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CHARACTERIZATION OF RESIDUES ARISING FROM SUSTAINABLE HYDROGEN GENERATION VIA METAL-MEDIATED REACTIONS

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Abstract. Faced with the growing consumption of energy worldwide, humanity is in search of a sustainable energy matrix. Such a change is extremely important and necessary so that the current challenges related to climate change, scarcity of natural resources, pollution, energy security, sustainable development and access to energy are faced. The transition to renewable energy sources is crucial to reducing greenhouse gas emissions, ensuring energy availability in the future, promoting a cleaner and healthier environment, stimulating economic growth, as well as enabling access to energy in regions and communities that still do not have adequate access. It is a fundamental shift towards a more sustainable and resilient future. The hydrogen-based economy should be part of a possible solution to the energy problem. Hydrogen is the known fuel with the highest calorific value on a mass basis, and the simplest and most abundant gaseous element on the planet. The generation of hydrogen can be obtained by metallic ways, for example, by the oxidation of aluminum in an alkaline solution. The use of recyclable metals, such as aluminum in this study, is an option for sustainable hydrogen generation processes. However, like any chemical reaction, part of the products generated are waste, some of which are harmful to the environment, thus making the production of sustainable fuels unfeasible if an appropriate industrial technological destination is not found for them. In this context, the Optical Emission Spectroscopy with Inductive Coupling Plasma (ICP-OES) technique was chosen as an essential characterization tool for studying the waste, particularly aiming for conscious disposal. Through this technique, it is possible to obtain information about the chemical composition of the samples, identifying the elements present and allowing complete control of the reaction. This provides a completely sustainable chain of processes for hydrogen production as a renewable energy source, making it a promising perspective for technological advancement and the transition of the energy matrix towards a more sustainable future. Consequently, besides gaining better control and safety in the reaction, these insights into the generated waste are valuable. Not only do they help comprehend the environmental implications, but they also aid in making decisions about waste management and recycling processes, with a primary focus on appropriate disposal and optimizing their applications.

Keywords: characterization; clean and renewable energy; hydrogen generation; reaction waste; ICP-OES technique

1. INTRODUCTION

Since the onset of the First Industrial Revolution, unparalleled industrial growth was primarily driven by the widespread use of coal, followed by oil. This unbridled reliance had a lasting global impact that persists to this day (Jacob-Furlan et al., 2023). The critical nature of this dependence on fossil fuels became evident in the 1970s, post the first oil crisis, when many nations grappled with shortages, leading to famine and societal upheaval. This crisis underscored the world's true reliance on fossil fuels (Ma et al., 2022). Consequently, the scientific community recognized the need for alternative energy sources, prompted by the finite nature and environmental pollution associated with fossil fuels (Alharthi et al., 2022).

Since then, extensive research has been dedicated to exploring ways to transition the global energy matrix. There are compelling incentives for this shift, given the fundamental role of energy in sustaining terrestrial existence. The escalating global population serves as a significant catalyst for the exploration of renewable sources, as the future of humanity hinges on ensuring a continued energy supply, especially to support existing technologies (Emmott, 2013; Ang et al., 2022).

The potential depletion of energy due to the finite nature of fossil fuels, coupled with the direct threat to human survival, marked a pivotal moment. The first global oil crisis not only highlighted the immediate challenges of fossil fuel scarcity but also catalyzed the scientific pursuit of renewable energy solutions (Pata, 2018).

Renewable energy, conceptualized as: *clean energy generated through cyclical processes, plays a crucial role in reshaping the global energy landscape* (Çoker et al., 2010; Manish et al., 2006).

This shift is evident in the consolidation of renewable energies within the world's energy matrix. Examples of renewable energy sources include hydroelectric, wind, biomass, and the utilization of H₂ as an energy carrier (Turner, 1999; Santika et al., 2019).

The excessive consumption of fossil fuels has received considerable attention in discussions about the future of our planet and the impacts of the release of greenhouse gases. As a result, the search for alternatives that reduce dependence on these fuels has intensified, with emphasis on research on renewable energy sources (Chang, et. al., 2022).

In this context, H₂ emerges as a solution of great potential due to several scientific reasons. First, H₂ is a highly attractive gas because it has a higher calorific value than other gases (Wanghon, 2018). In addition, its special combustion properties offer significant advantages, favoring the reduction in the use of fossil fuels and contributing to the mitigation of the environmental impacts associated with its burning.

In 2018, the International Energy Agency (IEA) reported that over 30% of global energy was sourced from oil and fossil fuels, with coal and natural gas contributing over 45%. Renewable sources, including hydroelectric, biomass, and nuclear, accounted for less than 20%. Various forms of renewable energy, such as photovoltaic cells, solar energy, fuel cells, and H₂ generation, have been extensively researched for their viability and profitability.

There are several techniques for the production of H₂, but it is important to highlight that some of them can cause significant damage to the atmosphere (Wang, et. al., 2009).

The Table 1 below provides a more detailed look at the different hydrogen production methods and their respective environmental impacts. It is essential to consider these aspects when assessing the sustainability and viability of hydrogen production sources.

Table 1. H₂ production techniques and environmental impacts involved

Raw Material	Approach	Production Method	Environmental Impact	References
Water	Photolysis	Naturally, this process occurs during plant photosynthesis and can be artificially generated in the laboratory using light to decompose water into H ₂ and oxygen. On a research scale, solar energy is employed to drive this process.	Although the process is considered slow, photolysis from an environmental point of view is seen as a very favorable form of hydrogen production, as it does not emit greenhouse gases or other pollutants during the reaction.	Mahbub et al. 2022
	Electrolysis	The technique of separating water into H ₂ and O ₂ is achieved by using electricity. This process can be carried out in electrolytic cells that consist of an electrolytic solution and two electrodes, namely a cathode and an anode.	May result in greenhouse gas emissions depending on the source of electricity used.	Maggio, et. al. 2022
Natural gas, propane, and methane.	The reforming of hydrocarbons.	The process involves heating the hydrocarbon in the presence of a catalyst, resulting in the production of H ₂ along with other compounds like carbon monoxide and carbon dioxide.	Releases carbon dioxide (CO ₂) as a by-product, contributing to the greenhouse effect	Woo et al. 2023
Biological processes	Photosynthesis natural	Certain algae and cyanobacteria have the ability to produce H ₂ through photosynthesis. This process entails the splitting of water into H ₂ and O ₂ in the presence of sunlight.	As a natural process, photosynthesis is beneficial to the environment as it does not generate any GHG. However, when applying it for the production of H ₂ through artificial photosynthesis, it is necessary to carry out life cycle assessments.	Abas, et. al. 2020
	Anaerobic digestion	Some bacteria found in the gastrointestinal tract of ruminant animals, such as cows and sheep, have the capability to produce H ₂ through anaerobic digestion of cellulose and other carbohydrates.	Anaerobic digestion can cause environmental impacts, including the emission of greenhouse gases, the production of effluents and waste, the use of natural resources and the possibility of competition with food production.	Córdova-Lizama et. al. 2022
	Fermentation	Some anaerobic bacteria can produce H ₂ through the fermentation of sugars. This process includes the breakdown of sugars into acetic acid, alcohol, and H ₂ .	The associated impacts are linked to the emission of greenhouse gases, the use of natural resources, the generation of effluents and the potential use of chemical additives.	Balachandar et al. 2020
	Photo-fermentation	Certain bacteria are capable of producing H ₂ through photofermentation. This process entails breaking down water into H ₂ and O ₂ in the presence of sunlight, with the H ₂ produced being used to generate energy.	Environmental impacts relate to the use of natural resources, greenhouse gas emissions, treatment of effluents and by-products, in addition to the dependence of energy efficiency on sunlight conditions	Shui, et al. 2023
Biomass	Gasification of biomass	The process relies on converting biomass into a synthetic gas known as "syngas," which comprises H ₂ , methane, carbon monoxide, and carbon dioxide. H ₂ can be extracted from syngas through purification procedures.	The production of hydrogen from biomass can generate greenhouse gas emissions, especially if the process involves the direct burning of biomass.	Valizadeh et al. 2022

From this, sustainable methods of hydrogen production are in high trend, one of the highlights is the use of recycled metals, for the generation of the gas in interest. The use of recycled aluminum is a great ally in the hydrogen production process based on metals (Jacob-Furlan, et. al, 2022).

2. METAL-MEDIATED REACTIONS

2.1 Periodic table: Families IA, IIA and other metals

Within the chemical context, some metals have higher reactivity levels than others, making them more apt to participate in reactions that produce hydrogen (Greenwood, 1997). Among these, the alkali metals and alkaline earth metals, which are found in groups IA and IIA of the periodic table, respectively, are the most commonly used (Atkins, 2006). Table 2 brings examples of reactions and the probability of the reaction occurring, either in aqueous or acidic medium.

Table 2. Reactivity of Metals with Water, Acids and Bases - Family IA, IIA and Other Metals

Classification	Metal (Symbol)	Reaction with Water	Reaction with Acids	Probability of Reaction
IA (Alkali metals)	Lithium (Li)	$H_2O + 2 Li \rightarrow 2 LiOH + H_2$	$2 Li + 2 HCl \rightarrow 2 LiCl + H_2$	Highly reactive, likely
	Sodium (Na)	$H_2O + 2 Na \rightarrow 2 NaOH + H_2$	$2 Na + 2 HCl \rightarrow 2 NaCl + H_2$	
	Potassium (K)	$H_2O + 2 K \rightarrow 2 KOH + H_2$	$2 K + 2 HCl \rightarrow 2 KCl + H_2$	
	Rubidium (Rb)	$H_2O + 2 Rb \rightarrow 2 RbOH + H_2$	$2 Rb + 2 HCl \rightarrow 2 RbCl + H_2$	
	Cesium (Cs)	$H_2O + 2 Cs \rightarrow 2 CsOH + H_2$	$2 Cs + 2 HCl \rightarrow 2 CsCl + H_2$	
	Francium (Fr)	$H_2O + 2 Fr \rightarrow 2 FrOH + H_2$	Reaction with acids is rare	Extremely rare and unstable
IIA (Alkaline earth metals)	Magnesium (Mg)	$H_2O(hot) + Mg \rightarrow Mg(OH)_2 + H_2$	$Mg + 2 HCl \rightarrow MgCl_2 + H_2$	Highly reactive, likely
	Calcium (Ca)	$H_2O + Ca \rightarrow Ca(OH)_2 + H_2$	$Ca + 2 HCl \rightarrow CaCl_2 + H_2$	
	Strontium (Sr)	$H_2O + Sr \rightarrow Sr(OH)_2 + H_2$	$Sr + 2 HCl \rightarrow SrCl_2 + H_2$	
	Barium (Ba)	$H_2O + Ba \rightarrow Ba(OH)_2 + H_2$	$Ba + 2 HCl \rightarrow BaCl_2 + H_2$	
	Radium (Ra)	$H_2O + Ra \rightarrow Ra(OH)_2 + H_2$	$Ra + 2 HCl \rightarrow RaCl_2 + H_2$	Extremely rare, radioactive and unstable.
Other metals	Aluminum (Al)	$2 Al + 6 H_2O \rightarrow 2 Al(OH)_3 + 3 H_2$	$2 Al + 6 HCl \rightarrow 2 AlCl_3 + 3 H_2$	Reactive, likely
	Zinc (Zn)	Does not react with water	$Zn + 2 HCl \rightarrow ZnCl_2 + H_2$	Reactive, may require acid
	Iron (Fe)	Does not react with water	$Fe + 2 HCl \rightarrow FeCl_2 + H_2$	

The mentioned metals have the ability to release hydrogen gas when reacting with water or waiting. Although Zn and Fe do not react directly with water, they can generate hydrogen gas when reacting with resistance. On the other hand, the metals francium and radium are rare and highly radioactive, making practical experiments intuitive. It is important to recognize that the reactivity of these metals can vary and the efficiency of reactions can depend on factors such as temperature, acid concentration and specific reaction conditions.

2.2 Aluminum

Millennia ago, the history of aluminum began. This light and versatile metal, with the chemical symbol Al and atomic number 13, played a crucial role in the development of human civilization, especially during the industrial revolution. Its unique properties have made it an invaluable material in many applications (Constantino et. al., 2001). With its low density (2.7 g/cm³) and resistance to corrosion, aluminum has become the ideal choice for aircraft, automobiles, packaging and light structure construction. Its light weight has provided significant improvements in the transportation industry and energy efficiency. Furthermore, aluminum's excellent electrical and thermal conductivity makes it a crucial component in the manufacture of wires, cables and various electronic devices (Greenwood, 1997).

These characteristics allow efficient transmission of electricity and heat, making it indispensable for modern technology. Over the centuries, aluminum has evolved from a rare and precious material to one of the most used elements in today's society. Its versatility, along with scientific and technological advances, shaped the history of aluminum and positioned it as one of the main pillars of our industrialized civilization (Kauffman and Adams, 1990).

The aluminum journey begins with the discovery of one of the most abundant elements in the earth's crust. Credit for discovering the metal is attributed to the Danish chemist Hans Christian Ørsted in 1825, although some records suggest that Sir Humphry Davy, in 1807, carried out similar experiments. Ørsted obtained the metal in small amounts by reacting alumina (aluminum oxide) with potassium (Kirk-Othmer, 1992). However, due to the high cost of production, aluminum was initially more valuable than gold and silver. Due to its high added value, aluminum was present on the royal banquet table and in the homes of nobles, considered a really valuable artifact (Evans, 1995).

With scientific progress over the years, innovations such as electrolysis emerged as a key milestone for modernizing the cheap use of aluminum. In 1886, two scientists working independently, Charles Martin Hall in the United States and Paul Héroult in France, simultaneously developed the process of electrolysis of aluminum from aluminum oxide dissolved in molten cryolite (Martin, 2011). This technique represented a true revolution in the aluminum industry, making its production significantly more efficient and accessible. Since then, aluminum has established itself as one of the most versatile and widely used materials in modern society, driving advances in several areas, such as aeronautics, automobiles and civil construction. Its wide-scale adoption was made possible by this scientific achievement, which changed the course of metal history. Aluminum is highly recyclable, and the recycling process requires only about 5% of the energy required for primary production. Large-scale recycling plays a crucial role in reducing the environmental impact and sustainability of the metal (Cassanelli, 2016).

2.3 Chemical reaction

In the quest to develop a sustainable H₂ production system, aluminum stood out as a reagent in chemical reactions that generate H₂ as a product (Bolt et al., 2020; Haller et al., 2021; Hurtubise et al., 2018). The economic aspect of this choice is promising, since the reagents used in the reaction, namely water and aluminum, are easily obtained. When combined in an alkaline medium with an aqueous solution of sodium hydroxide, they react to generate H₂ gas and sodium aluminate. This system is economical, as sodium hydroxide has considerable industrial importance and the process does not require highly expensive equipment to operate (Hiraki, 2007; Akiyama, 2009).

The reaction involving aluminum and sodium hydroxide is highly exothermic, releasing thermal energy of the order of 853 kJ/mol (Cassanelli, 2016). However, a challenge is that when aluminum comes into contact with atmospheric air, it oxidizes, forming a thin layer of aluminum oxide that isolates the metal from the external environment. To overcome this, a catalyst is used to minimize the reaction time, which naturally takes several hours. The catalyst used in this study is hydroxide (alkaline) solution - NaOH - due to its wide industrial use, making it readily available. However, other basic catalysts and chemical hydrides can also be employed to achieve similar effects. (Jacob-Furlan, et. al., 2023)

The presence of sodium hydroxide in the solution is essential, as it dissociates and forms OH⁻ ions, preventing the formation of aluminum oxide. This allows the metal to come into direct contact with water and initiate the reaction (Hsieh; Her; Chen, 2012). The overall reaction is represented by Eq. (1), which summarizes the main chemical processes involved.



From a chemical perspective, it is crucial to maintain precise reaction control to ensure optimal performance, where reactants and products can be easily consumed and generated. Moreover to the production of H₂, the reaction also leads to the formation of an aluminum compound, which can be sodium aluminate (Jacob-Furlan, et. al., 2023). This compound can be in the form of an ionizable complex, with aluminum present as Al³⁺ ions in an aqueous medium, when OH⁻ ions are present (Eq. 1). Another possibility is that the compound is alumina, an oxide-base, which can remain suspended in the NaOH solution (Eq. 2).



It is important to note that the basic solution is in a self-recycling system, which contributes to the sustainability of the chemical process, since OH^- ions are in high concentration and continue to react with Na^+ ions dispersed in solution (Eq. 3).



3. CHARACTERIZATION TECHNIQUES

To effectively characterize the residue generated by the reaction and give it a good destination in the future, the atomic absorption technique was used using the method of Optical Emission Spectroscopy with Inductive Coupling Plasma - (ICP-OES), which has as main objective to determine the concentration of chemical elements in several liquid samples. This analytical technique is widely used due to its advantages and applications in several areas of science and technology (Olesik, 1992). Some of the main purposes of the ICP-OES include:

- 1) Quantitative Element Analysis: ICP-OES allows precise quantification of elements in a sample, providing reliable and sensitive results even for very low concentrations (ppb to ppm).
- 2) Multi-element: The technique is capable of analyzing multiple elements simultaneously in a single analysis, which makes it efficient and economical, especially when it is necessary to evaluate several elements in a sample.
- 3) High sensitivity: It is capable of detecting and quantifying elements at levels of parts per billion (ppb) or even parts per trillion (ppt), making it a valuable tool for detecting trace elements and contaminants.
- 4) Analysis of complex matrices: Inductively coupled plasma is capable of efficiently atomizing and ionizing most liquid samples, even those with complex matrices, allowing for the analysis of diverse and challenging samples.
- 5) Assessment of transition elements and lanthanides: The ICP-OES is particularly useful for the analysis of transition elements and lanthanides, which are often found in low concentrations in many samples.

Six samples of recyclable aluminum from different sources were analyzed: industrialized beverage cans and industrial chips. Both samples were collected in experiments conducted at the State University of Maringá (UEM), under specific conditions made by batching inside a reactor, under a pressure that reached the limit of up to 20 bar and a continuous cooling system to maintain the internal temperature of the reactor at up to 60°C during the reaction.

3.1 Sample preparation

After collection, the samples were left to rest. At the end of this period, the samples that were in solution formed a suspension containing the residue and a basic NaOH solution. Using the vacuum filtration technique, the solid part was separated into fractions and subsequently dried in an oven, maintained at around 60°C, for a period of 72 hours.

The samples were properly named "*sample-1*" and coded as *S-1*, *S-2*, up to *S-6*. The Figure 1 below reveals the relationship between the identification of each sample and its respective image.

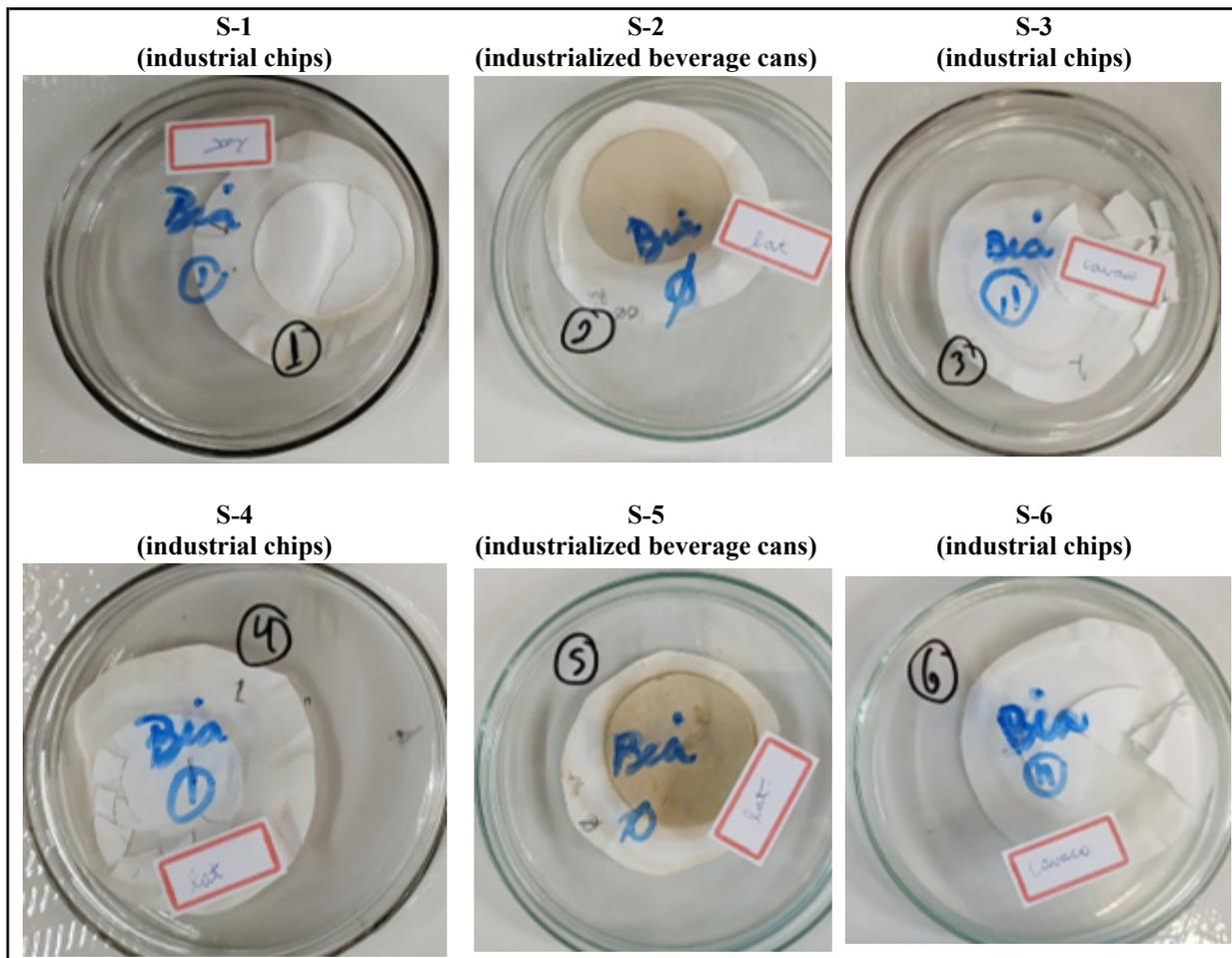


Figure 1. Identification of each sample on ICP-OES

The samples had distinct visual characteristics that suggested important information about their physical composition. The samples with a whitish hue come from aluminum chips (S-1, S-3, S-4, and S-6), exhibiting apparent purity due to the absence of impurities that were reflected in their color. On the other hand, the samples with a more yellowish hue were from industrialized beverage cans (S-2 and S-5), which had paint on their surface. In this context, the paint was considered a possible indicator of the yellowish color of the physical appearance of these samples, which is a preliminary observation for analysis.

3.2 ICP-OES: Results and discussion

After analyzing the samples with ICP-OES, the results obtained provided important information on the composition of recyclable aluminum waste from beverage cans and industrial chips. The Figure 2 shows the relationship of the results obtained:

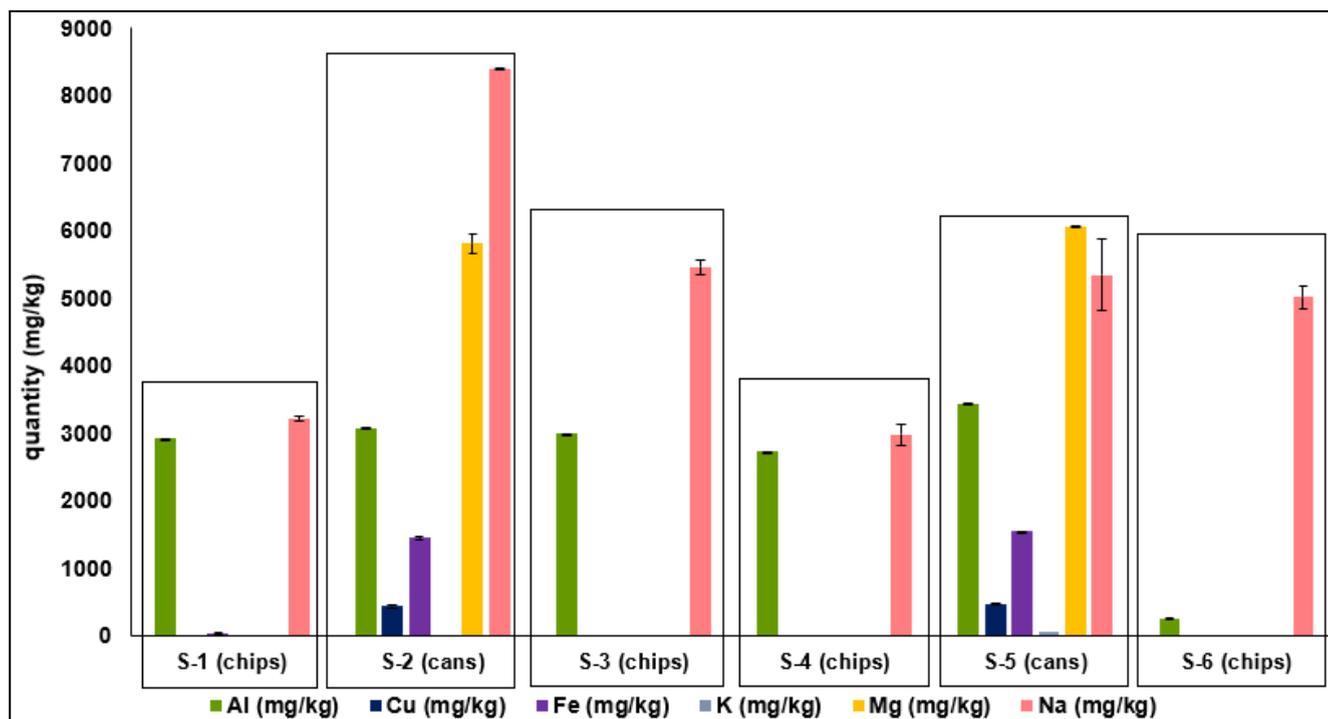


Figure 2. Sample characterization via ICP-OES

What can be noticed is that the preliminary physical analysis was really coherent. The samples that used chip aluminum in the reaction had a degree of purity associated with the results, where they hardly showed traces of concentration of other elements, such as Fe, Cu and Mg. On the other hand, the samples from the cans showed a high degree of concentration of other elements, such as Mg, which in S-5 was even higher in concentration than Na itself - present in the solution. What could also be noticed is that in S-2 the Mg also exceeds the concentration of residual Al, showing that using recycled cans can also result in a high impurity for the residue, thus impacting its destination and disposal.

In both samples, the K level was very low, almost negligible in the system. And considering the level of Cu, which is closely related to toxicity, it can be assessed that in addition to the level being low when it appears (S-2 and S-5 - cans), there are no traces of its presence in reactions with industrial chips.

The metals that were evaluated could come from contaminants present in the alloy of the industrialized beverage can, or could be due to the metallic alloy that makes up the reactor, so the ICP-OES analysis was crucial to assess how severe the basic reaction is with the environment, demonstrating a satisfactory efficiency in not attacking the metallic wall inside the reactor. The error values (standard deviation - SD) associated with the data system in Fig. 2 above is also described, and is low, bringing greater confidence to the chosen method.

4. CONCLUSION

Overall, the results suggest that the use of aluminum chips is a more suitable option in the reaction, as it results in a higher degree of purity and less impurities compared to the use of recycled cans. This information is valuable to understand the environmental implications of these reactions and can assist in making informed decisions about waste management and recycling processes, mainly aiming at the proper disposal of waste.

However, the impurities in cans are present at low levels and consist of low-reactive metals, which can even lead to the formation of a passivation layer under the surface of the aluminum, which favors spontaneity of reaction. Thus, the sustainability of redirecting industrialized beverage cans for hydrogen generation is considered an ecologically favorable application, regardless of the impurities present in the raw material, when compared to industrial waste chips, which are composed entirely of aluminum.

The presence of metallic sodium occurs due to the excess of the basic medium in which the sample is found. As NaOH acts as a homogeneous catalyst for the reaction, in the future it will be interesting to determine the concentration of the solution at the end of the reaction, in order to evaluate the feasibility of recycling the homogeneous catalyst for reuse in the reaction.

It is logical that more research may be needed to explore ways to improve the recycling process and minimize impurities when using recycled cans in reactions, so the next steps involve the evaluation of the morphological (physical) structure of the waste taking into account its morphology, for this, Scanning Electron Microscopy (SEM)

techniques will be used. In addition, the RAMAN and EDS/XPS spectrum will be carried out for greater accuracy of the total amount of elements present in the waste, in order to enable a better destination so that the system's production chain is complete and sustainable. Thermal analyzes and mechanical tests will be carried out to evaluate the potential application of the residue for the civil industry.

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