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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^0 is chemically deposited, serving as a conductive base. Electroplating then builds up additional Cu^0, then one or more layers on Ni^0 and a final Cr^0 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).

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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 (NH_3 5.0 M, $NH_4OH/(NH_4)_2CO_3$ 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 $(NH_4)_2CO_3$ as a buffering medium provided the highest recovery efficiency compared to other leaching agents such as $(NH_4)_2SO_4$ and NH_4Cl, 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 ($FeCl_3$, Comsa, 40%), iron (III) sulfate hydrate ($Fe_2(SO_4)_3 \cdot 3H_2O$, LabChem, test > 20%) and sulfuric acid (H_2SO_4, PanReac, ACS 96% reagent), Ferrozine/thioglycolate tablets, Lovibond water testing (IRON LR and IRON II LR).

Culture media: 0K solution (1 L H_2O, 3 g $(NH_4)_2SO_4$ Scharlau ExpertQ® ACS Reag; 0.1g KCl Merck GR for analysis; 0.5 g K_2HPO_4 Panreac ACS; 0.5 g $MgSO_4 \cdot 7H_2O$ Merk ACS; 0.01 g $Ca(NO_3)_2$ Sigma-Aldrich BioXtra >99.0%; 9K solution (700 ml 0K solution + 300 mL Fe^{2+} solution (44.2 g $FeSO_4 \cdot 7H_2O$ 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 (Fe^{3+}) and the acidic medium (H_2SO_4) were *Acidithiobacillus ferrooxidans* (DSM 14882) and 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 121ºC for 20 minutes (Brock, T.D. et al., 2018). Next, Fe solutions were prepared with a concentration of 8.84 g Fe^{2+}/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 Ferrozine/thioglycolate were used to calculate Fe^{3+} by total Fe and Fe^{2+}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^{2+} for 33 days at 27ºC. 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 microorganisms (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^{3+} 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^{2+} 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^0). 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

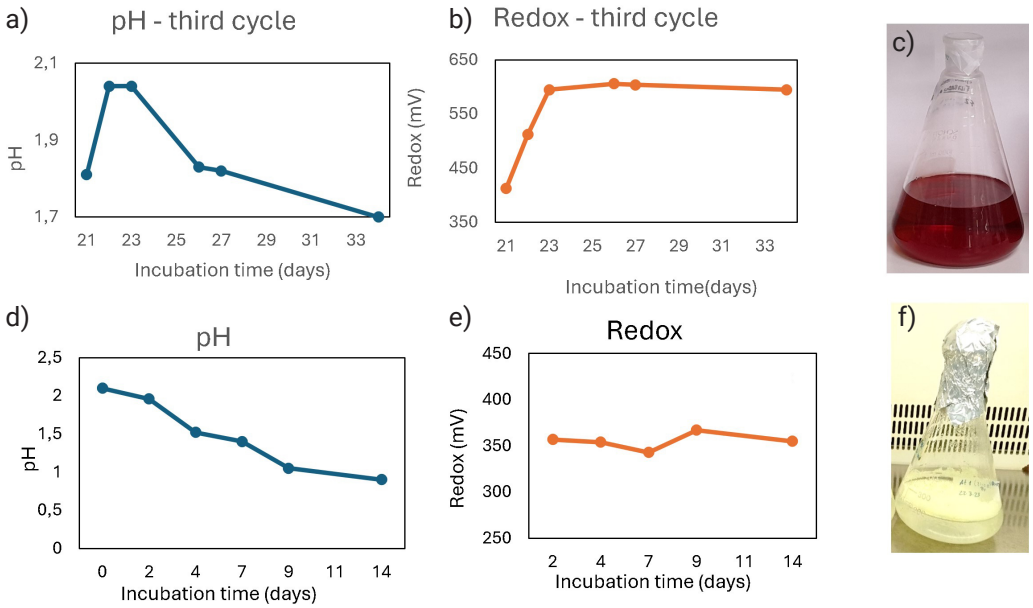

FIGURE 1: Variation during 33 days of (a) pH and (b) redox potential of the third cycle liquor obtained with *A. ferrooxidans*, and (c) aspect of leaching solution (F3) obtained with *A. ferrooxidans*; variation during 14 days of (d) pH and (e) redox potential of the acidic liquor obtained with *A. thiooxidans*.,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

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

$$g_{metal} = ICP_{metal}(g/L) \cdot Dilution \cdot Vol_{liquid}(L) \quad (2)$$

Where $g_{initial}$ is the mass of different types of ABS weighted at the start of each test, g_{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^-, 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.

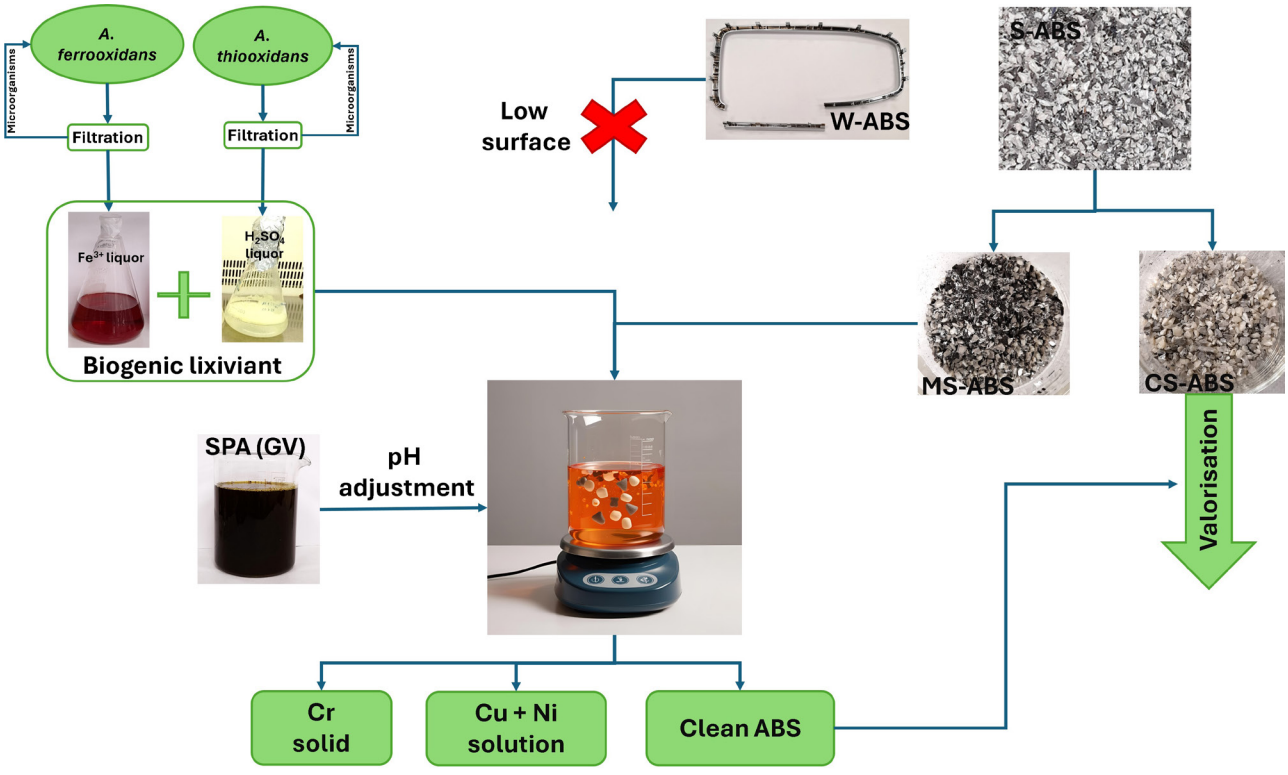

FIGURE 2: Scheme of the indirect bioleaching process.

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 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 Fe^{3+} to Fe^{2+} ions. The reduced Fe^{2+} ions further participate in the Fenton reaction to regenerate Fe^{3+} ions, maintaining a continuous Fe^{2+}/Fe^{3+} redox cycle and facilitating metal dissolution (Yken et al., 2020).

$$2Fe^{3+} + M^0 \longrightarrow M^{2+} + 2Fe^{2+} \quad (3)$$

$$Fe^{3+} + e\text{-} \rightleftharpoons Fe^{2+} \qquad (E^0 = +0.77\ V) \quad (4)$$

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:

$$Cu^0 + Fe_2(SO_4)_3 \longrightarrow 2FeSO_4 + CuSO_4 \qquad (E^0 = +0.43\ V) \quad (5)$$

$$Ni^0 + Fe_2(SO_4)_3 \longrightarrow 2FeSO_4 + NiSO_4 \qquad (E^0 = +1.00\ V) \quad (6)$$

The oxidation of metallic Cr with iron is difficult (Equation 7). In addition, metallic Cr has a passivating layer formed by Cr_2O_3 which makes it even more difficult its leaching (Milazzo et al., 1978; Reartes et al., 1995).

$$2Cr^0 + 3Fe_2(SO_4)_3 \longrightarrow 6FeSO_4 + Cr_2(SO_4)_3 \qquad (E^0 = -0.03\ V) \quad (7)$$

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 lixiviants containing different amounts of Fe (III), to confirm that Cu, Ni and Cr of W-ABS could be leached using 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 lixiviants 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

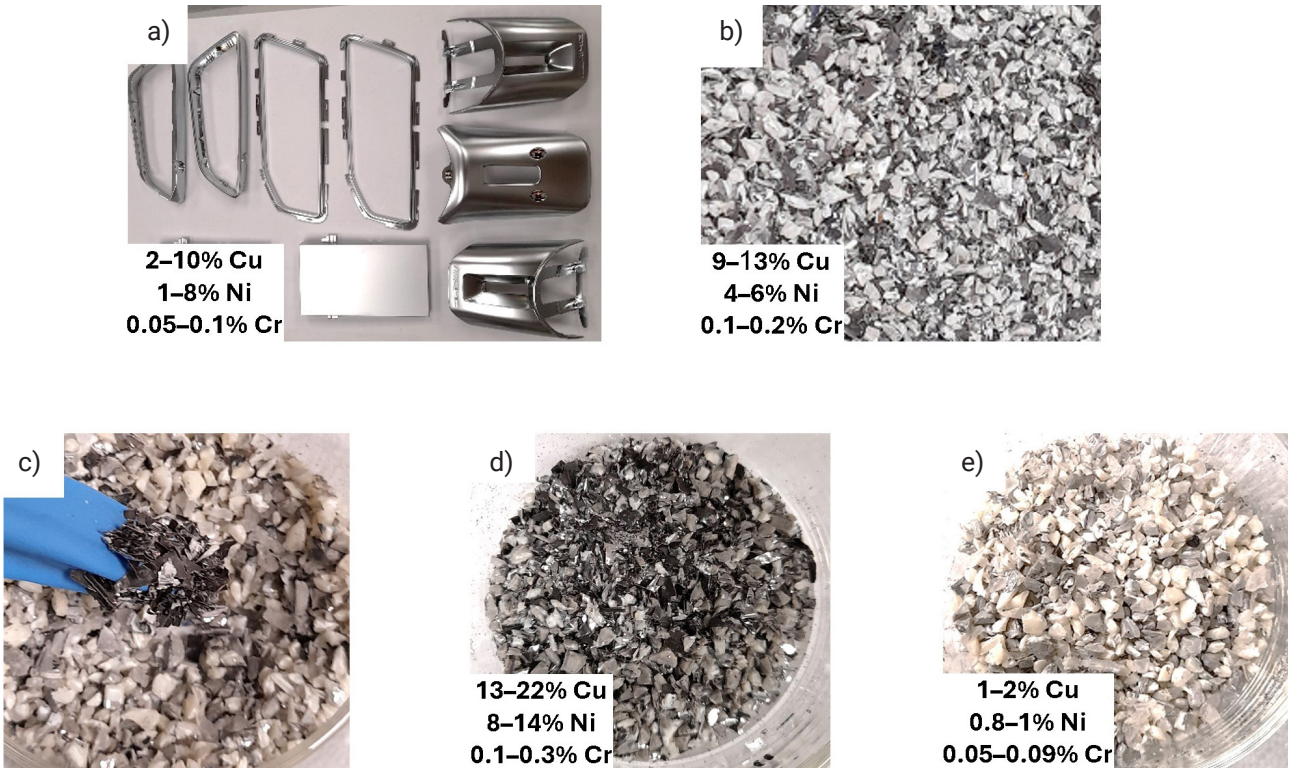

FIGURE 3: Aspect and metallic composition (% w/w) of (a) whole pieces of metallised ABS (W-ABS) and (b) shredded metallised ABS (S-ABS); (c) shredded metallised ABS being magnetically pretreated; aspect and metallic composition (% w/w) of (d) metallic fraction (MS-ABS); and (e) clean fraction (CS-ABS).

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 $FeCl_3$ and $Fe_2(SO_4)_3$.

As it can be observed, no metals were leached without the presence of Fe (III). When the concentration of $FeCl_3$ was 0.3 M a maximum Cu leaching was obtained, but not for Ni. When the concentration of $FeCl_3$ 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 $Fe_2(SO_4)_3$ was used as Fe^{3+} source, presenting a maximum quantity of dissolved Cu when its concentration was 1 M. At first, $FeCl_3$ shows higher extraction yields. Nevertheless, $Fe_2(SO_4)_3$ 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 $FeCl_3$ of $Fe_2(SO_4)_3$ as 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.

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

$[H^+]$ (M)	$[FeCl_3]$ (M)	$[Fe_2(SO_4)_3]$ (M)	Cu (%)	Ni (%)	Cr (%)
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

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 (≈ 50% of Cu leached; ≈ 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; $[Fe_2(SO_4)_3]$ = 0.2 M; and $[H_2SO_4]$ = 2 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 an 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 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.

$[H_2SO_4]$ (M)	$[Fe_2(SO_4)_3]$ (M)	Cu (%)	Ni (%)	Cr (%)	Temp (°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

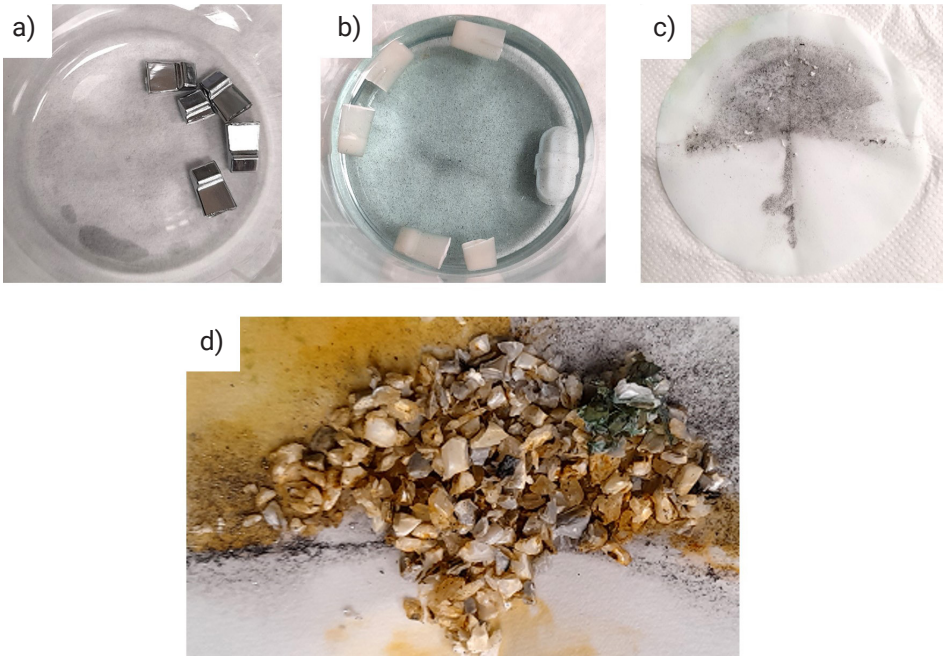

FIGURE 4: Aspect of (a) W-ABS; (b) the final leaching solution; (c) the filtered Cr; (d) MS-ABS treated at 80°C, showing a poor quality which implies that it would not be reused.

3.3 Leaching tests using biogenic lixiviants

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 ($[Fe^{3+}]$ = 0.4 M; pH = 2) or a mixture of F3 + T0 (1:1 v/v; $[Fe^{3+}]$ = 0.2 M; 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	$[Fe^{3+}]$ (M)	Liquor change	pH adjustment
A	100	F3 + T0 1:1 v/v	1.5	0.2	no	yes
B	100	F3	2	0.4	no	no
C	100	F3 + T0 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 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; $[Fe^{3+}]$ = 0.2 M; pH = 1.5), L/S = 100 mL/g, without solution replacement, adjusting every 24 h to pH = 1.5 by using H_2SO_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 H_2SO_4

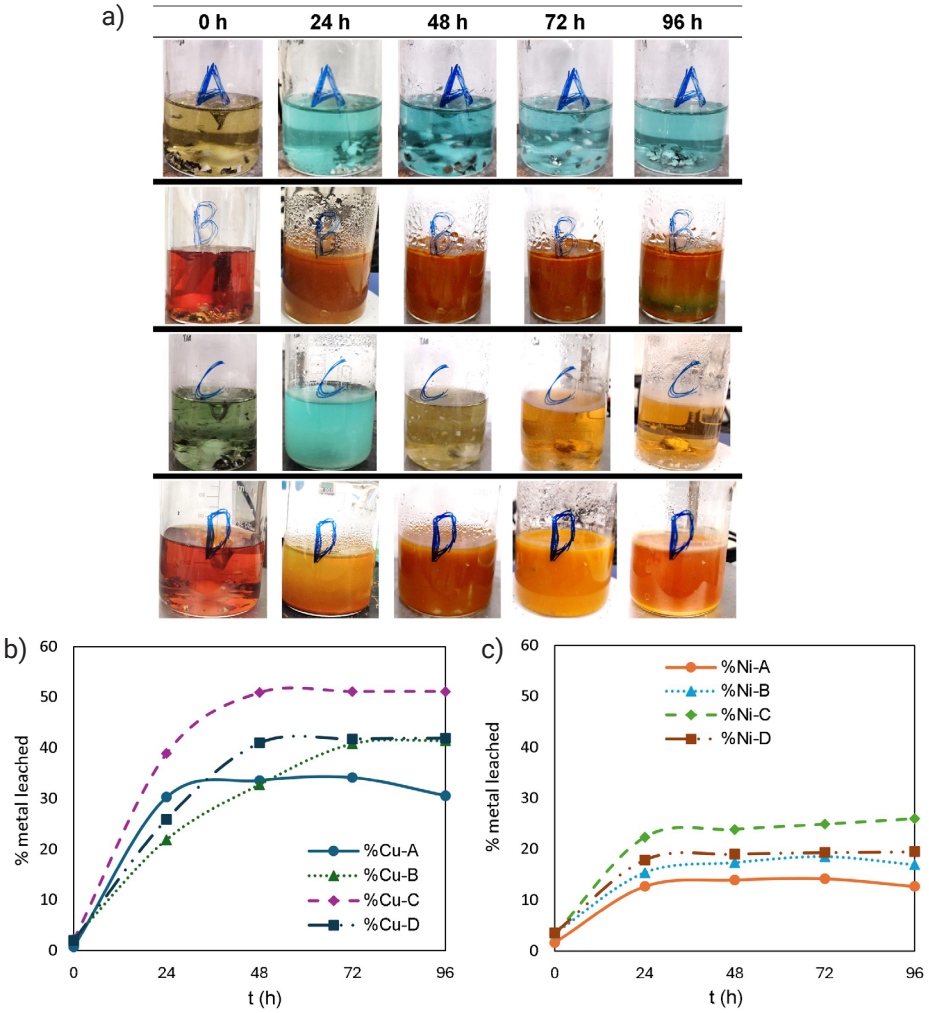

FIGURE 5: (a) Aspect of the solutions each 24 h; time evolution of leaching process of (b) Cu and (c) Ni for each test: A (circles and solid line), B (triangles and dotted line), C (diamonds and dashed line) and D (squares and dash-dots line). The proportions of dissolved metals are related with total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

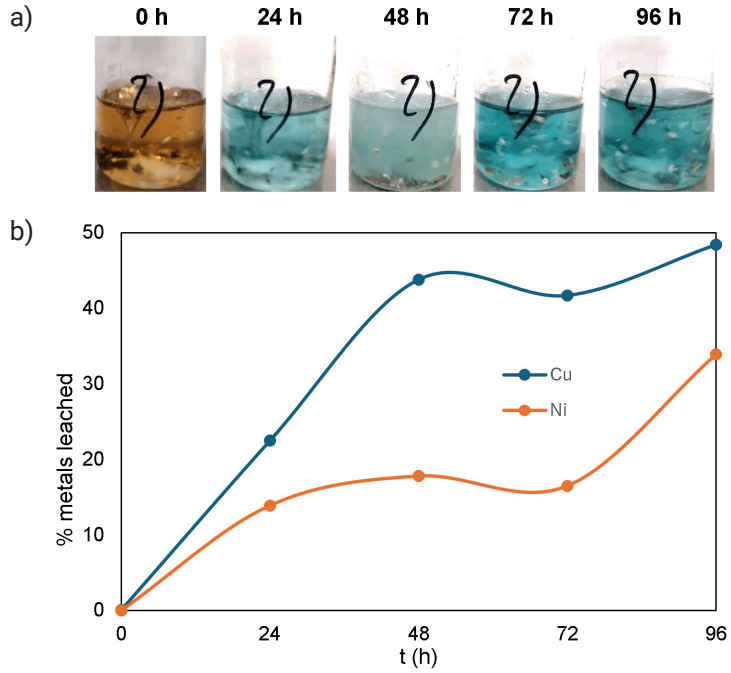

FIGURE 6: (a) Aspect of the solutions each 24 h; (b) time evolution of the proportions of metals leached. % were calculated as stated in Equation 1.

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 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 H_2SO_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 (≈70%) which could be valorised directly in injection-moulding, and MS-ABS (≈30%) which could be treated with biogenic lixiviants. 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 + Fe^{2+}/Fe^{3+}). To concentrate Cu and Ni, the dissolution can

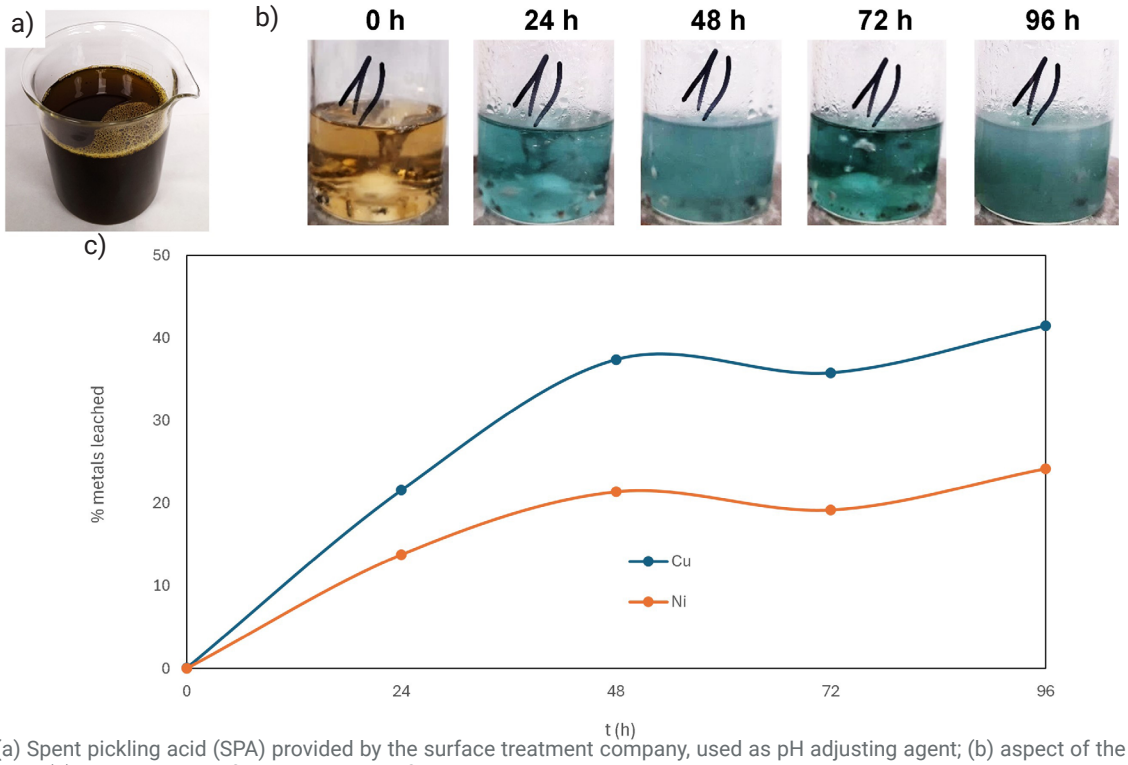

FIGURE 7: (a) Spent pickling acid (SPA) provided by the surface treatment company, used as pH adjusting agent; (b) aspect of the solutions each 24 h; (b) time evolution of the proportions of metals leached. % were calculated as stated in Equation 1.

be recirculated to the bioleaching reactor until the Fe^{3+} is depleted, enhancing the metal recovery. After the depletion of 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

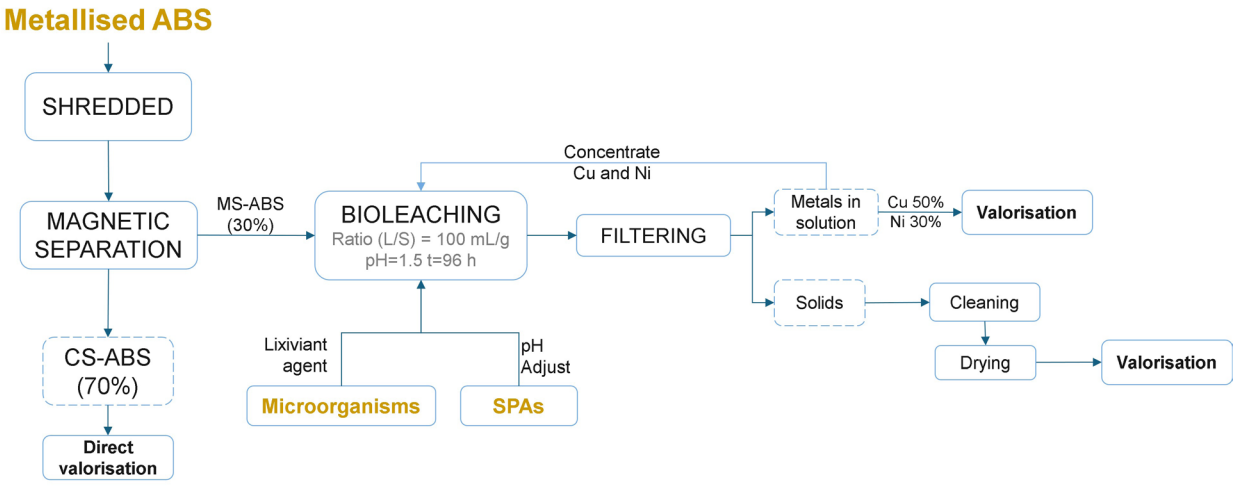

FIGURE 8: Proposed recovery process for rejected metallised ABS.

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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