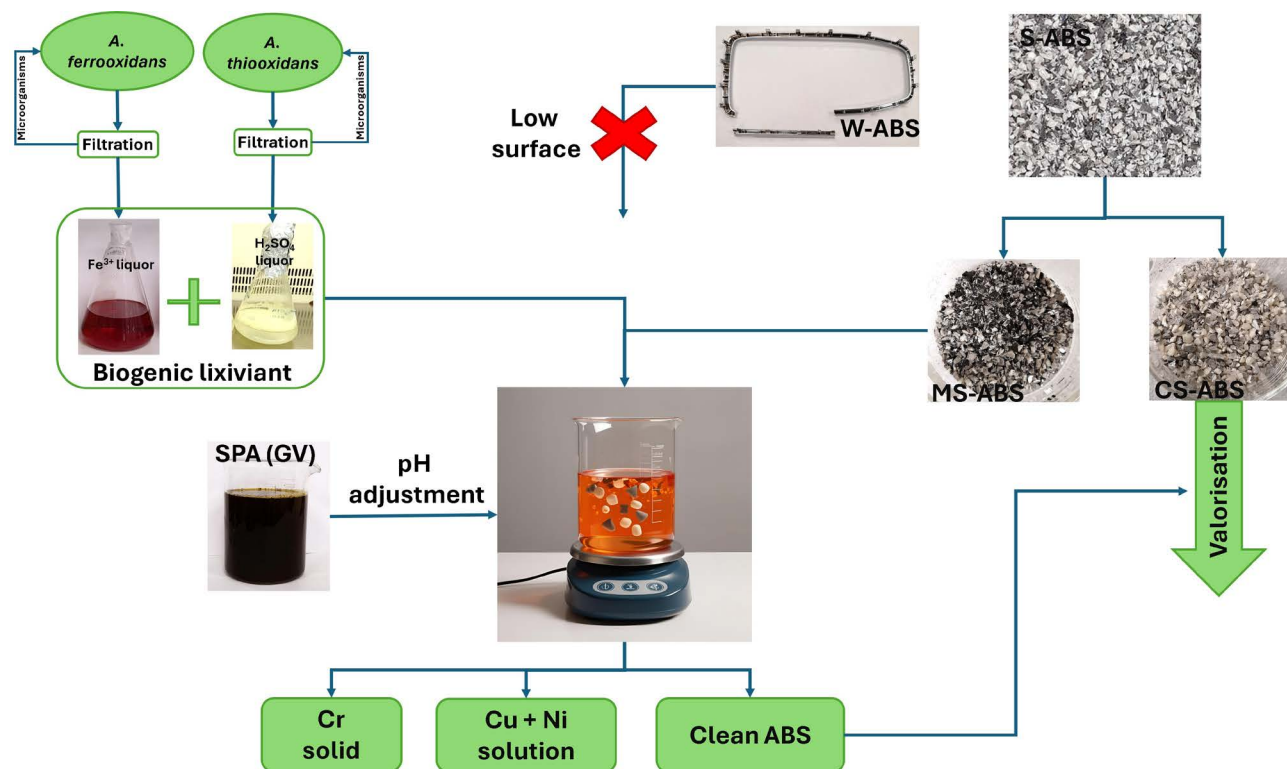


FIGURE 2: Scheme of the indirect bioleaching process.

Due to the low metal content in CS-ABS, the leaching tests in this study were done using the MS-ABS and the W-ABS. Optimal extraction yields of each fraction were defined as those close to the reference composition presented in Figure 3.

### 3. RESULTS AND DISCUSSION

#### 3.1 Mechanism of metal dissolution

The  $\text{Fe}^{3+}$  ions act as a strong oxidizing agent, oxidizing the metals present in the metallised ABS by increasing their oxidation state to a soluble form. This process leads to the dissolution of other metals with lower standard oxidation potential, reducing  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions. The reduced  $\text{Fe}^{2+}$  ions further participate in the Fenton reaction to regenerate  $\text{Fe}^{3+}$  ions, maintaining a continuous  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox cycle and facilitating metal dissolution (Yken et al., 2020).



Metallic copper and nickel oxidize slowly by the action of water (humidity) and oxygen (air) generating a surface covering layer constituted by their hydroxides and/or oxides. These compounds passivate the metal hindering further corrosion. Forced leaching can be realized in the presence of sulfuric acid and oxidizing agents such as ferric sulfate (Barlett, 1998; Bradley et al., 1992; UTEXAS, 2016) which reacts via the following stoichiometry:



The oxidation of metallic Cr with iron is difficult (Equation 7). In addition, metallic Cr has a passivating layer formed by  $\text{Cr}_2\text{O}_3$  which makes it even more difficult its leaching (Milazzo et al., 1978; Reartes et al., 1995).

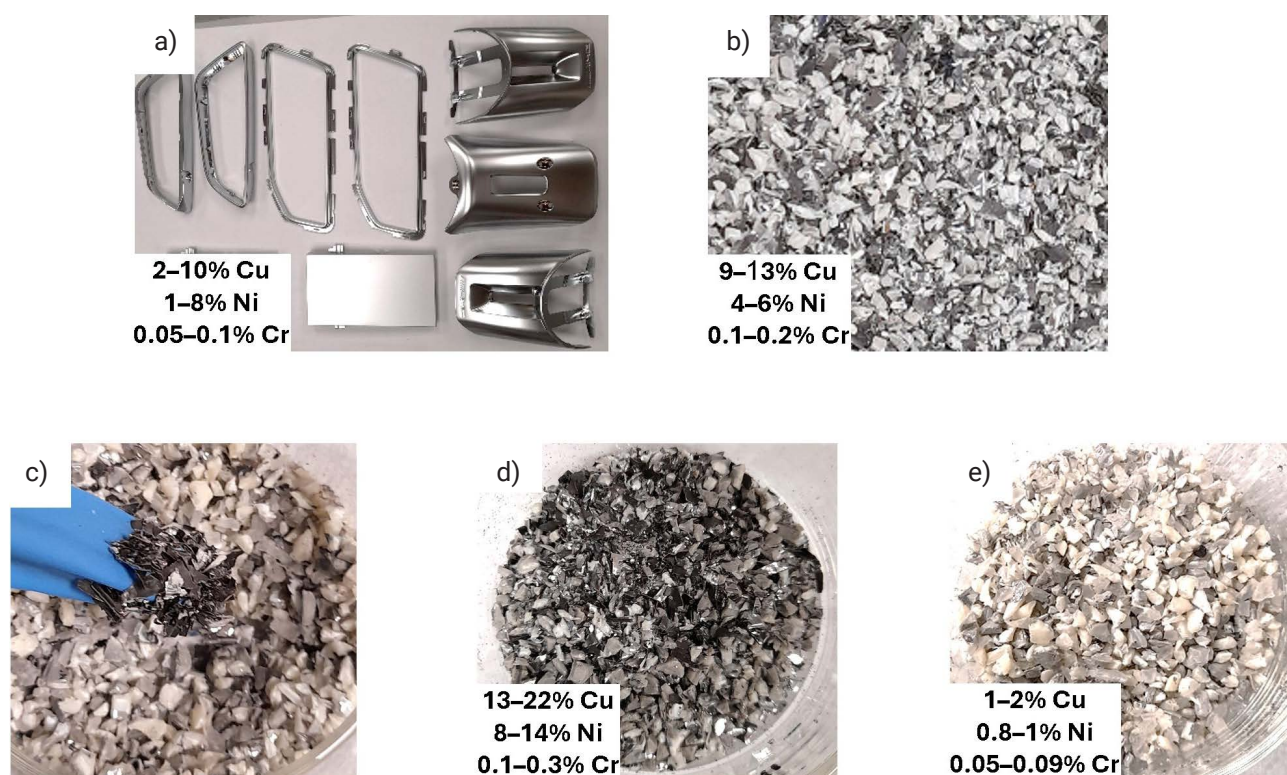


The bioleaching reactions presented in this work are performed in acidic media, since it is the media where the selected microorganisms grow and work. Thus, it is expected a low Cr dissolution during the tests.

#### 3.2 Preliminary leaching tests using synthetic lixiviants

##### 3.2.1 Leaching tests for Whole-ABS

Whole pieces of ABS were first treated using synthetic lixivants containing different amounts of Fe (III), to confirm that Cu, Ni and Cr of W-ABS could be leached using  $\text{Fe}^{3+}$ . The liquid-to-solid ratio (L/S) and leaching time are two important parameters to be considered. There are works in the literature where the Cu-containing waste (waste PCBs) is treated using biogenic lixivants to recover Cu and they use a L/S ratio of 100 mL/g or even higher, and a leaching time from 24 hours to 25 days. (Yken et al., 2020; Li et al., 2020; Shina et al., 2018; Iglesias-González et al., 2022). In the following tests, the L/S ratio and the leaching time were fixed and set to a reduced value; As W-ABS presents less quantity of Cu and Ni than PCBs, for preliminary tests the L/S ratio was adjusted to 20 mL/g and they were treated



**FIGURE 3:** Aspect and metallic composition (% w/w) of (a) whole pieces of metallised ABS (W-ABS) and (b) shredded metallised ABS (S-ABS); (c) shredded metallised ABS being magnetically pretreated; aspect and metallic composition (% w/w) of (d) metallic fraction (MS-ABS); and (e) clean fraction (CS-ABS).



for 4 h with continuous stirring at room temperature (RT). The results are shown in Table 1.

W-ABS shows a greater variability in metal composition (Figure 3), mainly due to the dependence of the amount of metallic coating with the morphology of the surface. Besides, only the outer part of the piece (and the sides in the manually cut parts) is in contact with the lixiviant; this represents a low reaction interface and therefore an inefficient mass transfer among the piece and the lixiviant. Therefore, the next tests will be carried out using the shredded ABS. The metallic composition variability of ABS could be the explanation for the differences between the results obtained with  $\text{FeCl}_3$  and  $\text{Fe}_2(\text{SO}_4)_3$ .

As it can be observed, no metals were leached without the presence of Fe (III). When the concentration of  $\text{FeCl}_3$  was 0.3 M a maximum Cu leaching was obtained, but not for Ni. When the concentration of  $\text{FeCl}_3$  was 0.5 and 1 M, the results in leaching capacity were almost the same for Cu and Ni, probably reaching the maximum demetallisation for this format of waste. Different behaviour was observed when  $\text{Fe}_2(\text{SO}_4)_3$  was used as  $\text{Fe}^{3+}$  source, presenting a maximum quantity of dissolved Cu when its concentration was 1 M. At first,  $\text{FeCl}_3$  shows higher extraction yields. Nevertheless,  $\text{Fe}_2(\text{SO}_4)_3$  is the chemical compound produced by the selected microorganisms; thus, it will be used in next preliminary tests.

The results obtained in these preliminary tests showed that no significant difference was observed when using  $\text{FeCl}_3$  or  $\text{Fe}_2(\text{SO}_4)_3$  as  $\text{Fe}^{3+}$  source in metals dissolution. Both were capable of leaching Cu and Ni from the ABS waste provided in similar proportions, demetallising and cleaning it for its reuse.

Regarding Cr, it mainly remains suspended as small particles in the media (Figure 4 b) and c)), so the presence in the leaching liquor was low. The same behaviour was observed in all the following tests. Therefore, the data referred to Cr are not shown in the following results for simplicity.

Chromium coatings are commonly applied to protect different surfaces due to their high resistance to oxidizing agents and acids (Milazzo et al., 1978; Reartes et al., 1995). In our experiments, we observed that chromium is minimally dissolved under the bioleaching conditions employed. This suggests that the demetallisation of metallised ABS likely initiates at the edges or corners of the pieces, where the underlying nickel and copper layers are exposed to the

bioleaching medium. Consequently, the leaching solution can penetrate the interface between the ABS polymer and the metallic layers, primarily attacking and dissolving copper and nickel. So, it is easier and faster to dissolve Cu and Ni coating S-ABS and MS-ABS than W-ABS pieces.

It was observed in preliminary studies that the Cu and Ni contained in W-ABS are not leached efficiently, even when used rough conditions. However, when the tests were performed using S-ABS and MS-ABS, the dissolution and demetallisation occurred faster, even in mild conditions. So the size of ABS particles influences the efficiency and time extension of the process.

### 3.2.2 Leaching tests using Shredded-ABS

#### Tests at higher temperature using S-ABS

Considering S-ABS have larger contact surface than W-ABS, it was decided for preliminary tests to set more aggressive conditions, thus the following tests were held at L/S 20 mL/g for 1 hour at 80°C. The results shown in Table 2 indicate that the increase in temperature combined with high acidic media does not mean a greater increase in metal leaching yield. Whereas, looking to the metallic composition of S-ABS (Figure 3), the highest concentration of iron combined with high acidic media extracts more metal ( $\approx 50\%$  of Cu leached;  $\approx 100\%$  of Ni leached, Table 2). However, the surface of the ABS after the heat treatment presented a significant deterioration in terms of colour and probably mechanic characteristics (Figure 4 d)), that would make the recovered ABS not suitable for an industrial reuse, therefore the heat treatment was discarded in all tests.

#### Tests at room temperature using MS-ABS

The following test was held in synthetic bioleaching (mild) conditions (48 h at RT;  $[\text{Fe}_2(\text{SO}_4)_3] = 0.2 \text{ M}$ ; and  $[\text{H}_2\text{SO}_4] = 2 \text{ M}$ ). Since MS-ABS contains the highest quantity of metals (Figure 3), the L/S ratio was increased to 40 mL/g. Samples were taken each 24 h. The quantity of metals leached after 48 h of treatment was high using these conditions: 29.8% of Cu and 18.2% of Ni. The reference quantities of Cu and Ni (Figure 3) obtained for MS-ABS are a bit lower to that obtained in this test. This result remarks the great variability in the composition of the material in study.

Otherwise, an increase in L/S ratio showed a better performance in Cu and Ni dissolution. Also, a higher reaction time is better for the process, increasing Cu and Ni dissolution. Since the iron content in biogenic lixiviant is limited, the combination of acid and iron along with greater L/S ratio or time is crucial for a high leaching yield.

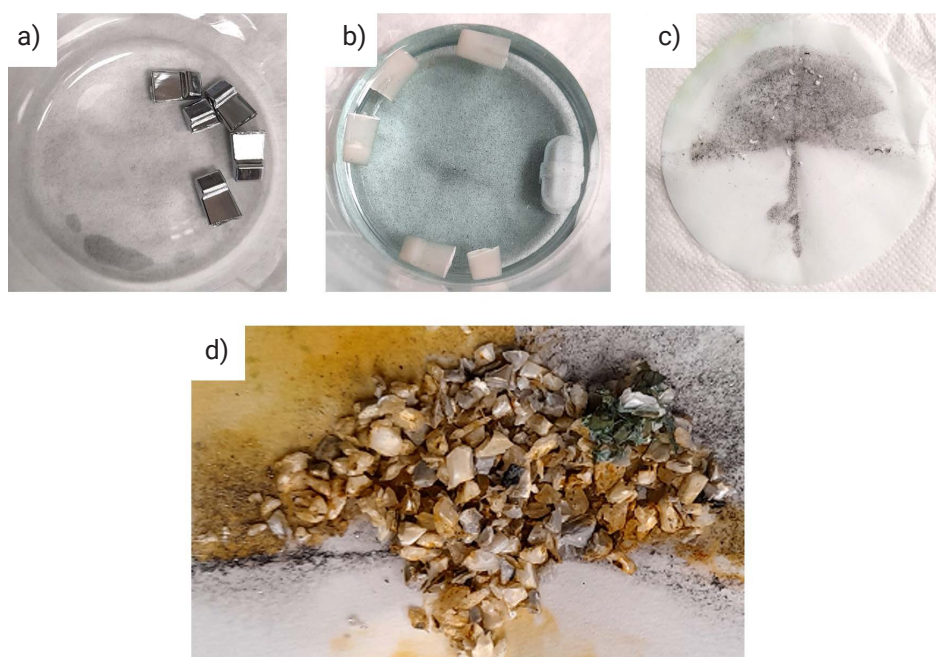
**TABLE 1:** Conditions and results of metal leaching yield obtained for W-ABS. % were calculated as stated in Equation 1.

| $[\text{H}^+]$<br>(M) | $[\text{FeCl}_3]$<br>(M) | $[\text{Fe}_2(\text{SO}_4)_3]$<br>(M) | Cu<br>(%) | Ni<br>(%) | Cr<br>(%) |
|-----------------------|--------------------------|---------------------------------------|-----------|-----------|-----------|
| 2                     | 0                        | 0                                     | 0         | 0.1       | <0.05     |
| 0.5                   | 0.3                      | 0                                     | 10.42     | 4.30      | 0.20      |
| 1                     | 0.5                      | 0                                     | 9.71      | 6.84      | 0.10      |
| 0                     | 1                        | 0                                     | 9.99      | 6.39      | 0.20      |
| 0.1                   | 0                        | 0.125                                 | 5.72      | 3.14      | <0.05     |
| 0.5                   | 0                        | 0.25                                  | 4.95      | 4.74      | <0.05     |
| 0.5                   | 0                        | 0.5                                   | 11.02     | 4.00      | <0.05     |

**TABLE 2:** Conditions and results of metal leaching yield obtained for S-ABS at 80°C for 1 h. % were calculated as stated in Equation 1.

| $[\text{H}_2\text{SO}_4]$<br>(M) | $[\text{Fe}_2(\text{SO}_4)_3]$<br>(M) | Cu<br>(%) | Ni<br>(%) | Cr<br>(%) | Temp<br>(°C) |
|----------------------------------|---------------------------------------|-----------|-----------|-----------|--------------|
| 0.5                              | 0.5                                   | 5.10      | 3.24      | < 0.05    | 80           |
| 1                                | 0.5                                   | 6.63      | 4.51      | < 0.05    | 80           |
| 1                                | 0.25                                  | 1.4       | 3.12      | < 0.05    | 80           |
| 2                                | 0                                     | 0.02      | 0.5       | < 0.05    | 80           |





**FIGURE 4:** Aspect of (a) W-ABS; (b) the final leaching solution; (c) the filtered Cr; (d) MS-ABS treated at 80°C, showing a poor quality which implies that it would not be reused.

### 3.3 Leaching tests using biogenic lixivants

#### 3.3.1 Defining bioleaching conditions

The bioleaching conditions, using real biolixiviant, for MS-ABS waste were evaluated. As a first approximation, two tests were done to verify if 24 h using a L/S ratio of 20 mL/g would be enough to obtain more than 10% of Cu leached. Two leaching liquors were used: F3 ( $[\text{Fe}^{3+}] = 0.4 \text{ M}$ ;  $\text{pH} = 2$ ) or a mixture of F3 + T0 (1:1 v/v;  $[\text{Fe}^{3+}] = 0.2 \text{ M}$ ;  $\text{pH} = 1.5$ ). The quantity of metals leached after 24 h using F3 was 4.1% of Cu and 0.1% of Ni. When the mixture of F3+T0 was used, the quantity of metals leached after 24 h was 3.7% of Cu and 2.0% of Ni.

Results show that, in all of the liquors, the proportion of leached metals was low (less than 25% of Cu and Ni present in the samples), taking into account the reference values (Figure 3). As a consequence, it was necessary to increase the leaching time as well as the L/S ratio for the next tests. The following tests performed evaluated the effect of pH and the need of changing leaching liquor containing iron. L/S ratio was increased to 100 mL/g (50 mL of lixiviant and 0.5 g of MS-ABS), at RT for 96 hours. The conditions used for each test are shown in Table 3.

The concentration of metals was analysed each 24 h. The pH experimented variations for each test, so pH was adjusted when necessary. In Figure 5 (a) the aspect of the solutions during the tests each 24 h is shown. The time evolution of the leaching reaction is shown in Figure 5 (b) and (c), in which the calculated percentages of leached metal are related to the total mass of MS-ABS added (Equation 1).

As it can be observed in Figure 5 (b) and (c), in all tests the proportions of Cu and Ni leached at 96 h, or less, are higher than those obtained as reference values (Figure 3). Again, this is clear evidence of the great variability of the MS-ABS. In any case, the stabilization in the amount of leached metal as well as the demetalized appearance of the processed plastic indicate that leaching has been complete.

The tests demonstrated that only the fact of maintaining a stable pH of 1.5 is not enough to increase Cu and Ni extraction, while Cr remains largely insoluble (<0.02%) (test A). The highest metal recovery was observed in Tests C and D achieving, respectively, Cu dissolution of 51.16 and 41.43%; tests C and D showed also the higher rate for Ni dissolution of 25.99% and 19.48%, respectively. Solution renewal impacted on metal recovery; continuous leaching

**TABLE 3:** Conditions used for tests A, B, C and D.

| Test | L/S (mL/g) | Lixiviant          | pH  | $[\text{Fe}^{3+}] \text{ (M)}$ | Liquor change | pH adjustment |
|------|------------|--------------------|-----|--------------------------------|---------------|---------------|
| A    | 100        | F3 + T0<br>1:1 v/v | 1.5 | 0.2                            | no            | yes           |
| B    | 100        | F3                 | 2   | 0.4                            | no            | no            |
| C    | 100        | F3 + T0<br>1:1 v/v | 1.5 | 0.2                            | yes           | no            |
| D    | 100        | F3                 | 2   | 0.4                            | yes           | no            |

without replacement (Tests A and B) led to steady metal dissolution over 96 hours, while frequent solution changes (tests C and D) resulted in rapid extraction within the first 48 hours, followed by a decline. In all cases, peak efficiency is taken when the plateau is reached. Peak efficiency was reached at different times in each test: 24 h for test A, 48 h for tests C and D, and 72 h for test B.

While changing frequently the leaching liquor was the most efficient leaching method, it is not considered an ecofriendly alternative, due to the high production of liquid waste. Taking this into account, alternatives A and B are considered more sustainable; so, comparing both tests, conditions of test A are considered the optimum for several reasons: 1) Cu and Ni were leached in higher quantities in less time; 2) less  $\text{Fe}^{3+}$  was present; 3) no sludge (Figure 5 (a), tests A and B) was generated during the process. Consequently, conditions of test A were used in the next studies.

### 3.3.2 Reusing bioleaching liquor for MS-ABS

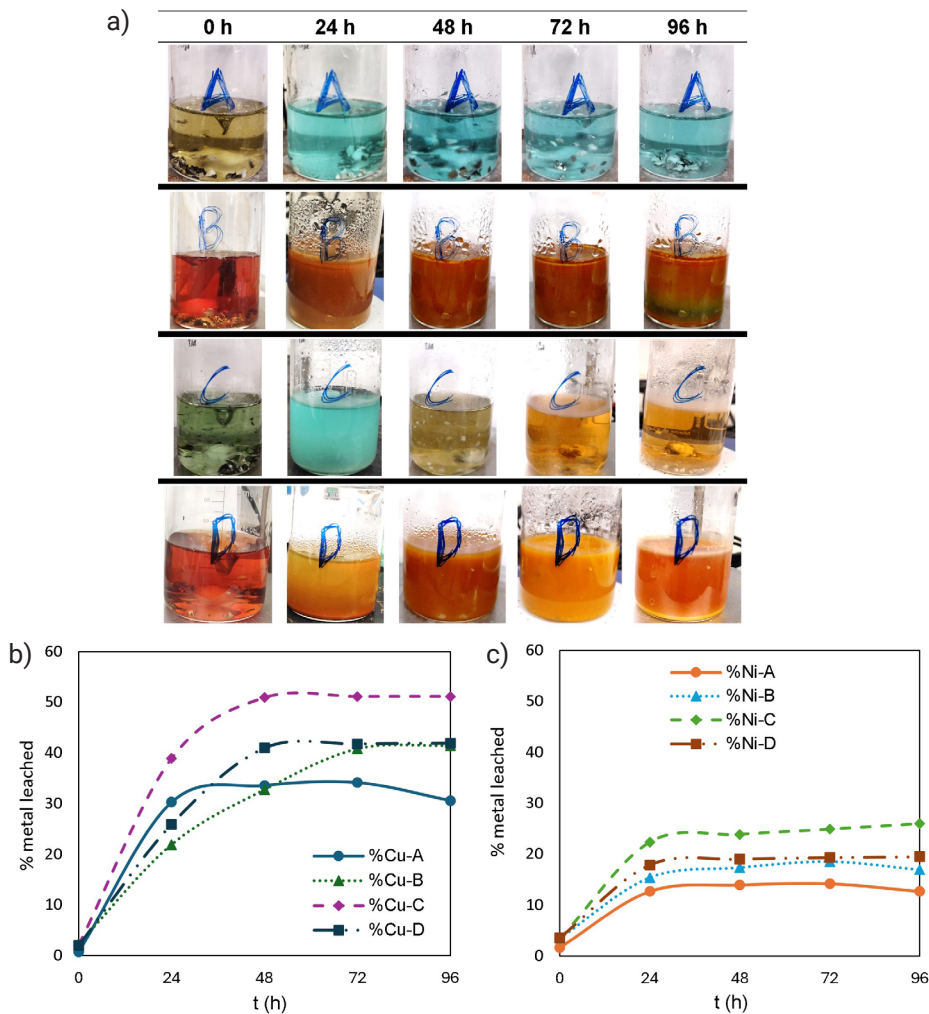
Experiments were conducted to evaluate the reuse of bioleaching mixture by increasing the ABS added to the solution each 24 h (10% of total mass each 24 h, 0.1 g each

24 h). The tests were performed under the following conditions: MS-ABS (0.51 g) was leached in a mixture of F3 + T0 (1:1 v/v;  $[\text{Fe}^{3+}] = 0.2 \text{ M}$ ;  $\text{pH} = 1.5$ ), L/S = 100 mL/g, without solution replacement, adjusting every 24 h to  $\text{pH} = 1.5$  by using  $\text{H}_2\text{SO}_4$  4 M. The experiments lasted 96 hours. Figure 6 shows the proportions of metals leached, measured each 24 h.

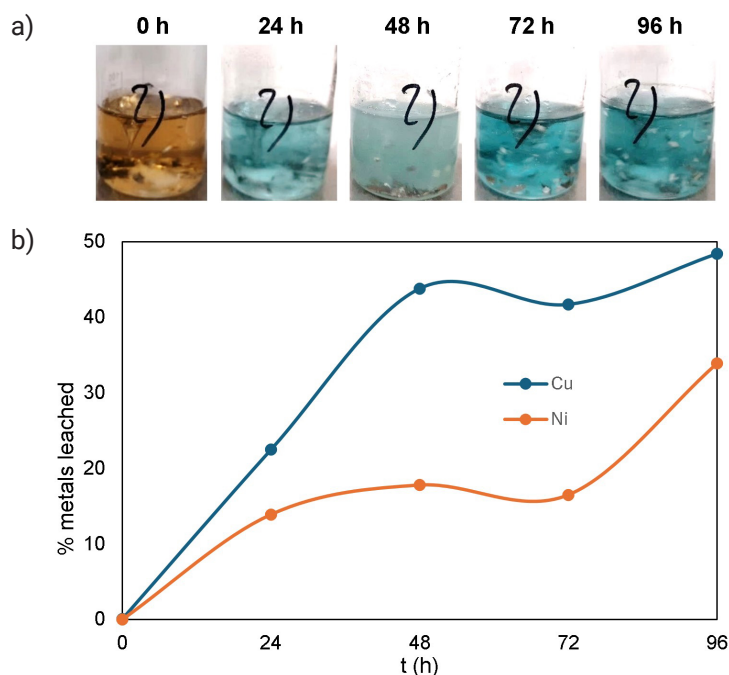
The reuse of bioleaching liquor for magnetically pretreated ABS waste shows distinct trends in metal dissolution over time. Also, in this test the proportions of Cu and Ni leached at 96 h, or less, are higher than those obtained as reference values (Figure 3), as observed in previous tests. Again, this is clear evidence of the high variability of the MS-ABS. In any case, the progressive increase in Cu and Ni in solution indicates that the liquor can be used in several successive cycles.

At 24 h, Cu dissolution reaches 22.7% (0.116 g) and Ni 13.7% (0.07 g). After 48 h, Cu dissolution rises sharply to 44.13% (0.271 g) and Ni dissolves to 17.9% (0.110 g).

At 72 h, Cu leaching not increased and remained to 42.1% (0.302 g) and Ni dissolution increased to 16.7% (0.120 g). In that moment, a significant quantity of  $\text{H}_2\text{SO}_4$



**FIGURE 5:** (a) Aspect of the solutions each 24 h; time evolution of leaching process of (b) Cu and (c) Ni for each test: A (circles and solid line), B (triangles and dotted line), C (diamonds and dashed line) and D (squares and dash-dots line). The proportions of dissolved metals are related with total mass of MS-ABS added in each test. % were calculated as stated in Equation 1.



**FIGURE 6:** (a) Aspect of the solutions each 24 h; (b) time evolution of the proportions of metals leached. % were calculated as stated in Equation 1.

4 M (10 mL) was needed to decrease the pH to 1.5. By 96 h, Cu reaches its highest concentration at 48.7% (0.401 g) and Ni 34.1% (0.281 g).

Overall, the data suggest that the  $\text{Fe}^{3+}$  contained in the liquor is sufficiently high to continue leaching metals, if pH is continuously adjusted.

### 3.3.3 Using SPAs for pH adjustment in MS-ABS tests

As stated above, the optimal eco-friendly conditions for ABS demetallisation were established, so experiments were conducted to evaluate the feasibility of using SPA, an acid waste which contains Fe (II) and HCl, to adjust the pH of the leaching solution. These experiments combine bioleaching and circular economy principles. The experiments were performed under the following conditions: magnetically pretreated crushed ABS waste (MS-ABS, 0.52 g) was leached in a mixture of F3 + T0 (pH = 1.5), L/S = 100 mL/g, with no solution replacement, adjusting the pH using SPA. The experiments were carried out up to 96 hours. Figure 7 shows the proportions of metals leached, measured each 24 h.

The use of SPA waste to adjust the pH of bioleaching liquor for MS-ABS demonstrates notable performance in metal dissolution. The addition of SPA to adjust pH showed a similar behaviour when compared with  $\text{H}_2\text{SO}_4$  adjustment. Once again, in this test the proportions of Cu and Ni leached at 96 h, or less, are higher than those obtained as reference values (Figure 3), as observed in previous tests. This result highlights the uttermost variability of the metals composition in MS-ABS samples. As happened in Figure 5 (b) and (c), the stabilization in the amount of leached metal after 48 h, as well as the demetallised appearance of the processed plastic indicate that leaching has been complete.

As can be seen in Figure 7, at 24 h Cu dissolution reaches 21.5% (0.112 g) and Ni 13.8% (0.072 g). By 48 h, Cu concentration continued increasing to 37.5% (0.195 g) and Ni to 21.3% (0.111 g).

At 72 h, Cu levels slightly decrease to 35.8% (0.186 g) and Ni 19.2% (0.100 g), suggesting a possible slowdown in metal leaching. By 96 h, Cu reaches its highest concentration at 41.5% (0.216 g), while Ni increases to 24.2% (0.126 g).

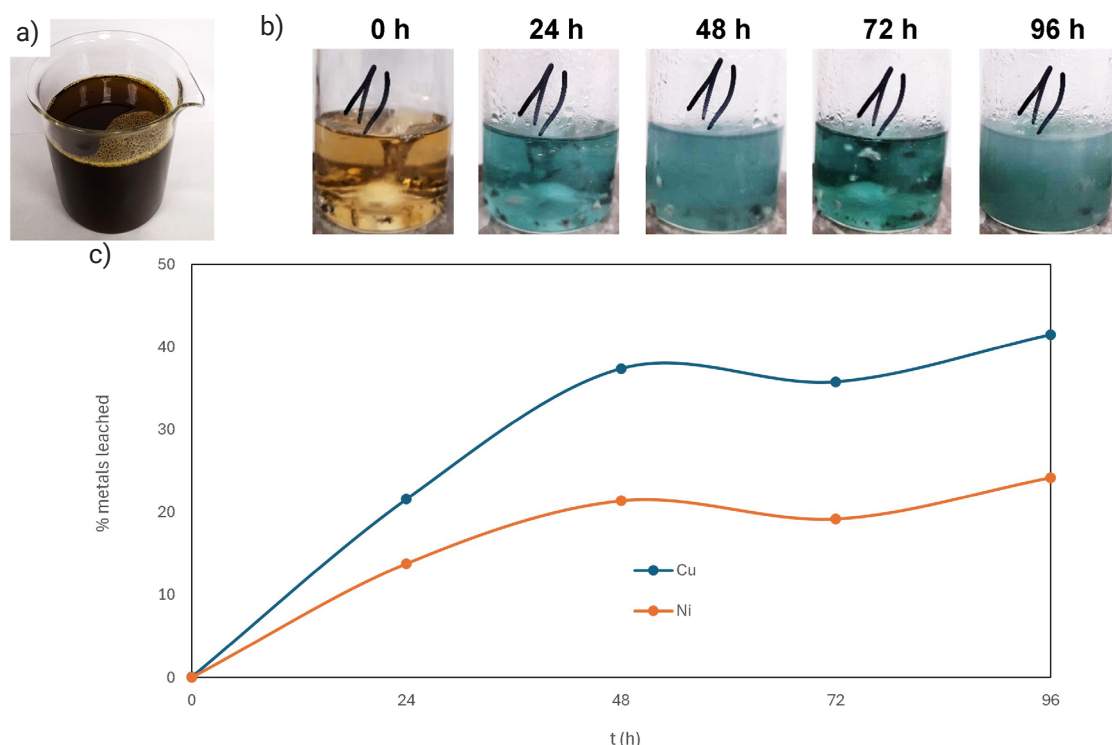
Overall, these results confirm that SPA can effectively regulate pH in bioleaching processes, maintaining metal dissolution efficiency, compared with previous tests. Cu leaching follows a progressive trend, while Ni dissolution appears more stable, but it also increases over time. This approach supports circular economy principles by valorising industrial waste (SPAs) to optimise the demetallization of metallised ABS.

### 3.3.4 Proposal of recovery process

In Figure 8 is proposed a recovery process for metallized ABS scrap. First, metallized ABS (W-ABS) should be shredded (S-ABS) to increase the surface area and facilitate de magnetic separation.

After the magnetic separation, two phases are obtained: CS-ABS ( $\approx 70\%$ ) which could be valorised directly in injection-moulding, and MS-ABS ( $\approx 30\%$ ) which could be treated with biogenic lixivants. Additionally, the pH of the biogenic lixiviant could be adjusted with SPAs when required, valorising this industrial acid waste, and implementing the circular economy model.

Once the bioleaching is finished (about 24-96 h) the solution is filtered, obtaining two streams: a solid (Cr particles + Clean MS-ABS), and a liquid solution (Cu + Ni +  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ). To concentrate Cu and Ni, the dissolution can



**FIGURE 7:** (a) Spent pickling acid (SPA) provided by the surface treatment company, used as pH adjusting agent; (b) aspect of the solutions each 24 h; (c) time evolution of the proportions of metals leached. % were calculated as stated in Equation 1.

be recirculated to the bioleaching reactor until the  $\text{Fe}^{3+}$  is depleted, enhancing the metal recovery. After the depletion of  $\text{Fe}^{3+}$ , the solution could be sent to valorisation. The solid current contains the ABS that, once rinsed and dried, can be directly valorized.

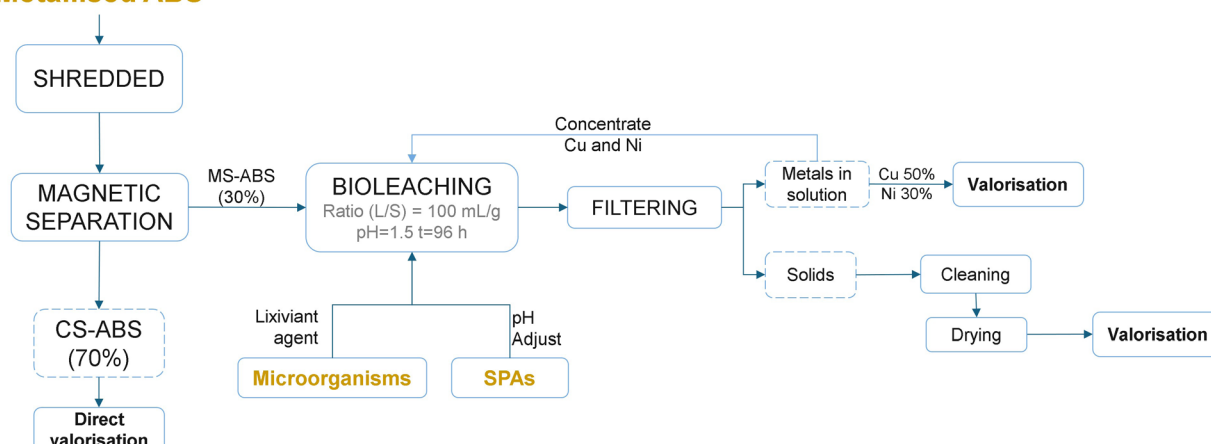
#### 4. CONCLUSIONS

Two different bacterial species (*Acidithiobacillus ferrooxidans* DSM 14882 and *Acidithiobacillus thiooxidans* DSM 504) were selected and grown to obtain the leaching liquors for the leaching test. During the bioleaching process of the different formats of ABS waste, it was observed

a different leaching behaviour depending on the format of the ABS treated. S-ABS is recommended as better fraction to be leached, confronted to whole ABS (W-ABS), due to its larger active surface.

For the S-ABS, a pretreatment consisting in magnetic concentration was used. The clean ABS (CS-ABS) obtained from this treatment had a low metal content, therefore it could be directly reused. The concentrated fraction (MS-ABS) was used for the bioleaching tests. The most promising L/S ratio for demetallisation was 100 mL/g, up to 24-72 h duration providing a remarkable Cu and Ni leaching performance. The Cr was recovered in metallic state by

#### Metallised ABS



**FIGURE 8:** Proposed recovery process for rejected metallised ABS.



filtering the solution. The obtained ABS was clean and suitable for its reuse. The bioleaching liquor could be reused for different leaching batches. In addition, SPAs, which are a hazardous waste, could be valorised by using it in the bioleaching process for pH adjustment. All the tests demonstrate the high variability in metal composition of any type of ABS treated.

The benefits of the novel and eco-friendly bioleaching process developed in this study comprise the use of environmentally friendly reagents, no gas emissions, room temperature and low energy consumption, allowing a recovery of the ABS and the metals in different streams. In addition, the valorisation of ABS is a great opportunity both for the environmental and economic point of view.

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# PRODUCTION OF BIO-DEGRADABLE PLASTICS USING DIFFERENT WASTE RESOURCES BY *STREPTOMYCES GEYSIRIENSIS* SP. VITJK02

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## ABSTRACT

Plastic polymers are invariably used every day for multiple applications causing huge environmental pollution globally. Biopolymers are biodegradable and considered to be a better alternative to synthetic plastics. This study explores the microbial production of Poly 3-hydroxyalkanoates (PHAs/ Poly 3-hydroxybutyrates (PHBs) using low-cost waste substrate. The polymer of hydroxyalkanoate is produced as intracellular granules, accumulates inside and serves as a source of energy for microorganisms. PHA-producing bacteria were isolated and screened using the Nile red and Sudan black B staining technique. Agro-industrial wastes like Rice bran. Sesame seed oil cake, used cooking oil, and glucose were used as carbon sources. The PHA-producing strain was characterized and identified by 16S rRNA partial genome sequencing. The extracted PHA was analyzed for PHA and PHB monomeric compounds by GC-MS analysis. PHA-producing isolate was identified as *Streptomyces* species and named as *Streptomyces geysiriensis* sp. VITJK02 by molecular taxonomic characterization. Among the carbon sources used rice bran served as a better carbon source for PHA production, and the yield was calculated to be 37.55%. Octadecanoic acid, 3-hydroxy-methyl ester, 2-butenic acid, 1-methyl ethyl ester, 9-hexadecanoic acid, butanoic acid, 2,7-dimethyl oct-7-en-5yn-4-yl ester, butanedioic acid, dimethyl ester, pentadecanoic acid, and valeric acid, 2-tetradecyl ester were a few of the major PHA monomeric compounds observed in our study. Since PHA/PHB bioplastics are a better alternative to petroleum hydrocarbon-based synthetic plastic polymers, cheap household wastes can be used to produce PHA to minimize the cost.

## 1. INTRODUCTION

One of the major causations of water pollution is the improper disposal of solid waste like garbage; the environment is currently suffering because of improper use and disposal of plastics. Plastic pollution has a huge impact on the environment, animals, plants, and humans directly and indirectly. We need to follow the three R's in plastics use: reduce, reuse, and recycle. Although plastics are frequently used in our daily lives, their use must be minimized as much as possible, and they need to be recycled properly to reduce plastic pollution. PHAs are a type of naturally occurring bio-polyesters produced by a variety of microorganisms. PHA synthase gene (*phaC*) is responsible for the synthesis of PHA by bacteria (Tan et al., 2019). PHA is commercially important due to its eco-friendly nature, biodegradability, biocompatibility, crystallinity, and chemical diversity, and it could be produced from cheap and renewable carbon resources (Shah et al., 2008). PHA molecule is made up of 600 to 35,000 (R)-hydroxy fatty acid monomer

units (Khanna & Srivastava, 2005). Based on number of carbon atoms, PHA monomers can be classified as short (3-5 carbon atoms), medium (6-14 carbon atoms), and long ( $\geq 15$  carbon atoms) chain length (Al-Hamdani, 2016). Some of the SCL-PHAs (Short chain length-PHAs) polymers are 3-hydroxypropionate (3HP), 3-hydroxybutyrate (3HB), 4-hydroxybutyrate (4HB), 3-hydroxyvalerate (3HV), 4-hydroxyvalerate (4HV) and 5-hydroxyvalerate (5HV). MCL-PHAs (Medium chain length-PHAs) polymers are 3-hydroxyheptanoate (3HHp), 3-hydroxyoctanoate (3HO), 3-hydroxyhexanoate (3HHx), 3-hydroxydodecanoate (3HDD), 3-hydroxynonanoate (3HN), and 3-hydroxydecanoate (3HD) (Ojha & Das. 2020). LCL-PHAs (Long chain length-PHAs) polymers are 3-hydroxypentadecanoate (3-HHxD), 3-hydroxyoctadecanoate (3-HOD), 3-hydroxy-9,12-octadeca-dienoate, 3-hydroxy-9-octadecenoate, etc (Roja et al., 2019; Koller. 2018). Structurally, mechanically, and thermally, the MCL-PHA was different from SCL-PHA. Due to expensive fermentation procedures and a lack of potential MCL-PHA-pro-

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ducing bacteria, the research on MCL-PHA is limited (Sathiyarayanan et al., 2017). This classification aids in understanding the differences in physical and mechanical properties of various types of PHA. PHBs possess thermoplastic characteristics and is biodegradable. PHAs can be completely broken down into CO<sub>2</sub> and water by a variety of microorganisms.

PHA can be commonly modified using physical and chemical methods (Zinn & Hany, 2005). However, recombinant DNA technology facilitates the production of PHA containing desired functional groups (Thompson et al., 1997). PHB is the most well-known polyester in the PHA series, with a similar molecular structure and physical properties (Hahn et al., 1994). PHA is a microbial thermoplastic that degrades into a potentially useful polyester that can replace petroleum-derived thermoplastics (Zhang Z et al., 2023). Based on their UV tolerance, water solubility, and good barrier from oxygen penetration, they have been used in agricultural, domestic, industrial, and Bio-medical applications (Vu et al., 2020; Saxena & Tiwari, 2011). Some other applications of PHA-based bioplastics in the industry include packaging, disposable bottles, preparation of bioplastic films for the protection of crops, hydrating agents, additives for animal nutrients, and textile fibers. Biomedical use includes wound healing, artificial blood vessels, tissue repair, regenerative medicine, cartilage regeneration, heart valves, bone implants, scaffold making, and drug carriers. Environmental uses include PHA surface coating, antifouling agent, and nanocomposite uses including biomedicine, hydrogels/nanogels, cancer treatment, stem cell engineering, coating for biomedical agents, coating for the paper board, automotive tools, microchips, and nanochips, etc. (Pratap & Krishnan, 2023).

When compared to synthetic plastics, PHA has much higher manufacturing costs. PHA costs are influenced by both carbon sources and fermentation processes. The cost of producing PHA from fossil-based polymers is very high. For large-scale production of PHA sugar-rich substrates and pure or recombinant bacterial strains are needed (Pratap & Krishnan, 2023). The production cost of PHA can be decreased by using cheap carbon sources such as household oil waste, fruit and vegetable waste, spent coffee grounds (SCGs), chicken feather waste, organic sludge, dairy waste, etc. Many reports are available on the production of PHA/PHB using various carbon sources and actinobacterium isolates. Some of these include *Arthobacter* sp. PCH145, which produces 15% of PHA, *Paenarthrobacter* sp. PCH191, which produces 26.6%, and *Microbacterium* sp. PCH192, which produces 67.2% of PHA (Kumar et al., 2018). *Rhodococcus* sp. strain BSRT1-1 yields 46.8% PHB content when fructose is utilized as a carbon source (Trakunjae et al., 2021). *Rubrobacter xylanophilus* produced 38.02%, 3%, 4.21%, and 51.53% of PHB content using glucose, arabinose, fructose, and glycerol as carbon sources, respectively. *Rubrobacter spartan* utilizes glucose and glycerol as substrates, producing 38.59% and 49.65%, respectively (Kourilova et al., 2021). *Propionibacterium* sp. produced 13% and 5% PHA content utilizing 1% palm oil and 2% waste glycerol as carbon sources, respectively (Jamil, 2022). *Streptomyces parvulus* created PHB by using

whey as a low-cost carbon source (Rasheed et al., 2013). *Streptomyces* sp. MAPPL011 produced 6.9%, 28.55%, 7.5%, and 7.94% of PHB content when agricultural waste like rice bran, oil cake, paddy straw, and cane molasses were chosen as carbon sources (Krishnan, Chinnadurai & Perumal, 2017). This study aims to isolate the PHA-producing microorganism from agricultural soil samples and produce PHA using cheap agriculture and household wastes including rice bran, used cooking oil, and sesame seed oil cake were provided as a carbon source for the bacteria for PHA production to minimize the production cost. To the best of our knowledge, this is the first report on the production of PHA using *Streptomyces geysiriensis* sp. VITJK02. The yield of PHA produced by *Streptomyces* sp. MAPPL011 was comparatively higher than earlier reports. The maximum growth was observed at 120h, and accumulation of PHA was observed on the same day by *Streptomyces geysiriensis* sp. VITJK02. When the rice bran was used as a cheap carbon source, the yield of PHA by *Streptomyces geysiriensis* sp. VITJK02 strain (37.55%) was more than *Streptomyces* sp. MAPPL011 (6.9%). Another innovative aspect of the study is to maximize the applications like bioplastics are used not only as an alternative to hydrocarbon-based plastic polymers but also in other biomedical applications.

## 1.1 Nomenclature

- PHAs (Polyhydroxyalkanoates)
- PHBs (Polyhydroxybutyrates)
- SCL-PHAs (Short chain length-PHAs)
- MCL-PHAs (Medium chain length-PHAs)
- LCL-PHAs (Long chain length-PHAs)
- CO<sub>2</sub> (Carbon dioxide)
- GC-MS (Gas chromatography- Mass spectrometry)
- phaC (Polyhydroxyalkonates synthase)
- r-DNA (Recombinant DNA)
- SCGs (Spent coffee grounds)
- MSM (Minimal salt medium)
- UV (Ultra violet)
- PCR (Polymerase chain reaction)
- MEGA (Molecular Evolutionary Genetics Analysis)
- BLAST (Basic Local Alignment Search Tool)
- NCBI (National Center for Biotechnology Information)
- rRNA (Ribosomal ribonucleic acid)
- SEM (Scanning electron microscopy)
- RT (Retention time)

## 2. MATERIALS AND METHODS

### 2.1 Collection of agricultural soil samples

Agricultural soil samples were collected from Chandrapa Naidu Kandriga Village, Taduku, Puttur Mandal, Tirupati district, Andhra Pradesh, India. The soil samples were collected in a sterilized sample collecting container after removing the surface soil. All samples were labeled, transported to the laboratory, and refrigerated at 4°C for further processing.

### 2.2 Isolation of PHA-producing organisms

The soil sample was serially diluted and plated on nutrient agar medium [0.5% of peptone- nitrogen source],



0.3% of beef extract (water-soluble consists of vitamins, carbohydrates, nitrogen, and salt), and 1.5% of agar] for the isolation of PHA producing organism. All the plates were incubated at 37°C for two days, pure colonies were isolated by the streak plate method on minimal salt medium [30 g/L of Na<sub>2</sub>HPO<sub>4</sub>·7H<sub>2</sub>O, 15 g/L of KH<sub>2</sub>PO<sub>4</sub>, 2.5 g/L of NaCl, 5 g/L of NH<sub>4</sub>Cl, 2 g/L of MgSO<sub>4</sub>, 0.1 g/L of CaCl<sub>2</sub>, 10 g/L of glucose and 20 g/L agar] (Sriyapai et al., 2022). The glycerol stock cultures were kept at -20°C on 20% glycerol stock.

## 2.3 Screening and Detection of PHA-producing Microorganisms

### 2.3.1 Nile red and Sudan black B staining for PHA-producing isolate

Nile red (0.5µg mL<sup>-1</sup>) was added to a sterilized MSM medium containing 1% glucose. The plates were incubated at 37°C for 48 h after adding microbial colonies (Tan et al., 2014). After incubation, the plates were exposed to UV light and observed for orange color fluorescence. Microbial colonies were cultured on MSM medium with 1% glucose and all the plates were incubated at 37°C for 72 h. To stain microbial colonies, the culture plates were flooded with 0.02% alcoholic Sudan black B incubated for 30 min (Al-Hamdani, 2016). The excess stain was removed by rinsing with 100% ethanol and observed for bluish-black color.

## 2.4 Identification of PHA-producing isolate

### 2.4.1 Phenotypic characterization of PHA-producing isolate

Morphological, biochemical, and physiological characterization of the isolate was carried out according to Bergey's manual (Bergey, 1994). The colony morphology like shape, margin, opacity, elevation, and texture was studied by microscopic examination.

### 2.4.2 Phylogenetic characterization of PHA-producing isolate

The genomic DNA was extracted from a PHA-producing isolate VITJK02 using the PCR template preparation kit (Roche) (Kieser et al., 2000). The extracted DNA was amplified by using 27F and 1492R and 518F and 800R universal primers and the PCR reaction mixture consist of double distilled water (18.3µl), tag DNA polymerase buffer (10x) (2.5µl), dNTP mix (2mM) (2.5µl), forward primer (10µM) 27F, 518F (0.5µl), reverse primer (10µM) 800R and 1492R (0.5µl), template DNA (0.5µl), taq DNA polymerase enzyme (5U/µl) (0.2µl) with amplification conditions of initial denaturation at 94°C for 5min, denaturation at 94°C for 45sec, annealing at 55°C for 45sec, extension at 72°C for 1min for 34 cycles and the final extension reaches to 72°C for 5min. After the program, PCR products were subjected to 1% agarose gel electrophoresis, and the amplified bands observed were compared with 1kb ladder. The 16S rDNA sequence obtained was subjected to BLAST search using NCBI GenBank database to find out the sequence similarity. The MEGA 5.1 software program (Tamura et., 2011) was used to construct a phylogenetic tree.

The 16S rRNA gene was 1500bp long and has conserved regions as well as hypervariable regions with spe-

cific codes useful for actinobacterial identification.

### 2.4.3 Scanning electron microscopic (SEM) analysis

The PHA-producing isolate was cultured in an MSM agar plate for SEM analysis (Carl Zeiss, Model No: EVO /18). The agar blocks were cut with a sterile blade and the culture was streaked around the edges, covered with a coverslip, and incubated for 7 days at 37°C. After incubation, 2.5% glutaraldehyde was added as a fixative. After overnight incubation, slide was washed with different ethanol gradients (30%, 60%, 70%, and 90%) to remove the loosely attached cells and excess of glutaraldehyde. It was allowed to dry and observed under SEM.

## 2.5 Growth kinetics

The PHA-producing isolate was inoculated into a 100ml MSM medium and incubated at 37°C at 200 rpm for various time intervals. The cell dry weight was determined after 24h, 48h, 72h, 96h, 120h, 144h, and 168h of incubation. To determine cell dry weight, microorganism-containing media was pelleted by centrifugation at 9000rpm for 10 minutes at 4°C. The supernatant was discarded, and a pellet containing cells was collected and dried overnight in a hot air oven at 100°C. The dry weight of the cells was calculated as g/L of the medium. All experiments were done in triplicates.

## 2.6 Extraction of PHA

PHA-producing isolate was grown on 250ml of MSM broth with 1% substrate in 500ml Erlenmeyer flasks. Different substrates like glucose, used cooking oil, sesame seeds oil cake, and rice bran were used separately for PHA production. It was incubated at 37°C for 7 days in a rotary orbital shaker at 200rpm. After incubation, the cells were harvested by centrifugation at 9000 rpm for 15min (Sriyapai et al., 2022). The pellet was collected, dried and the cell dry weight was determined in g/L. Sodium hypochlorite (10 ml) was added to the pelleted dry biomass and incubated for 2 hr at 50°C to lyse the cells before centrifugation at 9000 rpm for 10 min (Adnan et al., 2023). After centrifugation, a mixture of ethanol and acetone (1:2 ratio) was used to wash the pellet. The polymer-containing pellet was dissolved in chloroform and filtered through Whatman No.1 filter paper (Narayanan et al., 2022). The filtrate containing PHA was dried in a hot air oven at 60°C, and collected as a white precipitate. Experiments were performed in triplicates. The concentration of PHA (g/L) and percentage of PHA content was calculated as:

$$\text{Percentage of PHA} = \text{PHA weight/cell dry weight} \times 100$$

The extracted PHA was subjected to GC-MS (GC-7890B; MS-5977A) analysis to identify the PHA and PHB monomeric compounds. The split injection mode was used in the GCMS analysis, and its ratio is 50:1, liner volume: 0.99 ml, injection volume: 1.0 µl, injector temperature 260°C, column: DB-5-30m x 0.25 mm x 0.25 µ or equivalent, carrier gas: helium, column flow 1.0 ml/min, initial temperature 45°C, Interface temperature: 280°C, Mass range: 45-600 amu, Temperature rise/min:10-20°C.



### 3. RESULTS

#### 3.1 Isolation and screening of PHA-producing bacteria

Twelve bacterial strains (VITJK01 to VITJK12) were isolated from collected soil samples. All the isolates were screened for PHA-producing potential. Unstained isolates are shown in Figure.1 A. Four isolates emitted orange colour fluorescence light under UV light after Nile red staining (Figure 1 B), and bluish-black colonies after Sudan Black B staining (Figure 1C).

#### 3.2 Growth curve analysis

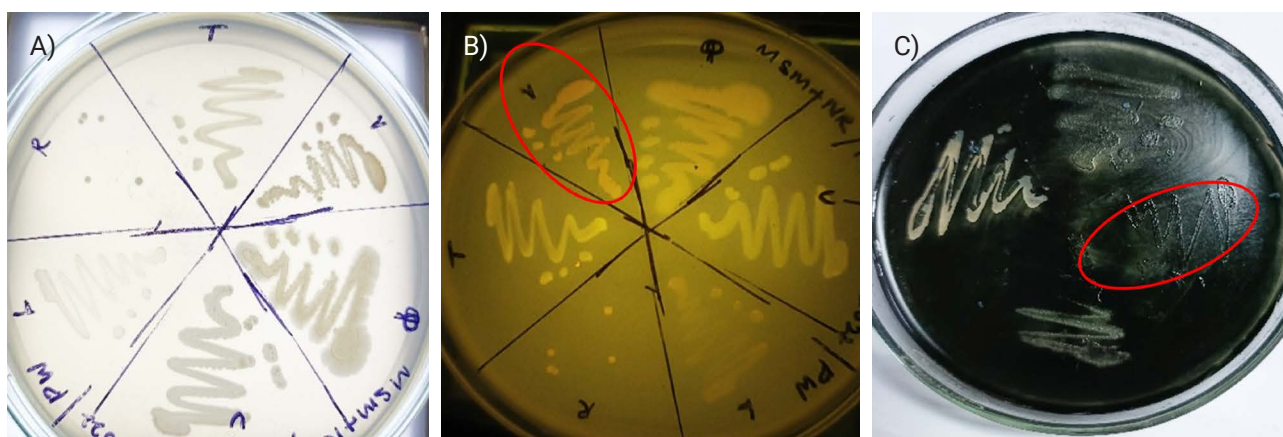
In order to identify the stationary phase for PHA extraction, a growth curve of the potential isolate was plotted based on the dry weight of the isolate. To plot the growth curve, the broth was centrifuged and the pellet obtained was dried, and the dry weight was recorded every 24 hours for 7 days. The stationary phase of the isolate was identified as 120 h and the PHA extraction was done on the same day. The growth curve was also used to study the growth rate of the isolate (Figure 2).

#### 3.3 Characterization of PHA-producing microorganisms

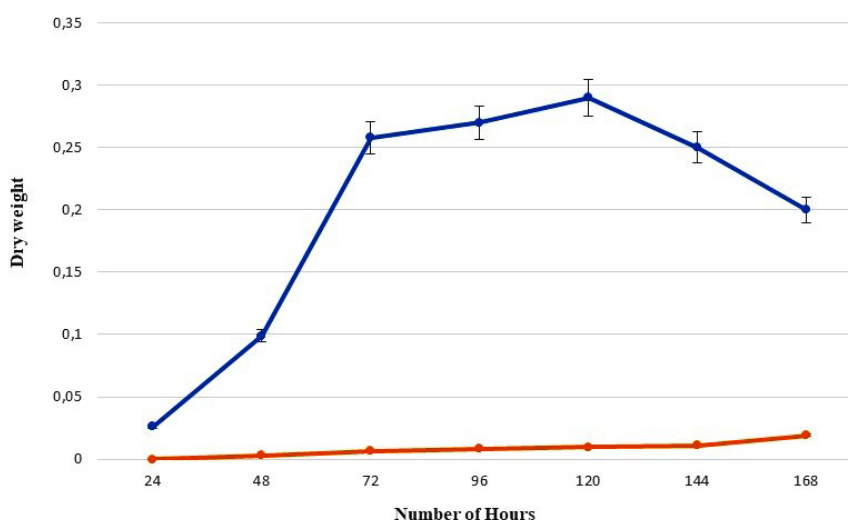
Based on physiological characterization, the isolate was irregular in shape, smooth surface, moist texture, raised elevation, undulated margin, and white in color on day 2 (Figure 3 A) and chocolate brown color on day 7 (Figure 3 B). The isolate was examined under SEM to study the structure and surface morphology and it was observed as a rod-shaped chain-like structure. The cell was approximately 0.5-1.0µm in size (Figure 3 C).

#### 3.4 16S rRNA partial genome sequencing

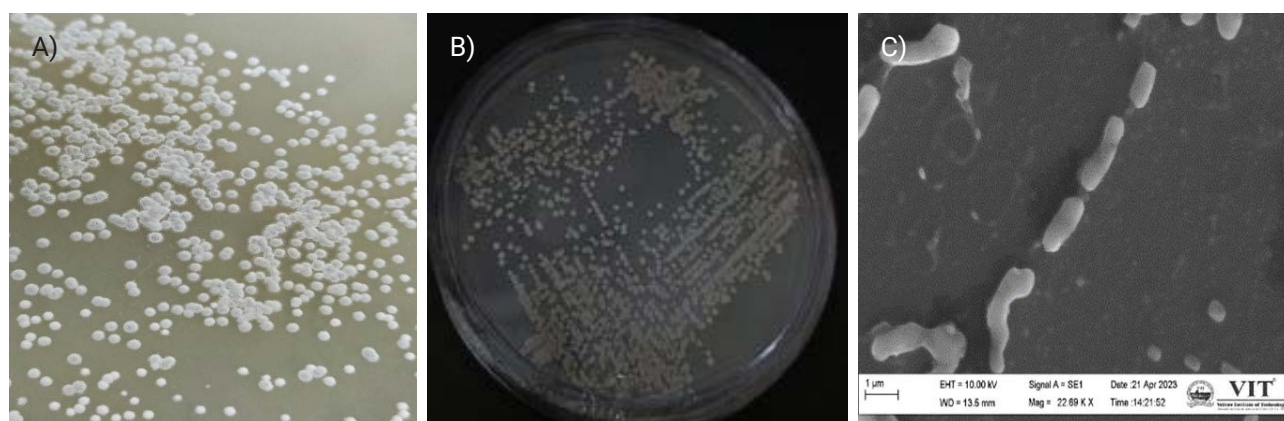
A BLAST search of the VITJK02 sequence showed a sequence similarity of 99.92% with *Streptomyces geysiriensis* (Accession number NR\_112459.1). The phylogenetic tree of VITJK02 was constructed using MEGA Software by the neighbor-joining method (Figure 4). Based on phylogeny and molecular taxonomy the PHA-producing isolate was identified as *Streptomyces* species and designated as *Streptomyces geysiriensis* sp. VITJK02. The 16S rRNA sequence of the PHA-producing isolate (VITJK02)



**FIGURE 1:** Nile red and Sudan black B staining for PHA-producing isolate VITJK02. A) Under normal light. B) Orange color fluorescence under UV light after Nile red staining. C) Bluish-black color after Sudan Black B staining.



**FIGURE 2:** Growth curve analysis of a potential isolate *Streptomyces geysiriensis* sp. VITJK02.



**FIGURE 3:** Morphological characterization of PHA-producing isolate *Streptomyces geysiriensis* sp. VITJK02. A) Growth at 48 hours, B) Growth at 7 days (producing brown color pigment), C) SEM image.

was submitted to GenBank under the Accession number OQ373315.

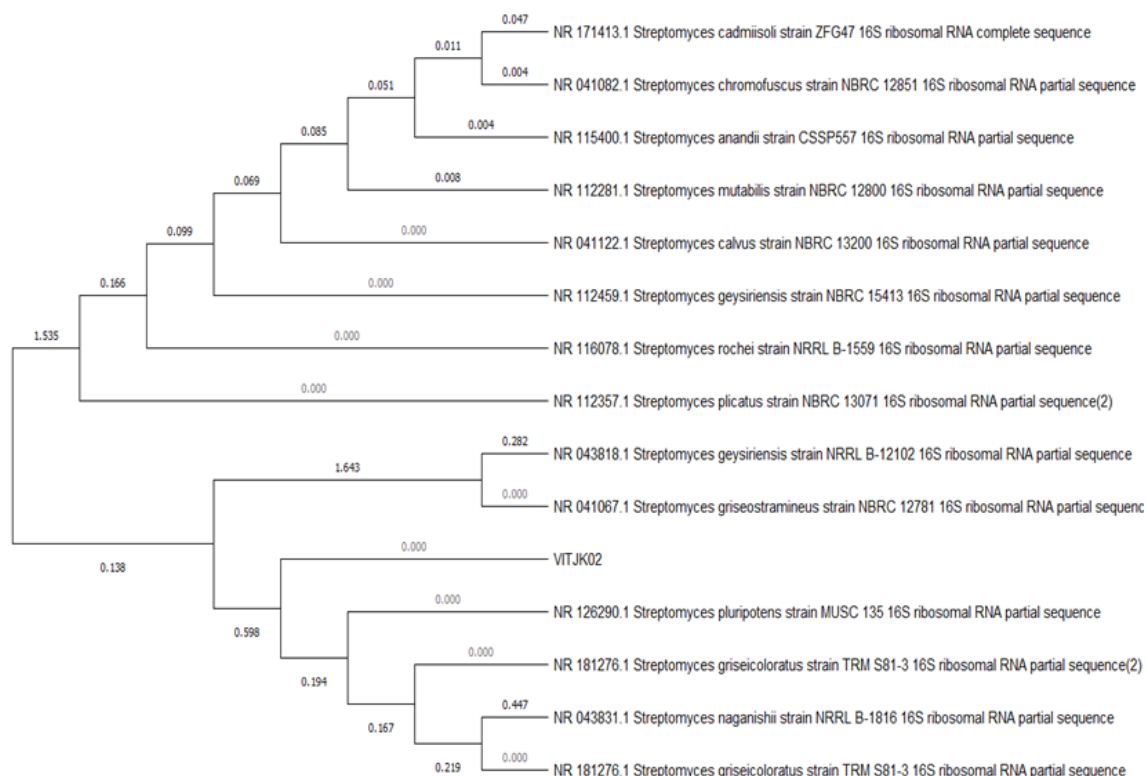
### 3.5 PHA Production and extraction

The PHA-producing isolate was cultured in 500 ml Erlenmeyer flasks each containing 250 ml MSM broth with 1% sesame seed oil cake, 1% of rice bran, 1% used cooking oil and 1% glucose (control) as a carbon source, and incubated for 7 days in an orbital shaker at 200 rpm at 37°C. For 1% rice bran the PHA yield was calculated to be 1.6 g/L from 3.5 g/L of cell dry weight. For 1% sesame seed oil cake it was 1.4 g/L from 4.2 g/L of cell dry weight. For 1% glucose it was 1.2 g/L from 3.8 g/L of cell

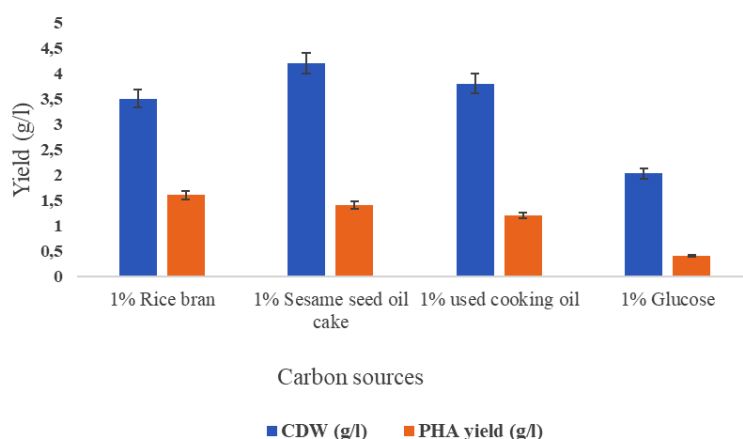
dry weight. The isolate VITJK02 with rice bran as a carbon source yielded the highest PHA (34%), sesame seed oil cake (33%), glucose showed (31.5%) and used cooking oil showed less PHA yield (Figure 5). The extracted PHA yield was analyzed using GC-MS for PHA and PHB monomeric compounds.

### 3.6 GCMS analysis

The monomeric chemical composition of the polyhydroxyalkanoate (PHA) produced was characterized by gas chromatography-mass spectroscopic analysis. Multiple peaks were observed in the test system when compared to the control system. The majority of the PHA monomer-



**FIGURE 4:** Phylogenetic relationship of *Streptomyces geysiriensis* sp. VITJK02 with other similar isolates based on 16S rRNA partial genome sequencing.



**FIGURE 5:** The yield of cell dry weight and extracted PHA using *Streptomyces geysiriensis* sp. VITJK02.

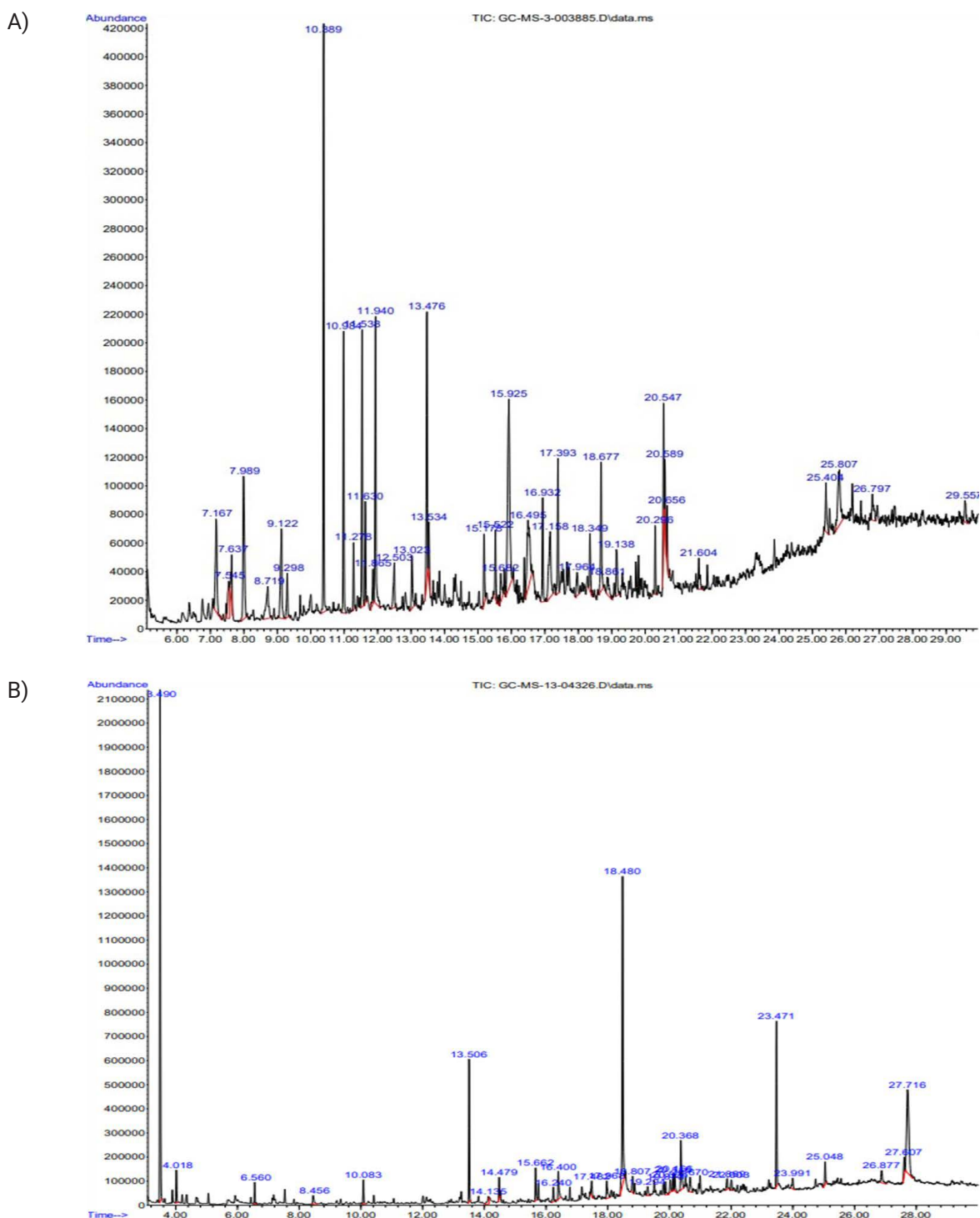
ic compounds observed in the GCMS spectrum have belonged to derivatives of decanoic acid and decanamide. When rice bran was used as a carbon source, the high-intensity peak of n-hexadecanoic acid (RT 18.48) and the low-intensity peaks of tetradecanoic acid (RT 16.4), tetradecanamide (RT 19.29), 9-Octadecanamide (RT 20.166), octadecanoic acid (RT 20.368) and the total area percentage of all PHA monomeric compounds were 37.55% (Figure 6 B). The retention time and area of the peak observed in the GC-MS spectrum are given in Table 1. When sesame seed oil cake was used the total area percentage of all PHA monomeric compounds was 29.28%, whereas in the case of glucose, the total area percentage of all PHA monomeric compounds was 21.92%. When compared to other carbon sources rice bran produced a maximum amount of PHA monomers. Hence, rice bran was selected as a cheap carbon source for PHA production.

When glucose was used as a carbon source which resulted in the highest peak intensity observed in octadecanoic acid (RT 20.54), moderate peak observed in pentanoic acid, 4-oxo-methyl ester (7.63), butanedioic acid, dimethyl ester (7.98), butanedioic acid, monomethyl ester (9.122), n-hexadecanoic acid (18.67), octadecenoic acid (20.58), 9,12, octadecanoic acid (20.65) whereas low-intensity peaks were observed in pentanoic acid, 4-oxo-methyl ester (7.54), pentanoic acid (8.71), pentadecanoic acid (17.15) were observed (Figure 6A).

The result analysis of the monomeric compounds was extracted from NIST libraries. The chromatogram showed the formation of monomeric compounds of many significant parent peaks, thus confirming the presence of PHA production as mentioned below. The predominant PHA monomers found was n-hexadecanoic acid, tetradecanoic acid, Phthalic acid, isobutyl octadecyl ester, Valeric

**TABLE 1:** GC-MS spectrum of PHA monomeric compounds produced by *Streptomyces geysiriensis* sp. VITJK02 in the presence of glucose and rice bran as a carbon source.

| Control (glucose)                            | Retention time (RT) (glucose) | Area of percentage (%) (glucose) | Test (Rice bran)                                     | Retention time (RT) (Rice bran) | Area of percentage (%) (Rice bran) |
|----------------------------------------------|-------------------------------|----------------------------------|------------------------------------------------------|---------------------------------|------------------------------------|
| Pentanoic acid, 4-oxo, methyl ester          | 7.545min                      | 1.56                             | Diethyl Phthalate                                    | 14.479min                       | 1.03                               |
| Pentanoic acid, 4-oxo-methyl ester           | 7.637min                      | 1.08                             | 2-propenoic acid, penta decyl ester                  | 15.662min                       | 1.67                               |
| Butanedioic acid, dimethyl ester             | 7.989min                      | 2.82                             | Tetradecanoic acid                                   | 16.400min                       | 1.88                               |
| Butanedioic acid, monomethyl ester           | 9.122min                      | 2.82                             | Phthalic acid, isobutyl octadecyl ester              | 17.482min                       | 1.02                               |
| Pentadecanoic acid                           | 17.158min                     | 3.24                             | n-hexadecanoic acid                                  | 18.48min                        | 18.91                              |
| n-Hexadecanoic acid                          | 18.677min                     | 2.92                             | Valeric acid, 2-tetradecyl ester                     | 20.11min                        | 0.73                               |
| 2-Ethylbutyric acid, 3-methylpent-2-yl ester | 20.296min                     | 1.17                             | Octadecanoic acid                                    | 20.368min                       | 3.58                               |
| 9-Octadecenoic acid, (E)-                    | 20.547min                     | 2.53                             | Butanoic acid, 2,7, dimethyl oct-7-en-5yn-4-yl ester | 21.869min                       | 0.82                               |
| Octadec-9-enoic acid                         | 20.589min                     | 0.84                             | Bis (2-ethyl hexyl) Phthalate                        | 23.471min                       | 7.91                               |
| 9,12-Octadecadienoic acid (Z,Z)-             | 20.656min                     | 0.84                             | -                                                    | -s                              | -                                  |
| 9-Octadecenoic acid, (E)-                    | 25.404min                     | 1.25                             | -                                                    | -                               | -                                  |



**FIGURE 6:** GC-MS Chromatogram of PHA monomeric compounds produced by *Streptomyces geysiriensis* sp. VITJK02 in the presence of A) glucose and B) rice bran as a carbon source.

acid, 2-tetradecyl ester, and octadecanoic acid, etc, when glucose was used as control system, predominant PHA monomers were butanedioic acid, dimethyl ester, n-hexadecanoic acid, octadecanoic acid and pentadecanoic acid.

#### 4. DISCUSSION

Plastic exerts a profound influence on the ecosystem, engendering adverse consequences affecting the soil, wa-

ter, ecosystem, and the environment. The release of greenhouse gases as a result of plastic degradation increases global warming. Increased production, widespread utilization, and improper disposal of conventional plastics lead to the accumulation of plastic waste in the soil, which remains in the soil for a prolonged period and their degradation lasts for several decades resulting in severe pollution affecting the well-being of the living systems. Multiple



strategies were followed for the control and management of plastic pollution. One such remedy is to decrease plastic production and their use and production of biodegradable plastics as an effective alternative to synthetic plastics. Bioplastics have demonstrated their superiority as a substitute for synthetic plastics, offering environmental benefits by avoiding the release of toxic compounds, plastic debris, and micro-nano plastics (Narancic et al., 2020). In order to mitigate the issue of plastic pollution, environmentalists are advocating the use of bioplastics, it is ecologically sustainable and readily degradable. The primary constituent of bioplastics is PHA/PHB. Many microbial species accumulate PHA/PHB compounds and used them as an energy source. A total of more than 150 unique hydroxy-alkanoic acids have been recognized for their integration into PHAs (Castilho et al., 2009). Furthermore, the accumulation of these specific polyesters has been seen in over 90 different genera of microbial species. The degradation of PHA/PHB can occur under both aerobic and anaerobic circumstances. Under aerobic conditions, the tricarboxylic acid (TCA) cycle participates in the process of oxidation and undergoes degradation, resulting in the production of water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>). Under conditions devoid of oxygen, methane (CH<sub>4</sub>) is generated. During this process, no hazardous chemicals were produced (Rai & Lee et al., 2009). The degradation process involves the participation of both biotic and abiotic factors.

In the current study, the PHA-producing *Streptomyces* *geysiriensis* sp. VITJK02 was isolated from agricultural soil samples. *Streptomyces* are a major group of soil bacteria belonging to the family actinomycetes are prolific producers of diversified compounds. It was reported that there are only 1-20% of culturable actinomycetes in the soil (Olanrewaju & Babalola, 2019). *Streptomyces* species play an essential role in agricultural soil due to their ability to create plant growth promoters, secondary metabolites, and enzymes (Vurukonda, Giovanardi & Stefani, 2018) and they also have the ability to resist both biotic and abiotic stress conditions. *Streptomyces* are recommended as prospective sources for the synthesis of PHAs with desirable characteristics that are acceptable for biomedical applications (Krishnan, Chinnadurai, & Perumal, 2017). Presence of the above reported monomers in PHA produced by microbes was reported by several researchers. Bacteria belonging to the actinomycetes family have been recognized as PHA-producers in recent past. Some of the PHA-producing actinomycetes are *Rhodococcus* species strain BSRT1 1 (Trakunjae et al., 2021), *Kineosphaera limosa* (Liu et al., 2002), *Nocardia* species, and *Streptomyces* species (Matias et al., 2009). PHA-producing *Streptomyces* species are *Streptomyces toxytricini* D2 (Narayanan et al., 2022), *Streptomyces coelicolor* A3(2) (Kalia, Lal, & Cheema, 2007), *Streptomyces plumbiresistens* CCNWHX 13-160T (Al-Hamdani, 2016), *Streptomyces gougerotti* and *Micromonospora matsumotoense* (Oliveira et al., 2022). PHA-producing *IsotERICOLA variabilis* species have been reported (Krishnan & Chinnadurai et al., 2021).

In this study, agro-based wastes like sesame seed oil cake, rice bran, and used cooking oil were used as a carbon source due to their easy availability, nutrient rich, and low-

er cost. Solid wastes like rice bran (Oh, Lee, & Jang et al., 2015), and food waste such as used cooking oil (Gómez Cardozo et al., 2016) have been reported to have high content of fatty acids and sugars for the production of PHA. Sesame seed oil cake is rich in carbohydrates, total solids, oils, and high chemical oxygen demand (Alsafadi, D., Alhesan et al., 2023). Agri waste is a low cost feed for bacteria making bioplastics (Mandal et al., 2024). Valorization of agri-food waste has been reported to contribute to the circular economy (Arriaga et al., 2025).

The monomeric compounds of PHA produced by VIT-JK02 were characterized using GC-MS analysis. PHA monomers such as 2-propenoic acid, penta decyl ester, tetradecanoic acid, phthalic acid, isobutyl octadecyl ester, phthalic acid, isobutyl octadecyl ester, n-hexadecanoic acid, valeric acid, 2-tetradecyl ester, octadecanoic acid, butanoic acid, 2,7, dimethyl oct-7-en-5yn-4-yl ester, bis (2-ethyl hexyl) phthalate, bis (2-ethylhexyl) ester was produced by VIT-JK02 when Rice bran was used as a carbon source. whereas, pentanoic acid, 4-oxo-, methyl ester, butanedioic acid, dimethyl ester, butanedioic acid, monomethyl ester, pentadecanoic acid, n-hexadecanoic acid, 2-ethylbutyric acid, 3-methylpent-2-yl ester, 9-octadecenoic acid, (E)-, octadec-9-enoic acid, 9,12-octadecadienoic acid (Z, Z)-, 9-octadecenoic acid, (E)- were produced when glucose was used. Based on GCMS analysis the total area percentage of the PHA monomeric compounds produced was 37.55% using rice bran and 23.09% for glucose. *Bacillus wiedmannii* AS-02 OK576278 produces octadecanoic acid, 3-hydroxy-, methyl ester, 2-butenic acid, 1-methyl ethyl ester, 9-hexadecenoic acid when different agricultural waste was used for PHA production (Danial & Hamdy et al., 2021). Production of PHB by *Bacillus cereus* SH-02 (OM992297) was reported earlier (Hamdy & danial et al., 2022). For comparison, the PHAs produced by the different *Streptomyces* species are listed. *Streptomyces griseorubiginosus* DBCC 719 (9.5%) (Manna, Banerjee & Paul et al., 1999); *Streptomyces toxytricini* D2 (86.56%) (Narayanan et al., 2022); *Streptomyces subutilus* (27.5%) (Malviya et al., 2021); *Streptomyces* sp.(4-8%) (Krishnan et al., 2017); *Streptomyces* species DG19 (100% of 3-hydroxyvalerate monomer) (Herrera et al., 2023); *Streptomyces gougeroti* (Oliveira et al., 2022); *Streptomyces coelicolor* A3(2) (Valappil et al., 2004). Production of PHA by *Bacillus paramycoides* strain KUMBNGBT-33 was reported recently (Nandish et al., 2023). Traina et al., 2024 have reported that the content of PHA is 0.46g/L, 0.20g/L, 0.19g/L, 1.48g/L, and 0.12g/L when sugar cane molasses, cheese whey, boiled mussel processing effluent, fruit waste and winery waste was used as a carbon source, respectively. Yoo et al., 2024 developed PHB from halophilic bacteria by improving salt tolerance. They created gamma radiation-induced mutants to improve salt tolerance. The Halo6 mutants produced 11% more PHA, which was associated with raised intracellular granule content and cell size. Petroleum-based polymers were replaced by biobased polymers in a wide range of applications like construction, biodegradable toys, automobiles, cosmetics products, medical applications like sutures, tissue engineering, heart valve engineering, organ transplantation and reconstruction, drug carrier, liver tissue

engineering, blood vessels, antibiotic delivery, etc. (Yeo et al., 2018). This study promotes a biocircular economy by utilizing waste for the production of PHA which can be used for bioplastic production.

## 5. CONCLUSIONS

VITJK02 was isolated from agricultural soil sample, which produced PHAs and PHBs. 16S rRNA partial genome sequencing of VITJK02 (Accession number OQ373315) showed 99.92% sequence similarity with *Streptomyces geysiriensis* (Accession number NR\_112459.1). Production of PHAs and PHBs by *Streptomyces geysiriensis* sp. VITJK02 by utilizing Sesame seed oil cake, Rice bran, used cooking oil as exclusive carbon sources was not been previously reported to the best our knowledge. Optimization of culture conditions of *Streptomyces geysiriensis* sp. VITJK02 would yield higher production of PHAs/PHBs by utilizing household and agricultural wastes. Large scale microbial production of PHAs/PHBs using the household wastes with reduced cost is of higher commercial value.

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# MATERIAL RECOVERY FROM PHOTOVOLTAIC PANELS BY MEANS OF THERMAL TREATMENT: THE EFFECT OF BACKSHEET REMOVAL

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## ABSTRACT

The thermal combustion of polymers contained in PV has been studied by 9-Tech, and it has been shown to be an efficacious way to recover from end-of-life (EoL) photovoltaic secondary raw materials with high efficiency and purity. In this work, the removal of the backsheet from photovoltaic (PV) panels has been investigated as a pre-treatment step in the thermal recycling process, assessing its impact on material recovery, energy consumption, and environmental emissions. The backsheet has been removed by means of an innovative technology developed by CEA based on sanding. The analysis of the materials recovered from PV panels with and without backsheet indicated that backsheet removal improves material purity by eliminating contamination with titanium dioxide (TiO<sub>2</sub>) powder. Furthermore, it reduced dust emissions and avoided the production of toxic hydrofluoric acid. Finally, it also slightly increased energy consumption due to the removal of combustible polymeric material.

## 1. INTRODUCTION

The global solar photovoltaic (PV) modules reached an installed capacity of 1 TW at the end of 2022 (IRENA, 2023), and according to the International Renewable Energy Agency, this value is predicted to increase to 5 TW by 2050 (Weckend et al., 2016). With an estimated PV module lifespan of 25-30 years, the volume of end-of-life (EoL) PV panels is expected to rise significantly in the coming decades, creating both environmental challenges and opportunities for resource recovery.

To survive for a long time, PV panels are made of different layers, each of which has a specific function. A soda lime glass is placed on top of the module to ensure mechanical stability and transparency to the incident light. It is characterised by a low iron content since the latter causes light absorption in the glass, which can result in losses. Moreover, the glass is tempered to boost its impact resistance (Jäger et al., 2014). Two encapsulant layers incorporate the solar cells; the most often used material is ethylene vinyl acetate (EVA). The final layer consists of the backsheet, a critical component of PV modules protecting against environmental stressors such as UV radiation, moisture, and mechanical damage (Fraunhofer, 2017). Backsheets are commonly made from materials like poly-

vinyl fluoride (PVF), polyvinylidene fluoride (PVDF), or polyethylene terephthalate (PET) (Chitra et al., 2022), and they often include additives such as titanium dioxide (TiO<sub>2</sub>) (Dobra et al., 2022) for UV resistance and pigmentation.

Recycling PV modules is essential to mitigate waste, recover valuable materials such as silicon, silver, copper, aluminium, and glass, and reduce the environmental footprint of solar energy systems (Fraunhofer, 2017).

The complexity of PV module design, particularly the strong encapsulation, poses significant challenges to efficient recycling processes.

End-of-life (EoL) PV panels contain valuable materials: recovering these materials efficiently is essential for maximising economic and environmental benefits. Among the different recycling techniques, the thermal, mechanical, and chemical are the most traditional according to the panel type (Deng et al., 2022; Rubino et al., 2021; Savvilotidou & Gidarakos, 2020). Investing in advanced and feasible recycling technologies, expanding treatment capacities, and promoting sustainable methods are crucial to scaling up PV recycling. These efforts reduce environmental risks, simultaneously unlocking market opportunities through material recovery and waste valorisation. Thermal-based strategies have recently gained attention as viable end-of-life (EoL) treatment routes for PV modules, especially

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when aiming for high-purity material recovery. In its inert atmosphere, pyrolysis allows for the degradation of EVA and the other backsheet polymers at temperatures typically between 400 and 600°C, enabling the recovery of silver and silicon while minimising oxidation of metallic fractions (Dobra et al., 2022). One of the main disadvantages of pyrolysis concerns the generation of a complex mixture of volatiles, requiring sophisticated gas treatment infrastructure. In contrast, combustion processes operating in oxidative environments simplify off-gas composition by oxidising volatile species to CO<sub>2</sub> and H<sub>2</sub>O, but introduce challenges when processing fluorinated backsheets due to HF formation (Chitra et al., 2022). Several projects in Europe have already demonstrated the feasibility of thermal approaches at the pilot scale (Fraunhofer, 2017; Weckend et al., 2016). In this framework, a novel approach comprising thermal delamination and mechanical separation has been validated by 9-Tech at the pilot scale (Cerchier et al., 2024).

The process can correctly separate glass, characterised by high purity, copper ribbons and pieces of silicon cells. These cells can further be treated by hydrometallurgical processes to recover the silver. In the abovementioned process, both encapsulant and backsheet are burned during the thermal treatment and therefore are not recovered. Backsheet recovery could have some advantages for the process. Fluorinated backsheets release hazardous hydrogen fluoride (HF) during thermal treatment, requiring mitigation measures. Additionally, TiO<sub>2</sub> powder can be present in the fumes or can contaminate the recovered materials like silicon and glass.

In this study, the removal of backsheets before thermal recycling has been studied as a solution to these challenges. By eliminating fluoropolymer layers, HF emissions during thermal processes can be avoided, reducing environmental risks and simplifying waste treatment. Furthermore, preventing TiO<sub>2</sub> contamination improves the purity of recovered materials, in particular silicon, increasing their potential for reuse in new PV modules or other applications.

This study aims to address this knowledge gap by conducting a comparative analysis of PV module recycling processes with and without backsheet removal.

The backsheet removal in literature has been studied to be obtained with hot knife (Wahman et al., 2014) or chemicals (Xu et al, 2029, Su et al. 2019).

In this study a novel approach, based on sanding, has been used for backsheet removal. In fact, using mature industrial sanding equipment, CEA developed a mechanical delamination process based on the use of abrasive belts. After determining the most suited abrasive nature, shape and size, a process was developed in order to remove all the materials present on the backside of a PV panel. Process control enables precise determination and selective removal of specific material layers from the PV panel. For this study, in order to remove the fluorinated polymers present in the backsheet, CEA was able to remove the backsheet layer from PV panels using this novel abrasion technology. Furthermore, as a complementary step, the encapsulant and the cells can also be removed using the

same technique, allowing to the recovery of the front glass sheet in a single piece, clean from metals, allowing the glass to be later recycled in the form of a cullet.

In the present study, by controlling the process, the removal of the backsheet was done using an industrial-sized equipment at CEA. The PV panels without a backsheet were later processed by 9-Tech using their proprietary combustion process. By evaluating key metrics such as material recovery rates, energy inputs, and emission profiles, this research seeks to elucidate the benefits and trade-offs associated with backsheet removal. The findings are intended to inform the development of optimized recycling protocols that align with environmental sustainability and economic viability objectives.

## 2. MATERIALS AND METHODS

### 2.1 Sample preparation

In this study, 12 c-Si photovoltaic panels of the same model (Trinasolar TSM-230PC05) were divided into 3 samples (4 PV panels each).

All panels were dismantled from the aluminum frame and junction boxes. After dismantling, the samples underwent different treatments:

- sample (A) has been treated with sanding technology to completely remove the backsheet
- sample (B) has been treated with sanding technology to partially remove the backsheet.
- sample (C), used as a reference, has not been treated and remained with the backsheet.

The sanding process, performed on samples A (Figure 1), and sample B by CEA, was performed using a Format 4 sander from the Felder group. The backsheet was removed using a 3 m/min PV panel speed and 19 m/s abrasive belt speed.

### 2.2 Recycling process

After dismantling and backsheet removal, the panels were cut into 33 cm wide strips, see Figure 2a, and each of the three samples was processed in the 9-Tech recycling line “9PV”, a system designed for thermomechanical recycling of PV modules (Figure 2b). The thermal treatment, in particular, was conducted in a patented tunnel furnace part of 9PV line that was developed by 9-Tech. It has dimensions 140 cm (L) × 60 cm (W) × 60 cm (H) and insulated with high-density ceramic wool. The panels are placed on a conveyor belt, and combustion gases are extracted through a heat exchanger and multistage filtration system.

The recycling process was conducted in two main phases: thermal treatment and mechanical separation.

The thermal treatment was performed using a controlled heating process designed to separate encapsulant layers and polymeric components from the panels.

The panels were exposed to high-temperature thermal treatment in air (>450°C) to ensure complete degradation of organic constituents (Figure 3).

Following thermal treatment, the panels underwent mechanical separation to recover individual material frac-



**FIGURE 1:** The PV panels pre-treated with a sanding process to remove the backsheet.

tions. Mechanical separation was carried out in multiple stages, involving first copper separation and then two sieving processes for separating glass and photovoltaic cells. The four recovered components are glass, PV cells, copper ribbons, and a powder fraction consisting of residual glass and photovoltaic cells.

### 2.3 Analytical techniques

Before any treatment, a Fourier-transform infrared spectroscopy (FT-IR) was employed to identify the chemical composition of both the encapsulant and the backsheet whereas Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive X-ray Spectroscopy (EDS) was performed to analyze the surface morphology and elemental composition of the recovered materials: glass, PV cells, copper ribbons, and residual powder fractions.

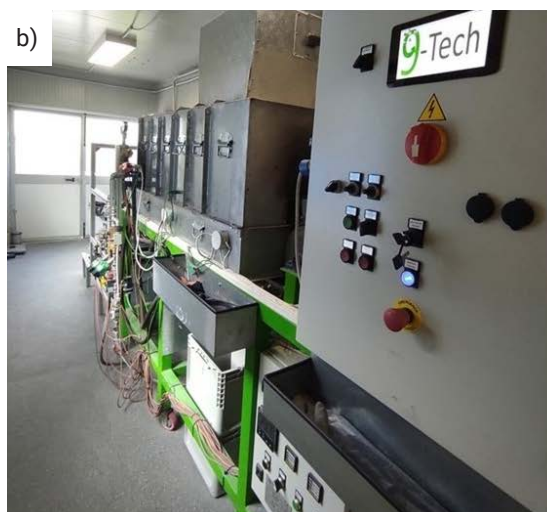
The efficiency of material recovery was evaluated by comparing the weight of the fractions obtained from panels with and without a backsheet, analyzing their composition, integrity, and contamination levels.

The fume analyses covered various parameters, each determined in accordance with specific standardized methods. Each sampling involved a continuous one-hour analysis of the fumes, thereby reducing the influence of transient variations in the measured parameters.

Powder concentration was measured according to UNI EN 13284-1:2017 using the gravimetric method. Carbon monoxide was determined following UNI EN 15058:2006 through a non-dispersive infrared (NDIR) technique, using a Horiba PG 350 analyzer. Hydrofluoric acid was analyzed in compliance with Ministerial Decree 25/08/00, through absorption in solution followed by ion chromatography, and particular attention was given to this acid, as its presence in the off-gases is directly related to the combustion of fluoride-containing materials within the PV panel structure. Metals, excluding mercury, were determined in accordance with UNI EN 14385:2004 using inductively coupled plasma optical emission spectrometry (ICP-OES). Lastly, volatile organic compound (VOCs) was continuously monitored using flame ionization detection (FID), with a Polaris model analyzer.

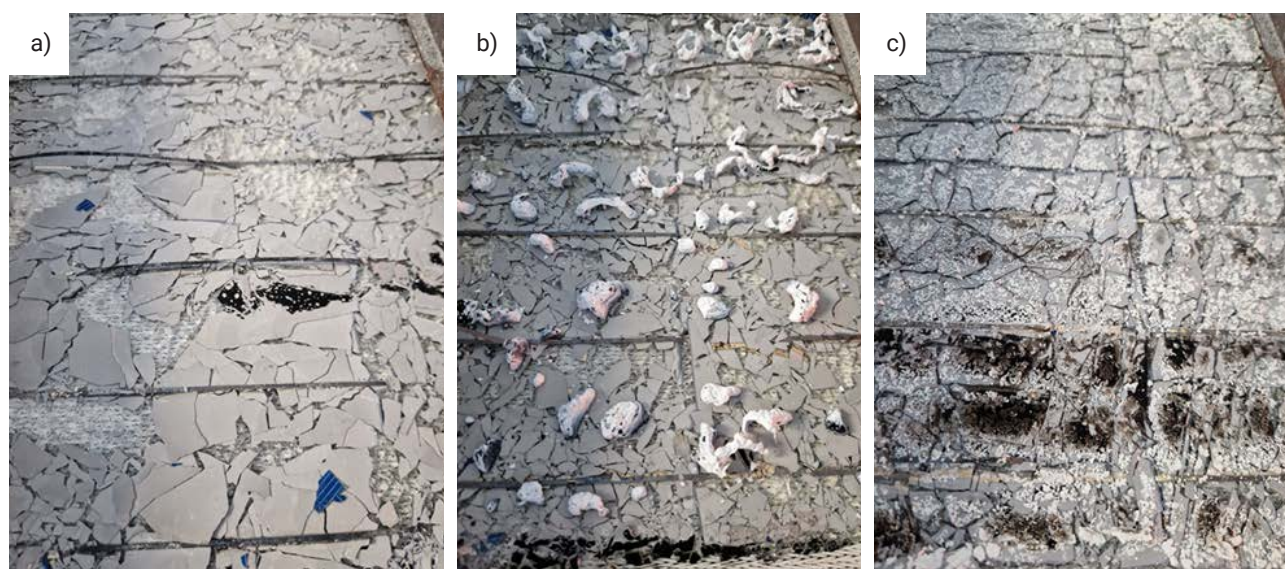
Finally, dioxin sampling was carried out according to UNI EN 1948-1:2006, using a filter/condenser system without flow diversion. The sampling equipment and the nozzle components in contact with flue gases were made of titanium.

To evaluate the impact of backsheet removal on process efficiency, the energy consumption of the recycling process was measured in two categories: propane consumption for thermal treatment and electricity consumption for flue gas treatment and material separation. Gas consumption was recorded using inline flow meters (Metrix Italia, UG G 2.5 ALU), while electricity usage was monitored with a multifunctional network analyzer (FRER, Nano 5H - Q52P3H005XCQ2U) at various stages of the process.



**FIGURE 2:** The three samples of PV panels strips: A, B, and C (a) and the 9PV pilot plant (b).





**FIGURE 3:** The PV samples after the heating treatment: a) sample A; b) sample B; c) sample C.

### 3. RESULTS AND DISCUSSION

#### 3.1 Material recovery and composition

The analysis confirmed that the encapsulant was composed of ethylene vinyl acetate (EVA), the backsheet, instead, was made of polyvinylidene fluoride (PVDF) in combination with PET. In this study, the backsheet was a typical multi-layer backsheet used in the PV industry in the 2010s. The backsheet is mainly composed of PVDF/PET/PVDF layers with additional adhesive layers and  $\text{TiO}_2$  powders. The thickness of the backsheet is 500  $\mu\text{m}$ , and its weight is close to 1 kilogram per PV panel. Owing to the differing responses of the various polymers to abrasive grains, the backsheet can be effectively removed with minimal removal of the encapsulant. This approach was employed in the preparation of Sample A.

In the case of sample B, the sanding process was carried out so it would not remove any encapsulant and rather leave a small layer of the internal layer of the backsheet that may contain some of the fluorinated polymer (PVDF). Depending on the abrasive used during the process, the granulometry of the powders varies, but a typical size of 200 to 300  $\mu\text{m}$  is common. The polymeric constituents

of the backsheet powders—poly(ethylene terephthalate) (PET), ethylene-vinyl acetate (EVA), and polyvinylidene fluoride (PVDF)—exhibit distinct physicochemical properties that enable their effective separation, thereby enhancing the feasibility of their individual recovery and recycling.

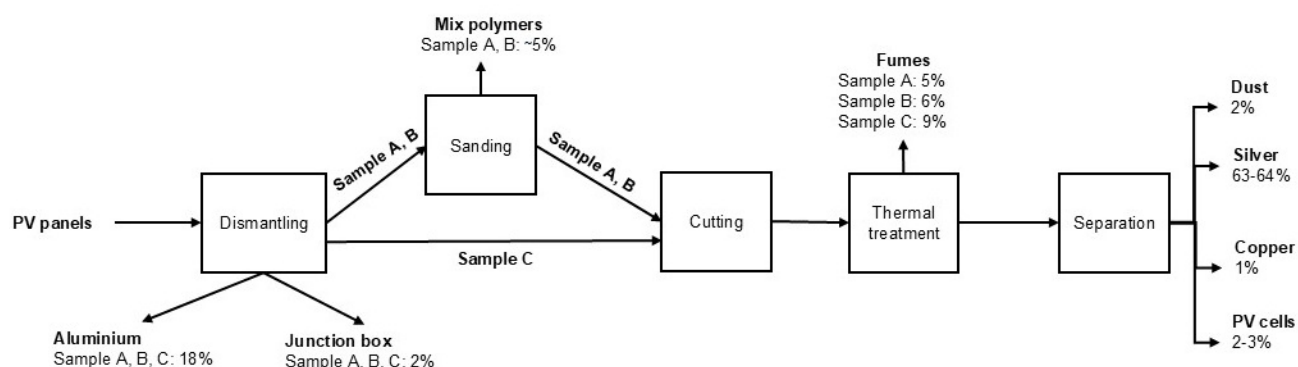
The mass balance of the process is reported in Figure 4, where are indicated the percentage of recovered material with respect to the initial weight of PV panels treated.

The recovered glass accounted for 62–64% of the total panel weight, with no significant variation between panels with and without a backsheet. The removal of the backsheet before thermal processing did not lead to any noticeable mechanical degradation of the glass, and no significant fracturing or fragmentation was observed. Similarly, the integrity of the PV cells remained largely unaffected by the absence of the backsheet, suggesting that pre-treatment did not introduce mechanical stress that could compromise material recovery.

The recovered materials are aligned with typical composition that can be found in literature, reported in Table 1.

The materials are shown in Figure 5.

The recovery of metallic fractions, including aluminum, copper, and photovoltaic cells, was consistent across all



**FIGURE 4:** Process scheme with mass balance.

**TABLE 1:** Approximate Bill of Materials for c-Si PV Panel (Belançon et al., 2022; Divya et al., 2023).

| Component           | Material                     | Approx. wt% |
|---------------------|------------------------------|-------------|
| Front Glass         | Tempered solar glass         | ≈ 66-72 %   |
| Aluminum Frame      | Anodized aluminum alloy      | ≈ 10-12 %   |
| EVA Encapsulant     | Ethylene-vinyl acetate       | ≈ 6-8 %     |
| Silicon Cells       | Polycrystalline silicon      | ≈ 4-6 %     |
| Backsheet           | PET/PVF polymer              | ≈ 2-3 %     |
| Copper Ribbons & JB | Copper, tin, plastic, diodes | ≈ 1-2 %     |

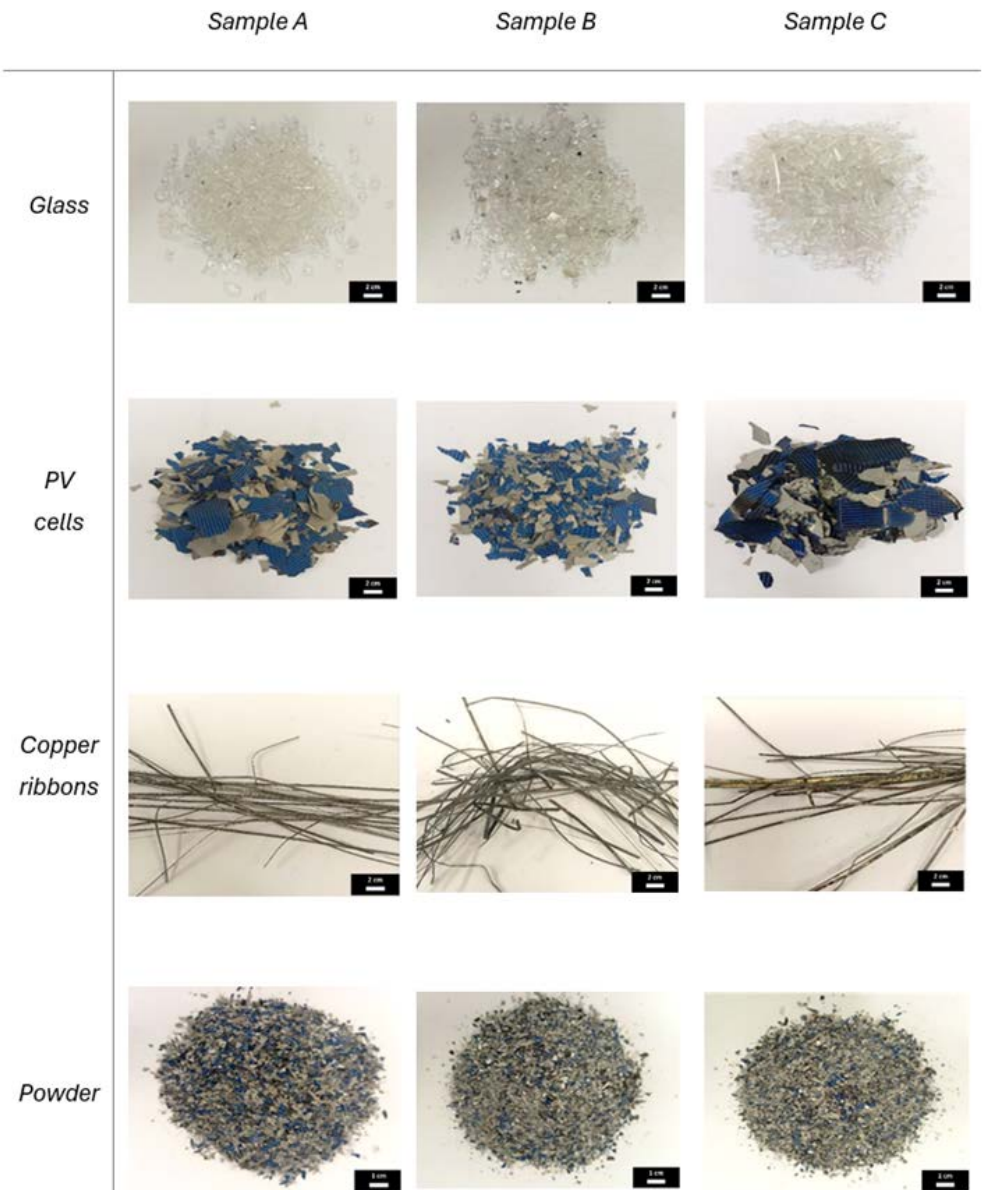
test conditions. The aluminum frame, which comprised approximately 18% of the panel weight, was fully recovered in both cases with no observable contamination. Copper ribbons, constituting approximately 1% of the total panel weight, were successfully extracted and characterised us-

ing scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS).

The SEM analysis is reported in Figure 6.

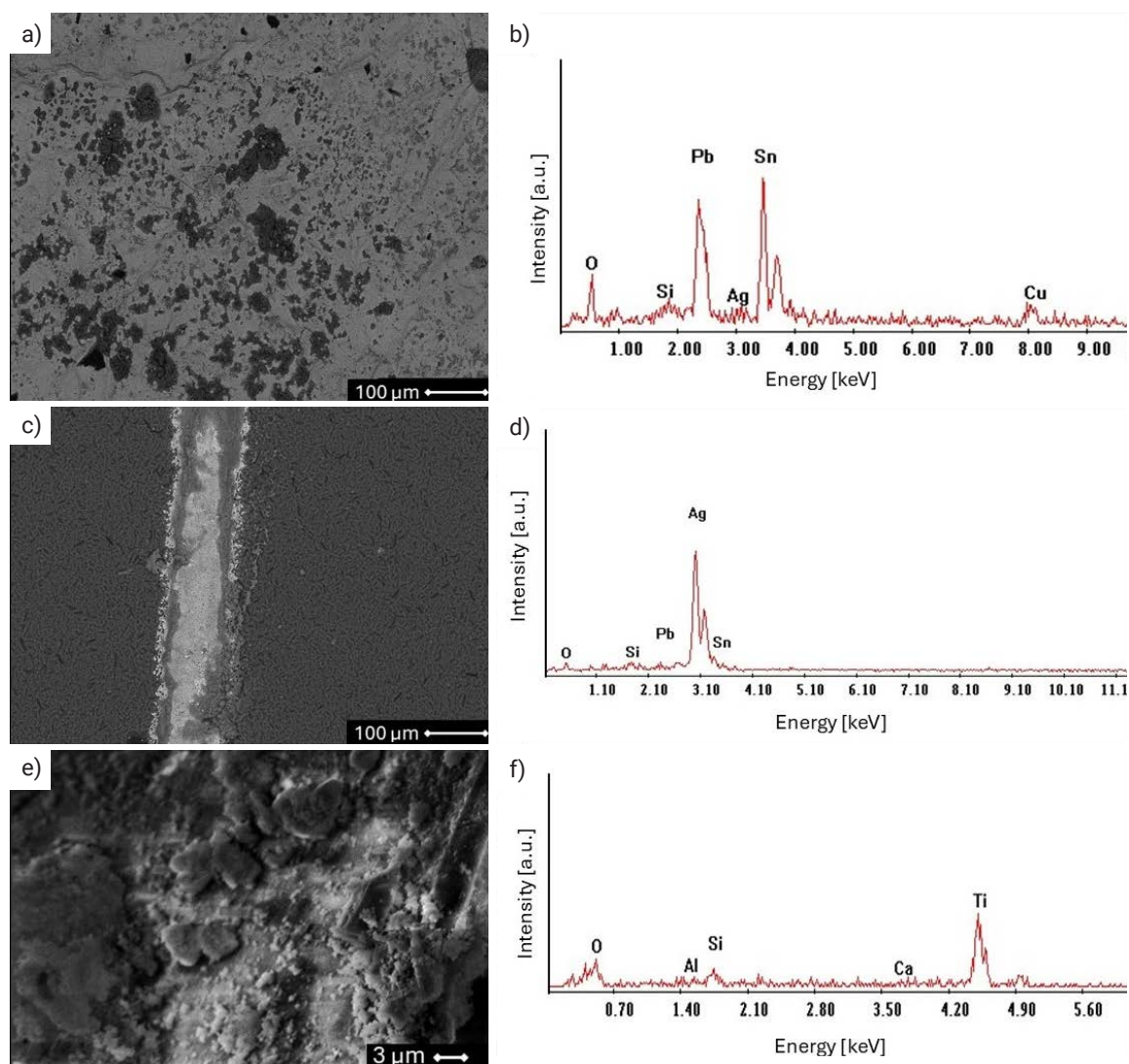
The analysis confirmed that the ribbons are composed of copper coated with a tin-lead alloy (Figure 6b). The silver contacts on the PV cells contained trace amounts of lead and zinc, with no significant compositional differences between samples with or without backsheet (Figure 6d).

Notable differences were observed in the composition of the powder fraction, which consists of fine residues of glass and PV cells. In panels that retained the backsheet, the powder contained a high concentration of titanium dioxide (TiO<sub>2</sub>), which originates from the degradation of the polymeric backsheet material (Figure 6f). In contrast, the powder recovered from backsheet-removed panels was free from TiO<sub>2</sub> contamination, indicating that backsheet removal significantly improved the purity of this fraction. The elimination of TiO<sub>2</sub> is particularly relevant for downstream



**FIGURE 5:** Images of the materials recovered from different samples of PV panels.





**FIGURE 6:** BSD-SEM and EDS analysis Images of: a-b) the surface of the copper ribbons; c-d) the front face of the PV cell with contact; e-f) glass surface with  $\text{TiO}_2$  powder contamination.

recycling applications, as it reduces the need for additional purification steps.

These findings demonstrate that backsheet removal has no impact on the recovery of glass, metals, or PV cells while significantly improving the purity of the recovered powder fraction by eliminating  $\text{TiO}_2$  contamination.

### 3.2 Energy consumption

A detailed analysis of the energy requirements associated with the recycling process was conducted to evaluate the influence of backsheet removal, considering both electricity and fuel (propane). Polymeric backsheets, typically composed of materials such as poly(ethylene terephthalate) (PET) and polyvinylidene fluoride (PVDF), possess intrinsic calorific values, this can sensibly contribute to thermal energy recovery during combustion-based treatments. Therefore, their presence within the module structure is expected to reduce the energy demand required for achieving and maintaining process temperatures. This analysis aims to quantify such reduction.

In fact, measurements of propane consumption indicated that the removal of the backsheet led to a notable increase in the demand for external thermal energy input. The backsheet is estimated to contribute approximately 21% of the total calorific value of a photovoltaic (PV) module. In comparison with sample C (with intact backsheet), the propane consumption increased by 40% in the case of Sample A, where the backsheet was completely removed, and by 16% in the case of sample B (with partially removed backsheet). The more pronounced increase observed in Sample A suggests that, in addition to the backsheet, portions of the ethylene-vinyl acetate (EVA) encapsulant were also removed during the pre-treatment phase. This further reduction in combustible material likely contributed to the increased external fuel requirement. In contrast, Sample B retained its encapsulant layer, which helped to partially offset the loss of the backsheet's thermal contribution.

Electricity consumption was monitored throughout the process, particularly in relation to the flue gas treatment

system and material separation operations. The flue gas treatment system, which includes an extractor fan, was responsible for the majority of electricity consumption, accounting for approximately 2.8 kW of power usage. Additional power was required for the mechanical separation of copper ribbons, powder fractions, and glass-cell mixtures, contributing to an overall electricity consumption of 10.5 kWh per 100 kg of PV panels processed. Unlike propane consumption and as expected, electricity usage was not significantly affected by the presence or absence of the backsheet, as the fundamental requirements for gas extraction and mechanical separation remained constant.

Overall, these results indicate that backsheet removal reduces the internal energy contribution of the panels, necessitating an increase in external fuel consumption. However, the impact on electricity consumption is negligible, suggesting that any additional energy requirements are limited to the thermal phase of the process.

### 3.3 Environmental performance

The concentrations of key gaseous pollutants were measured in the flue gas stream upstream of any filtration or treatment system, to comprehensively compare the environmental performance of the treatment on the different samples. This approach provided an accurate representation of the raw emissions generated during thermal processing.

The results of the analysis is reported in Table 2.

Gas chromatography and FTIR analysis confirmed the complete elimination of hydrogen fluoride (HF) emissions in cases where the backsheet was removed prior to treatment. This observation is consistent with the known chemical composition of typical PV module backsheets, which may contain fluoride-based polymers such as polyvinylidene fluoride (PVDF) or fluorinated additives.

From an environmental standpoint, the suppression of HF emissions is particularly significant. Hydrogen fluoride is a highly corrosive and toxic compound that poses substantial risks to both human health and industrial equipment. Its presence in flue gas necessitates the deployment of scrubbing systems, typically involving alkaline neutralization and particulate filtration, which increase operational complexity and cost (Le et al., 2021). On the

other hand, uncontrolled HF release must be avoided as it contributes to atmospheric acidification and represents a non-trivial regulatory compliance challenge under air quality directives (Ardenete et al., 2019). Therefore, the removal of the backsheet prior to thermal treatment not only improves process safety but also reduces the environmental impact and post-treatment burden of the recycling operation.

The concentration of particulate matter in the flue gases was markedly reduced in panels with a totally or partially removed backsheet (Sample A, B). Titanium dioxide (TiO<sub>2</sub>) powder, widely used as a filler in polymeric backsheets, was identified as the primary contributor to dust emissions in intact panels (Sample C). The elimination of the backsheet effectively removed this source of particulate contamination, resulting in significantly lower dust concentrations and thereby improving the overall air quality of the exhaust stream. This reduction in particulate emissions is environmentally advantageous, as airborne dust can contribute to respiratory health issues and necessitates filtration infrastructure to meet regulatory standards (Anderson et al., 2012).

Volatile organic compound (VOC) emissions exhibited variability dependent on processing conditions but showed no definitive correlation with the presence or absence of the backsheet. Carbon monoxide (CO) concentrations ranged between 20 and 70 mg/Nm<sup>3</sup>, while nitrogen oxides (NOx) levels varied from 5 to 30 mg/Nm<sup>3</sup>, with Sample C demonstrating the highest emissions for both gases. Dust concentrations spanned a broad range, from a low of 20 mg/Nm<sup>3</sup> in Sample B (backsheet removed) to a peak of 200 mg/Nm<sup>3</sup> in Sample C (intact panels), underscoring the influence of pre-treatment on particulate emissions.

Heavy metal analysis of the flue gas revealed minor reductions in chromium (Cr) and nickel (Ni) emissions following backsheet removal. Conversely, lead (Pb) emissions were elevated in Sample A, likely attributable to the abrasion and subsequent aerosolization of the tin-lead alloy coating on copper ribbons during mechanical pre-treatment. These findings highlight the complex trade-offs inherent in recycling processes, where material removal can mitigate certain pollutant sources while potentially exacerbating others.

**TABLE 2:** Fumes produced during the panel's thermal treatment (before treatment).

| Pollutant                                 | Sample A [mg/Nm <sup>3</sup> ] | Sample B [mg/Nm <sup>3</sup> ] | Sample C [mg/Nm <sup>3</sup> ] |
|-------------------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Carbon monoxide, CO                       | 24.2 ± 1.5                     | 31.8 ± 1.9                     | 73.9 ± 4.4                     |
| Dust                                      | 54.8 ± 1.8                     | 18.6 ± 0.61                    | 205 ± 6.7                      |
| Volatile organic compounds, VOCs          | 2.5 ± 0.22                     | 2.8 ± 0.25                     | 2.1 ± 0.18                     |
| Hydrofluoric acid, HF                     | < 0.2                          | < 0.2                          | 0.37                           |
| Sulphur dioxide, SO <sub>2</sub>          | < 0.5                          | < 0.5                          | < 0.5                          |
| Lead (Pb)                                 | 0.107 ± 0.0200                 | 0.017 ± 0.0040                 | 0.042 ± 0.0098                 |
| Total Chromium (Cr)                       | 0.004 ± 0.0011                 | 0.014 ± 0.0034                 | 0.020 ± 0.0048                 |
| Copper (Cu)                               | 0.005 ± 0.0011                 | 0.005 ± 0.0012                 | 0.005 ± 0.0012                 |
| Nickel (Ni)                               | < 0.003                        | 0.046 ± 0.0093                 | 0.006 ± 0.001                  |
| Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V | 0.12                           | 0.093                          | 0.073                          |

Importantly, analyses of dioxins and polychlorinated biphenyls (PCBs) demonstrated negligible emissions across all samples, indicating that the thermal treatment of photovoltaic panels under the conditions tested does not produce significant quantities of these highly toxic and persistent organic pollutants.

Overall, the data suggest that the removal of polymeric backsheets prior to thermal recycling significantly reduces particulate and hydrogen fluoride emissions, thereby mitigating critical environmental hazards associated with flue gas treatment. However, this benefit must be balanced against the potential increase in lead emissions due to mechanical processing of copper components.

## 4. CONCLUSIONS

The present study systematically analyzed the impact of backsheet removal on the thermal recycling of photovoltaic (PV) panels, focusing on material recovery, energy consumption, and environmental performance. The comparative analysis between panels with and without backsheet demonstrated that the pre-treatment technique aimed at removing the backsheet offers distinct advantages, particularly in terms of material purity and emission reduction, while also introducing some challenges related to energy consumption.

Specifically, the study found that:

- Backsheet removal did not affect the efficiency or structural integrity of recovering key materials such as glass, PV cells, aluminum, and copper ribbons.
- Removal of the backsheet significantly improved the purity of recovered powder by eliminating titanium dioxide (TiO<sub>2</sub>), reducing the need for additional purification steps.
- Backsheet removal eliminated hydrofluoric acid (HF) emissions by avoiding the processing of fluoride-containing materials.
- Dust emissions were substantially reduced due to the absence of TiO<sub>2</sub>, a primary source of particulates.
- Backsheet removal process led up to a ~40% increase in external fuel consumption, attributed to the complete lot of backsheet material and of partial loss of EVA encapsulant, which reduced the panel's overall calorific value.
- Electricity consumption remained stable, as downstream processing steps were unaffected.

In conclusion, the study highlights an important trade-off: while backsheet removal improves material quality and environmental performance, it also increases fuel consumption in the thermal phase of recycling. This raises questions about the overall energy demand of the process and suggests that further optimization is needed to compensate for the loss of internal energy provided by the backsheet during combustion.

From a future perspective, the feasibility of valorizing the removed backsheet material is also crucial and should be further investigated. The backsheet powder recovered with sanding process must not become a waste and alternative pathways such as chemical recycling, material upcy-

cling, or secondary applications in other industries are under investigations. The backsheet recovery and recycling would further enhance the circular economy potential of PV panel recycling and minimize material losses within the system.

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# ADVANCING WATER CIRCULARITY: A SIMULATION OF HYDRODYNAMIC CAVITATION AND MEMBRANE PROCESSES FOR SUSTAINABLE INDUSTRIAL WASTEWATER REUSE

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## ABSTRACT

Water scarcity is a growing global challenge, exacerbated by population growth, industrialization, and climate change. As freshwater resources become more limited, water reuse has emerged as a promising solution to alleviate shortages. Reusing treated wastewater for agricultural use in arid and semi-arid regions is considered a sustainable approach to conserving freshwater and supporting food production. However, for this to be viable, treated wastewater must undergo rigorous treatment processes to ensure both food safety and environmental sustainability. A water circular economy is central to this approach, emphasizing the recycling and reuse of water in a closed-loop system to minimize waste and maximize resource efficiency. In this model, wastewater is treated, purified, and reused across multiple sectors, reducing overall water consumption. For agriculture, reusing treated wastewater transforms what would be waste into a valuable resource, reducing dependence on freshwater sources. This study examines the integration of advanced treatment technologies into wastewater treatment plants to facilitate the safe and effective reuse of agricultural water. The research focuses on a simulation of a wastewater treatment plant designed for agricultural reuse, starting from a real industrial effluent. The treatment process incorporates innovative methods such as hydrodynamic cavitation, advanced oxidation processes, and membrane filtration to remove organic contaminants and inactivate pathogens. These technologies ensure that the treated wastewater meets the stringent water quality standards required for agricultural irrigation of all types of crops. This work demonstrates how integrating cutting-edge treatment technologies within a circular economic framework can significantly contribute to water sustainability, especially in water-scarce regions.

## 1. INTRODUCTION

Water scarcity is an increasingly urgent global problem, accentuated by the growth of the world population and climate change (Tow et al., 2021). The need for innovative strategies for water resource management has become essential to ensure a sustainable water supply for agriculture and other sectors (Gupta et al., 2012).

Historically, water reuse has been practiced since ancient civilizations, with examples of the use of urban wastewater in agriculture dating back thousands of years (Goyal & Kumar, 2021). Over time, water reuse practices have evolved from simple irrigation systems to complex wastewater treatment plants. Today, water reuse is a widespread practice in many parts of the world, with applica-

tions ranging from agricultural irrigation to industrial use, environmental restoration, and even potable reuse.

Currently, water reuse represents a well-established solution for water scarcity, with thousands of successful projects around the world. Agricultural reuse is widespread, especially in arid and semi-arid regions, where the demand for water for irrigation is constantly increasing. However, water reuse in agriculture requires adequate treatment to ensure food safety and environmental protection (Lazaro-va, 2020).

Among the emerging technologies for treating wastewater for reuse, hydrodynamic cavitation (HC) and advanced oxidation processes (AOPs) have attracted considerable attention. Hydrodynamic cavitation exploits the



formation and collapse of microbubbles in a liquid to generate extreme temperature and pressure conditions, capable of degrading organic pollutants and inactivating microorganisms. AOPs, in turn, are based on the production of highly reactive free radicals, such as the hydroxyl radical ( $\cdot\text{OH}$ ), to oxidize and mineralize pollutants.

The effectiveness of hydrodynamic cavitation depends on several operational parameters, including pressure, temperature, residence time, and reactor geometry. Furthermore, it has been shown that HC can act synergistically with other treatment processes, such as ozonation and UV radiation, improving the overall efficiency of the process. Despite the promising results obtained in the laboratory, the large-scale application of hydrodynamic cavitation in wastewater treatment requires further studies to optimize operating parameters and reduce energy costs (Prisciandro & Innocenzi, 2023).

This work presents the results of a simulation of a wastewater treatment plant (WWTP) designed for water reuse in agriculture starting from a real industrial effluent. The simulation was conducted using the commercial software SuperPro Designer and aims to evaluate the plant's performance under different operating conditions and to identify strategies to optimize process efficiency. The simulated plant integrates a hydrodynamic cavitation and AOP system for tertiary treatment of wastewater to remove organic contaminants and inactivate pathogens, ensuring compliance with quality requirements for agricultural reuse.

## 2. MATERIALS AND METHODS

The design and simulation of the treatment plant were carried out using the commercial software SuperPro Designer, to optimize the pollutant removal efficiency and evaluate the quality of the treated water for potential reuse in agriculture.

The following effluent quality metrics were monitored in both plant configurations (with and without Hydrodynamic Cavitation): COD,  $\text{BOD}_5$ , TOC, TSS, TKN, TP,  $\text{NO}_3\text{-NO}_2$ . The results were compared to the regulatory limitations for

**TABLE 1:** Properties of the effluent to be treated.

| Parameter                                    | Value |
|----------------------------------------------|-------|
| Flow rate                                    | 100   |
| Chemical Oxygen Demand (COD)                 | 2500  |
| Biochemical Oxygen Demand ( $\text{BOD}_5$ ) | 1000  |
| Total Kjeldahl Nitrogen (TKN)                | 17    |
| Total Protein (TP)                           | 3,10  |
| Chlorine ( $\text{Cl}_2$ )                   | 490   |
| $\text{NO}_3\text{-NO}_2$                    | 37,3  |
| pH                                           | 8,5   |

agricultural reuse (Classes A and B under European Union Regulation (UE-2020/741). The percentage reduction of each parameter in the Hydrodynamic Cavitation section was also calculated to determine the efficiency of the advanced oxidation process.

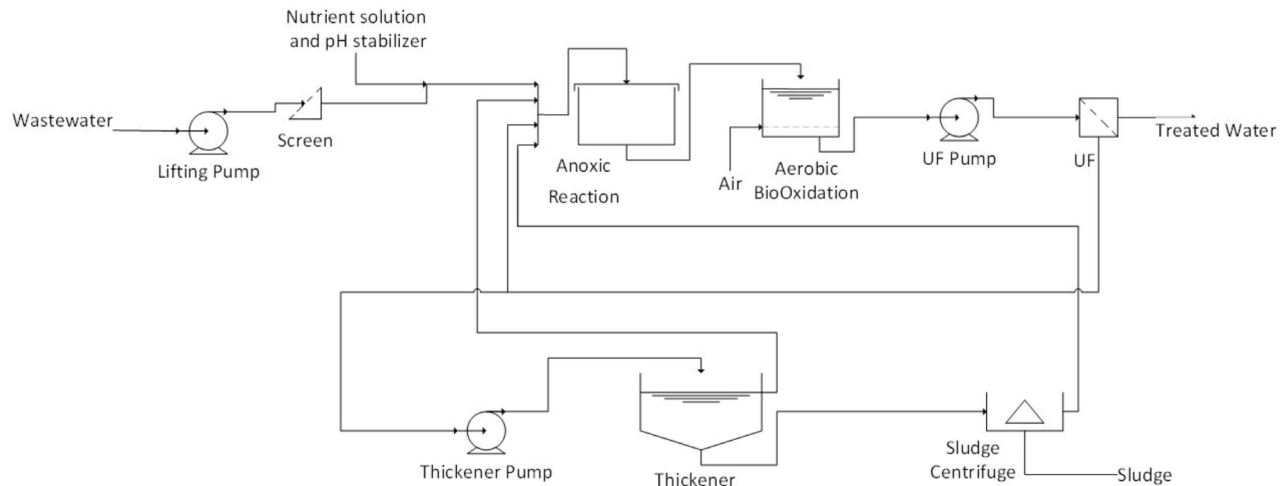
## 3. PLANT DESCRIPTION

This plant layout is intended to treat real industrial wastewater with the composition described in Table 1. The system depicted here can handle a current of  $100 \text{ m}^3/\text{h}$  of effluent (35000 E.I.).

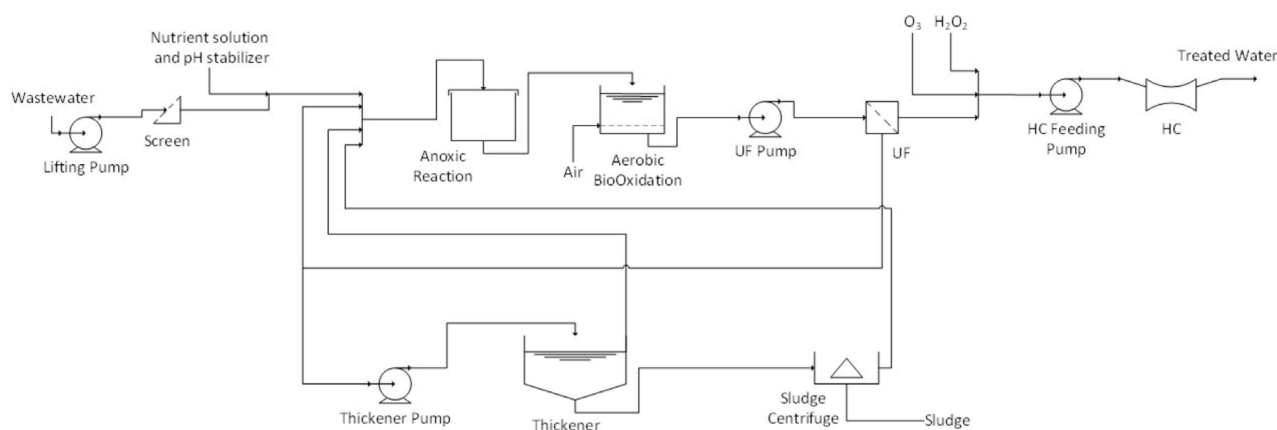
### 3.1 Wastewater treatment plant description

The basic scheme, shown in Figure 1, is intended to discharge effluent to municipal wastewater collection and treatment plants following Italian legislation (Italian Republic, 2006).

The wastewater to be treated is finely screened to remove particle materials. Given the effluent's initial composition, it is added with chemicals to supplement nutrients and balance the pH. Thus, 33% HCl is added until a concentration of  $45 \text{ mg/l}$  (pH 7,6) is obtained. In addition, nitrogen and phosphorus sources are provided in quantities of  $20,5 \text{ mg/l}$  and  $4,4 \text{ mg/l}$ , respectively. The overall consumption of these combinations will be  $4,55 \text{ kg/h}$  of HCl (33%) and  $13,5 \text{ l/h}$  of nitrogen/phosphorus mixture (18%).



**FIGURE 1:** Process flow diagrams for the basic wastewater treatment plant.



**FIGURE 2:** Wastewater Treatment Plant equipped with the Hydrodynamic Cavitation section.

Then, the effluent is sent to the biological treatment section to undergo denitrification in the first tank and aerobic oxidation in the second.

### 3.2 Hydrodynamic Cavitation Section

The same plant can be equipped with an advanced oxidation section, as shown in Figure 2.

Specifically, the advanced oxidation section includes hydrodynamic cavitation treatment, composed of a pump and a Venturi tube. HC is a process of generation, growth, and subsequent collapse of vapor-filled cavities within a liquid due to variations in local pressure. The cavities are generated in a low-pressure region, as in the throat of a Venturi tube. When these cavities travel to a region of higher pressure, they implode. The cavity collapse under certain conditions results in very high pressure and temperature near the location of collapse. These extreme local temperatures ( $> 2000\text{ K}$ ) and pressures ( $> 100\text{ MPa}$ ) result in the generation of highly reactive radical species (from water and dissolved air), with extreme physio-chemical effects that have been of interest to engineers and scientists due to their potential to damage equipment. On the other side, the strongly oxidizing hydroxyl radicals and local hot spots can be used for treating pollutants in water as well as for intensifying a variety of organic reactions in water (Capocelli et al., 2014). Therefore, among various AOPs, the  $\cdot\text{OH}$  yield, removal efficiency, and energy efficiency are the main evaluation indicators. In general, less  $\cdot\text{OH}$  is produced and higher energy consumption is required by hydrodynamic cavitation alone, but it can remarkably enhance oxidative degradation of organics by promoting the mass transfer and  $\cdot\text{OH}$  formation in combination with other AOPs, such as Fenton oxidation (Innocenzi et al., 2019) and ozonation (Wu et al., 2012). Several studies also by this research group have confirmed the synergistic effect of hydrodynamic cavitation and oxidants like ozone and hydrogen peroxide, (Ayedi et al., 2024; Innocenzi et al., 2022) to create a hybrid advanced oxidation process that achieves significantly greater degradation in a shorter period. In this treatment scheme, the inlet water stream of hydrodynamic cavitation is enriched with  $7.5\text{ mg/l}$  of ozone and  $0.3\text{M}$  of hydrogen peroxide. These are average concentrations used in previous stud-

ies carried out on polluted water streams with different organic loads.

The permeate from ultrafiltration is thus first added up with hydrogen peroxide ( $0.5\text{ kg/h}$ ) and ozone ( $1\text{ kg/h}$ ). It is then pumped into a Venturi tube-type hydrodynamic cavitation reactor via a pump. This pump must produce a sufficient  $D_p$  to initiate cavitation, with the ensuing synergistic effects on the previously supplied oxidants. 99% bacterial degradation was assumed for the simulation of this section, consistent with results found in the literature (Sun et al., 2020).

## 4. RESULTS AND DISCUSSION

The findings of this study focus on the reuse of industrial wastewater for irrigation purposes, while future research will investigate plant energy use. The described plant configurations produce a treated water flow rate of  $71.23\text{ m}^3/\text{h}$ .

### 4.1 Plant Characteristics

Table 2 summarizes the main characteristics of the wastewater treatment plant equipment.

Advanced Oxidation Processes increase the quality of treated water by mineralizing chemical species that can pass through traditional wastewater treatment without

**TABLE 2:** Wastewater treatment plant equipment.

| Equipment               | Main Characteristic |
|-------------------------|---------------------|
| Lifting Pump            | 5                   |
| Screen Number           | 1                   |
| Anoxic Tank             | 3450                |
| Aerobic BioOxidation    | 5200                |
| Ultrafiltration Pump    | 50                  |
| UF Membrane Type        | Dft Membrane        |
| UF Membrane Number      | 86                  |
| Thickener Charging Pump | 1                   |
| Thickener               | 8.5                 |
| Sludge Sentrifuge       | 15                  |
| Venturi Feeding Pump    | 15                  |

degradation (Prisciandaro and Innocenzi. 2023). In this study, a hydrodynamic cavitation system with a Venturi tube is proposed. As demonstrated in various investigations, hydrodynamic cavitation has a synergistic effect on conventional oxidants when combined with the output of earlier treatments (Wang et al. 2021).

#### 4.2 Treated water composition

Table 3 depicts the characteristics of water discharge from the two alternative system setups. The table also indicates the constraints imposed by current European guidelines on water reuse for irrigation applications (EUROPEAN PARLIAMENT, 2020).

As demonstrated in Table 3, the water leaving the ultrafiltration treatment may be appropriate for reuse as irrigation water for crops classified as Class B water applications. However, EU Regulation 741/2020 mandates that the water be disinfected before its reuse; therefore, the water exiting the Ultrafiltration section is not appropriate for irrigation reuse. The environmental parameters of this stream should be attributed to bacterial or viral remnants in the treated effluent.

Advanced oxidation methods are also covered in the guidelines for potable water reuse issued by the USEPA in 2017 as a disinfection method (USEPA, 2017).

According to EU 741/2020, hydrodynamic cavitation treatment yields Class A water suitable for all forms of culture. It has also been demonstrated in the literature that such a process can be efficient at removing numerous pathogens with great efficiency (Sun et al.,2020).

The reduction efficiency in environmental parameters (TOC, TP, TKN, COD, BOD<sub>5</sub>, TSS) of the current output from the cavitation section resulted always higher than 98%. This performance can be also attributed to the degradation of residual bacterial or viral load in the output current from Ultrafiltration (Mazziotti di Celso & Prisciandaro, 2013).

#### 5. CONCLUSIONS

In this study, modeling results for two possible layouts of an industrial wastewater treatment facility are provided. In the first plant design, the discharge meets all the standards for discharge to the municipal wastewater management network. This is mostly owing to the Ultrafiltration portion, which enables complete compliance with current

Italian rules on the issue. The outflow from the ultrafiltration section contains COD, BOD<sub>5</sub>, and TSS concentrations that would allow the reuse of Class B water for irrigation purposes under current European Union regulations. Still, the lack of a disinfection step makes them unsuitable for the purpose.

The literature indicates higher than encouraging yields for wastewater disinfection using Advanced Oxidation Treatments, specifically Hydrodynamic Cavitation in combination with other oxidants. The implementation of one stage of Hydrodynamic Cavitation to the initial plant scheme, in addition to disinfecting the effluent, enables further reductions in COD and TSS levels, as well as the reuse of Class A water for irrigation applications under European Union regulations.

However, the treated wastewater retains residual chlorine, making it suitable for certain crops. This limitation could be readily addressed with a Reverse Osmosis step. This operation ensures that the water is of adequate quality to be reused for processing. However, the topic stems from the current study's objectives.

Future research will focus on energy optimization using simulation tools, as well as assessing the environmental impact of the schemes employed through Life Cycle Assessment.

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Extra contents

# COLUMNS AND SPECIAL CONTENTS

This section comprises columns and special contents not subjected to peer-review



## DETRITUS & ART / A personal point of view on Environment and Art

by Rainer Stegmann

*It is often more important what someone sees, what something might be, than to know what it is.* In my view, this is an important statement worth considering in life; life might become more intense, varied, and creative. I will explain this statement using the presented photo. If you look at the Alternative Text of this photo, it says: a picture that contains grey, concrete, cement, and limestone. This view on the photo gives me hope that artificial intelligence AI is still a long way away from showing human emotions.

Now, let me present my interpretation. Having visited many art museums in China and Singapore, I see a landscape painted in a style that some Chinese artists use. I see the clouds above a mountain, with a small fir tree forest on the middle right side in a mountain landscape. If you look at this photo for longer, you may get a similar impression or see something different, but it is not just grey, concrete, cement, or limestone. I hope to make it clear what I want to share with you.

Where did I take this photo? I made this photo from a section of the wall of the house I live in. It is a plastered wall covered with a variety of these blackspots and lines. The black patterns on the wall may consist of black algae, as well as mosses and lichens; additionally, they may be deposits of air pollutants.

To take a photo of the wall with some content, one has to select the "right" section of the wall. Examining the entire wall, one may agree with the description of AI.

What does this have to do with waste? I have already pointed out earlier the health risks that may arise from micro- and nanoparticles. Such particles may originate from rust, abrasions from brakes and tires, as well as from paints and plastered walls. We must consider that parti-

cles, per se, are dangerous when they enter the lungs; the particle material itself does not need to be toxic. Examining the wall, it may require a paint job because material from the wall surface has eroded, producing microparticles. To get an idea about the dimension of the number of paints used, we can expect that approximately 30 liters of paint are needed to paint 100 m<sup>2</sup> of a facade. Of course, from one paint job to another, not all the paint may be eroded. We must always consider that these eroded paint particles do not disappear and will remain in the environment.

To reduce/avoid such small particle emissions, further research is needed, as well as the avoidance of using nanoparticles in products. The use of longer-lasting or different materials, along with improved preservation, must be enforced.

Let me close my brief remarks with my initial statement: *it is often more important what someone sees what something might be than to know what it is.*



*In the next issue of DETRITUS I will present Waste and Artificial Art.*







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