Selective Leaching and Recovery of Er, Gd, Sn, and In from Liquid Crystal Display Screen Waste by Sono-Leaching Assisted by Magnetic Separation

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ABSTRACT: We report a facile, economic, and ecofriendly method for selective recovery of Er, Gd, Sn, and In from liquid crystal display (LCD) screen wastes by ultrasound-assisted leaching, followed by magnetic separation. Thermodynamic analysis showed that the pyrophosphate ion is an excellent leaching agent for Er, Gd, and In at pH values below 8. Dissolved screen waste powder was subjected to leaching at room temperature using aqueous solutions of 0.05 M of sodium pyrophosphate ($Na_4P_2O_7$) as the leaching agent; hydrogen peroxide (H_2O_2) (3 v/v %) was added as an auxiliary reducing agent, and an ultrasonic source was used in the process. Once completed, magnetic separation was applied to the leached residue. The average contents of Er, In, Sn, and Gd in the LCD screen were found to be 477, 2422, 835, and 93 mg·kg^{-1}, respectively, of which 93, 97, 72, and 99% were selectively recovered from the waste material by this method at pH 3 after 2 h of leaching. The proposed method emerges as an easy and selective process for leaching Er from LCD screen wastes and concentrating In, Sn, and Gd in a separable magnetic solid.
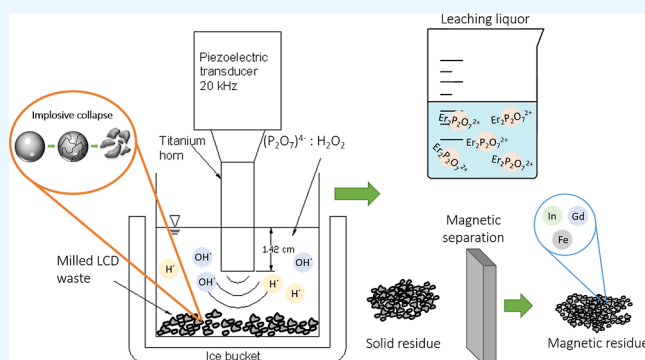
1. INTRODUCTION

At present, there is an imbalance between supply and demand for rare earth elements (REEs) and indium due to their extensive use in technological developments. For this reason, In and REEs are considered strategic elements for their applications in optics, lighting, screens, magnets, rechargeable batteries, renewable energy generation, and clean production, among many others.[1] As an example, the production of a smartphone requires a wide range of metals such as lithium, indium, tin, silver, palladium, copper, gold, and REEs.[2] Furthermore, the supply of these elements has become a worldwide concern since the scarcity of these resources is becoming increasingly evident, generating ecological, social, economic, and political repercussions.[3]

The aforementioned situations have prompted the search for alternative recovery methods for these elements, such as their recycling from electronic devices, since this waste has proven to be an important secondary resource for obtaining valuable elements such as gold, copper, silver, indium, and REEs. However, current practices for recycling electronic devices urgently require innovations in their processes to promote adequate and sustainable recycling.[2]

Annually, 1.3 billion tons of electronic waste are generated, and it is expected that by 2025 this amount will triple; this represents one of the major contributors to environmental pollution, containing heavy metals and toxic organic compo-

nents.[4] On the other hand, these wastes contain a wide range of valuable materials, such as rare earths, that are currently considered critical raw materials due to their scarcity and high risk of supply. This situation justifies the extensive research for the REE recovery from electronic waste;[2] however, only about 1% of rare earths contained in electronic devices are recycled, with the rest going to landfills, which removes them from the production cycle. One of the difficulties of recycling these metals is the small amount of REEs found in most electronic devices, combined with the difficulty of collecting, extracting, and recovering the rare earths. The presence of REEs in LCD (liquid crystal display) has been reported previously as doping elements[5] to improve the quality and intensity of RGB colors for different color displays (color filters)[6] and even in thin film transistors.[7] Currently, REE recycling is mainly focused on permanent magnets, fluorescent lamps, and Ni−MH (nickel−metal hydride) batteries using pyrometallurgical methods for REE alloys, gas phase extraction methods (where REEs are

transferred to a volatile chloride phase), and hydrometallurgical methods. These last mainly employ inorganic acid leaching[8] with nitric, sulfuric, and hydrochloric acids.[9−11] Despite being efficient and fast, these media are detrimental to the environment and to human health because they generate effluents with a high level of contamination.[12,13] Furthermore, these techniques are not selective, requiring complicated subsequent separation processes.

LCDs also contain indium-tin oxides (ITO) in low concentrations. Considered a critical metal, indium recovery from LCD has been the subject of several patents and academic studies.[14,15] However, all the proposed methods require strong acidic or basic leaching, as well as several additional recovery steps.

Therefore, it is important to find ecologically viable alternatives that lead to the efficient recovery of REEs and indium from electronic devices. One way to achieve this goal is to employ less aggressive and more ecofriendly reagents that form strong interactions with the desired metal, resulting in much more stable soluble products.[16] The ligand that most closely meets these requirements is the pyrophosphate ion (PPi), which is a selective ligand for metal ions with a high oxidation number, such as REEs and indium.[17,18]

The PPi is a tetra anion diphosphate $(P_2O_7)^{4-}$ and is a ligand of interest due to its versatile coordination modes, aqueous solubility, and low toxicity.[19] PPi has been used in the food and health industries for both humans and animals,[18,20−22] in addition to its catalytic role and uses in magnetic studies.[23] PPi has been employed as a chelating agent for metals, such as copper,[23] vanadium,[24] and magnesium;[25] however, at present, it has been scarcely used for metal leaching processes.

On the other hand, sonochemistry is a simple and environmentally friendly technique used to intensify metal leaching processes. In this technique, by means of a sonoreactor, a liquid medium is capable of transmitting large amounts of energy to the reagents, resulting in faster reactions, better conversions, improved or new products, and fewer by-products. This translates into process simplification and lower production costs on an industrial level.[26−28] In terms of chemical reactions, when the ultrasonic energy is sufficiently strong, a negative pressure is produced within the liquid, which generates bubbles or cavities that experience an implosive collapse; these consecutively generate new bubbles that will collapse again. The process takes place in ∼40 ms, in which time extremely high temperatures and pressures (5000 °C and 1000 bar, respectively) are reached upon collapse of the bubbles, and the cooling after the collapse of a bubble is extremely fast (10 billion °C·s^{-1}). These phenomena promote the formation of free radicals H$^\bullet$, OH$\bullet$, and hydrogen peroxide, which greatly enhance leaching.[28,29]

In previous work, it was proposed, for the first time, the use of sono-leaching of LCD powder in pyrophosphate solution, followed by magnetic separation, to find an ecofriendly leaching process for recovering REEs.[30] However, the research was limited to study the process at pH 6, without additional reducing agents. The results not only showed an unexpected phenomenon, a minimal dissolution of Pr and Gd into the leach solution, but also the formation of a magnetic residue (this residue is a product of the leach) consisting of metallic iron into which over 85% of these rare earths were incorporated. This was a significant finding; however, at the conditions used in these preliminary tests, very limited Er and practically no In were removed from the LCD waste.

For that reason, this paper is focused on the in-depth study of the recovery of the REE and indium contained in waste LCD screens by using the proposed method of ultrasonic-assisted leaching with PPi solutions, varying the solution conditions. This technique disrupts the conventional treatment of electronic waste and the recovery of valuable elements contained within, as well as being a selective leaching method for erbium.

2. MATERIALS AND METHODS

2.1. Materials. The reagents used in this investigation were of analytical grade: sodium pyrophosphate (PPi) (Alfa Aesar, 98%) and sodium hydroxide solution (1 M NaOH, Fisher Chemical). The sulfuric acid (H_2SO_4) (95.0−98.0%), hydrochloric acid (HCl) (36.5−38.0%), and nitric acid (HNO_3) (69.0−70.0%) were used for the digestion of the sample (LCD) and, to adjust the pH value in the solution, were acquired from J.T. Baker, as well as hydrogen peroxide (H_2O_2) was used as a reducing agent in ultrasonic leaching. The waste LCD screens were collected from different brands, models, and types (cell phones, televisions, tablets, cameras, and laptops).

2.2. Methods. LCD screen waste was used as the raw material in this study. First, the screens were manually removed from LCD equipment. Subsequently, the polarizing film was removed from the glass of the LCD panels. The screens were crushed and ground using an automatic agate mortar at 220 rpm. The powder was screened through a −325 mesh (−0.0445 mm) sieve since previous studies demonstrated that REEs are exposed, increasing dissolution when the particle is smaller than 0.0445 mm.[30] The raw material was characterized by scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM−EDS-JEOL, model IT 300). A sample was digested in aqua regia (HCl: HNO_3, 3:1), and the liquors were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, PerkinElmer, Optima 3000 XL) to quantify the chemical composition (digestion was also carried out using hydrofluoric acid, obtaining very similar results in relation to digestion with aqua regia).

A 3 g sample of milled screen waste was contacted with 150 mL of an aqueous solution of hydrogen peroxide (H_2O_2, 3 v/v %) and sodium pyrophosphate (PPi) as the leaching agent; the concentration of the latter was varied from 0.00 to 0.05 M. The obtained suspension was transferred into a 500 mL glass beaker, and magnetic stirring was initiated. The pH was then adjusted and maintained constant with a pH meter every 15 min in the range of 3 to 6 by additions of sulfuric acid (1 M). The leaching time was varied from 1 to 3 h. These experimental conditions were selected in accordance with preliminary studies, where some preliminary results at pH 6 were also shown, including a characterization of the raw material and the magnetic solid product, as well as an explanation of the processes occurring during the leach.[30] During the leaching process, a flow-through ultrasonic cell homogenizer, 300 VT, with a piezoelectric transducer at 90 kHz frequency and a titanium tip of 9.5 mm was used. The experiments were performed at a sonication output power of 120 W during the leaching process. The flask was placed into an ice bucket in order to keep the solution temperature near 25 °C (with the objective of achieving high percentages of leaching at room temperature); no appreciable changes were noted in the leaching volume during the experiment. Once the leach was complete, the solution was filtered and the solid residue was air-dried at 80 °C. A conventional iron bar magnet was passed over the solid residue, obtaining two components, which will be referred to as the
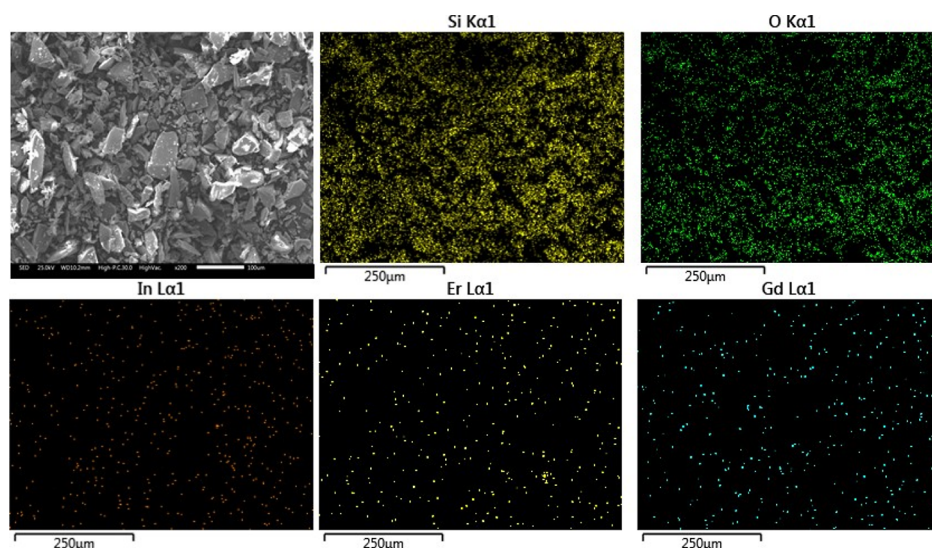
Figure 1. EDS elemental mapping showing the elemental composition of raw material (LCD screen powder).

magnetic and the non-magnetic residue. To quantitatively determine the elements present in the LCD powder (-0.0445 mm), a sample of the initial material was digested with aqua regia (HCl/HNO_3, 3:1) for ICP analysis. The results show interesting and economically profitable amounts for the recovery of gadolinium, erbium, and indium (93, 477, and 2422 mg·kg^{-1}, respectively)[31] (in relation to the steps or procedures and reagents necessary to obtain the material of interest by operating at a low temperature with relatively cheap and recyclable reagents using less equipment and considering the current prices of rare earths and indium), in addition to a significant amount of iron (2217 mg·kg^{-1}), which is analyzed by the additional process of magnetic separation.

2.3. Analysis. The leach liquor was analyzed by ICP to determine the dissolution percentages of the elements of interest (Er, In, and Gd, as well as other REEs present in a lesser proportion). Each solid residue (magnetic and non-magnetic) was examined by SEM−EDS-JEOL (model IT 300) in order to qualitatively determine its elemental distribution. The solid residues were later digested in aqua regia and characterized by inductively coupled plasma (ICP, PerkinElmer, Optima 3000 XL) in order to quantify their chemical composition.

The elemental dissolution (% Lix) (leaching percentage) and the element recovery (% R_M) are defined as shown below

$$C_i = V_{ICP}\left(\frac{L_d}{P_{LCD}}\right)(1000) \tag{1}$$

$$Lix = V_{ICP}\left(\frac{L_L}{P_{LCD}}\right)(1000) \tag{2}$$

$$\%\ Lix = \frac{(Lix)(100)}{C_i} \tag{3}$$

$$D_M = V_{ICP}\left(\frac{L_d}{M_M}\right)(1000) \tag{4}$$

$$\%\ R_M = \frac{(D_M)(100)}{C_i} \tag{5}$$

where C_i (mg·kg^{-1}) is the initial concentration obtained from the digestion of the LCD powder sample and analyzed in ICP, V_{ICP} (mg L^{-1}) is the value of the ICP analysis of the liquors obtained in the leaching or, where appropriate, in the digestion of the magnetic material, L_L (L) is the liters of solution used in the leaching of each sample, L_d (L) is the liters of aqua regia used in the digestion of the LCD power sample, P_{LCD} (g) is the LCD screen powder sample (-325 mesh), Lix (mg·kg^{-1}) is the amount of the element of interest leached, D_M (mg·kg^{-1}) is the result of the ICP analysis of the liquor obtained by digesting the magnetic material with aqua regia, M_M (g) is the grams of digested magnetic material, and % Lix and % R_M are the percentages of leaching of the elements of interest and of the recovery by magnetic means, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Starting Material. The elemental composition and distribution in the LCD powders were determined by ICP[30] and SEM−EDS (view Figure 1). The SEM−EDS analysis (element wt %) of the raw materials (LCD screens) indicated that silicon is the main component detected (37.5 % wt) in addition to oxygen, attributed to the presence of SiO_2. On the other hand, the metallic content from the analysis in ICP of the economically interesting elements is approximately 93 mg·kg^{-1} of gadolinium, 477 mg·kg^{-1} of erbium, and 2422 mg·kg^{-1} of indium.[30] The presence of REEs in LCD screen wastes is not usually reported; however, it is in good agreement with previously published studies focused on the recovery of REE from electronic wastes.[5−7,32]

In addition, a qualitative chemical analysis was carried out by means of EDS by elemental mapping (Figure 1). The presence of different elements, such as silicon, oxygen, indium, erbium, and gadolinium, was observed, which are uniformly distributed in the sample. Furthermore, the presence of oxygen can be inferred since the predominant material in LCD panels is SiO_2 (this may also indicate that the REEs are in the form of oxides).[33] The powder consists of particles of irregular shapes with diameters less than 70 μm.

3.2. Leaching Agent. In the search for optimal leaching agents (ligands) to improve the recovery efficiency of the elements of interest by hydrometallurgical methods, the metal−ligand complex stability constants (K_p) were consulted.[34] It is

well known that the solubility increases as the K_p is increased. Using this logic, the PPi was found among other effective complex agents such as EDTA[35,36] and citrate[37−39] to favor the solubility of metal ions in their III+ or IV+ oxidation states and, in particular, rare earth elements. As was noted previously, this agent is nontoxic since it is widely used in the food processing industry and is accessible and ecofriendly.[30,40]

The thermodynamic analysis of the PPi as a complexing agent for the elements under study was performed using the MEDUSA software package and the HYDRA database, complemented with the (K_p) critical stability constants of Er, Gd, Sn, and In reported in the NIST database.[17] The results of this analysis are presented in Figure 2, as the species distribution diagrams of
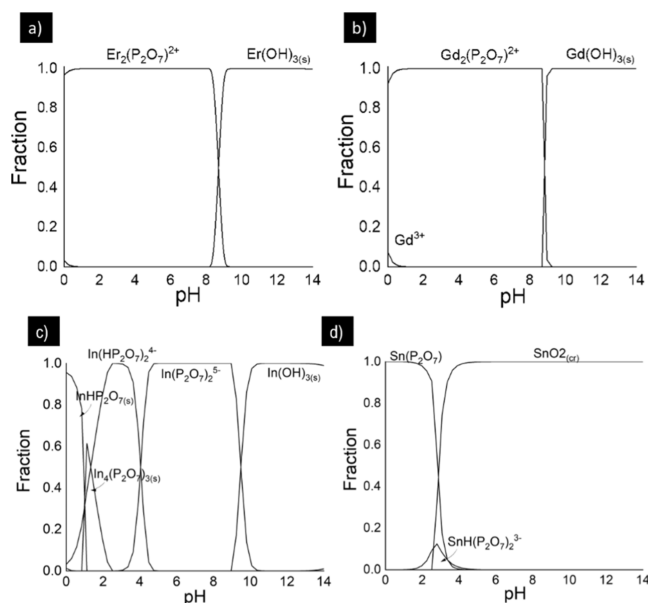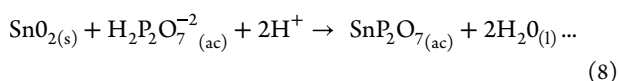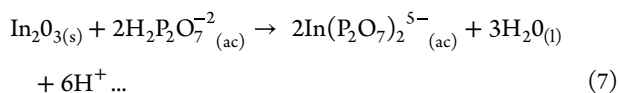

Figure 2. Species distribution diagrams of (a) Er $^{3+}$, (b) Gd^{3+}, (c) In^{3+}, and (d) Sn^{4+} as a function of pH using $P_2O_7^{4-}$ (0.1 M) as a complexing agent at room temperature (25 °C).

each element. As can be appreciated, to achieve the solubility of the Er ion, the pH values must be below 10; Gd requires a pH below 9 and In, a pH in the range of 3 to 10 to remain as soluble complexes.

According to Figure 2, it is observed that the PPi, when in contact with the rare earth ions, forms complex ions $(RE_2P_2O_7^{2+})$ as shown in the following equation

$$RE_2O_{3(s)} + H_2P_2O_7^{-2}{}_{(ac)} + 4H^+ \rightarrow RE_2P_2O_7^{2+}{}_{(ac)} + 3H_2O_{(l)} \cdots \tag{6}$$
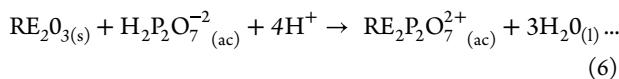
and with the tin and indium as soluble complexes, SnP_2O_7, $In_4(HP_2O_7)_2{}^{4-}$, and $In(P_2O_7)_2{}^{5-}$, these last according to the solution pH.

$$In_2O_{3(s)} + 2H_2P_2O_7^{-2}{}_{(ac)} \rightarrow 2In(P_2O_7)_2{}^{5-}{}_{(ac)} + 3H_2O_{(l)}$$
$$+ 6H^+ \cdots \tag{7}$$

$$SnO_{2(s)} + H_2P_2O_7^{-2}{}_{(ac)} + 2H^+ \rightarrow SnP_2O_{7(ac)} + 2H_2O_{(l)} \cdots \tag{8}$$

The $H_2P_2O_7{}^{2-}$ species that appear in the above reactions predominate in the 3−6 pH range considered in this study, as shown in Appendix A (Figure A2).

To evaluate the effects of various process parameters on the recovery of these elements, as well as Fe, from LCD waste powder, their percentages of dissolution in the leaching liquor
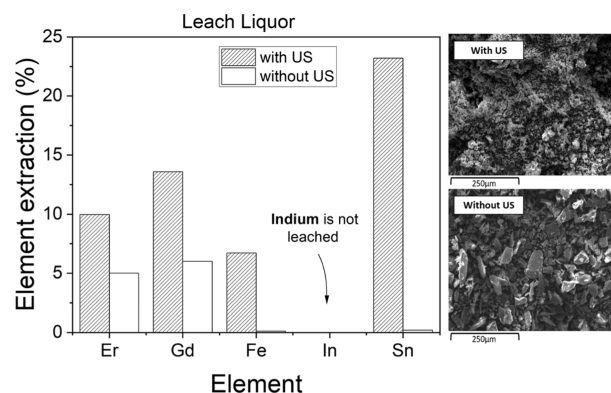

Figure 3. Morphology and percentage of extraction after the leaching process with and without US for 1 h, with 0.05 M of PPi and H_2O_2 (3%) at pH 6. SEM micrographs of the residue of the LCD powder treaded with and without US are included as insets.

and into the magnetic residue were determined and reported below.

3.3. Ultrasound Effect. According to different leaching studies,[28,30] the application of ultrasound (US) during the leaching process yields auxiliary energy for the accelerating leaching process.[27,41] Furthermore, it increases the leaching efficiency since US energy can cause particle fracture, with a consequent increase in the surface area available for reaction.[27,42] This process can produce freshly exposed, high temperature, and contrasting surfaces during the ultrasonic irradiation of powder suspensions in liquid; the cavitation and shock waves created can accelerate solid particles to high speeds, allowing collisions between particles capable of inducing dramatic changes in surface morphology, composition, and reactivity.[43] In order to confirm the positive effect of US in this waste, the morphology and extraction percentages of Er, In, and Gd are shown in Figure 3 after leaching with and without US for 1 h under experimental conditions of (PPi) = 0.05 M, H_2O_2 (3 v/v %) and pH 6. These experimental conditions were selected in preliminary studies.[30]

As may be observed in Figure 3, the extraction percentage is improved with US during the leaching process for all the elements studied, except for In, which is not leached in either case. It is important to note that the application of ultrasonic energy allows selective dissolution of the REEs into the pyrophosphate solution, which can be attributed to physical liberation and perhaps local pH variations (conditions that the use of US generates in the leaching process). It is also possible to observe in the micrographs of Figure 3, one of the effects of US, specifically in the reduction of the particle size of the LCD screen powder by the collisions between the particles. Therefore, all the experiments were performed using US throughout the leach (sono-leaching process). In addition, to qualitatively study the particle size and morphology of the residue, in Figure 3, some representative SEM micrographs of the residue of the LCD powder, treaded using US and without, are included as an inset. It is evident that there are important differences between the residues. As can be appreciated, the residue treated with US is composed by aggregates of rounded and fine particles, which can be attributed to the effect of the US on the LCD powders. In
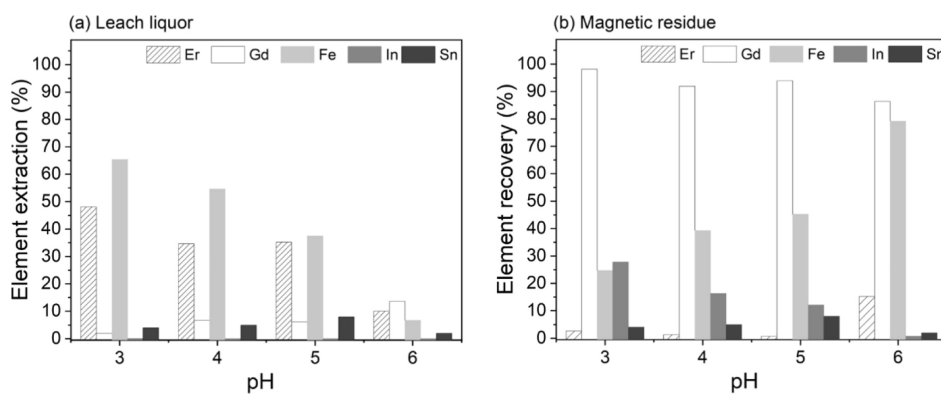
Figure 4. Effect of pH on the % of the elements extracted or recovered in the magnetic residue from the sono-leaching process: (a) leaching liquor and (b) magnetic residue for 1 h of process, 0.05 M of PPi concentration, H_2O_2 (3%), and at room temperature (25 °C).
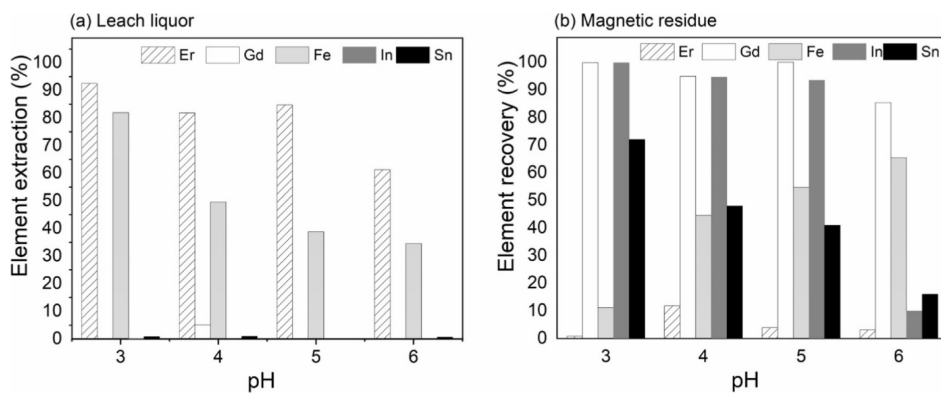

Figure 5. Effect of the pH on the % of the elements leached or recovered in the sono-leaching process: (a) leaching liquor and (b) magnetic residue for 2 h of the process, 0.05 M of the PPi concentration, H_2O_2 (3%), and at room temperature (25 °C).
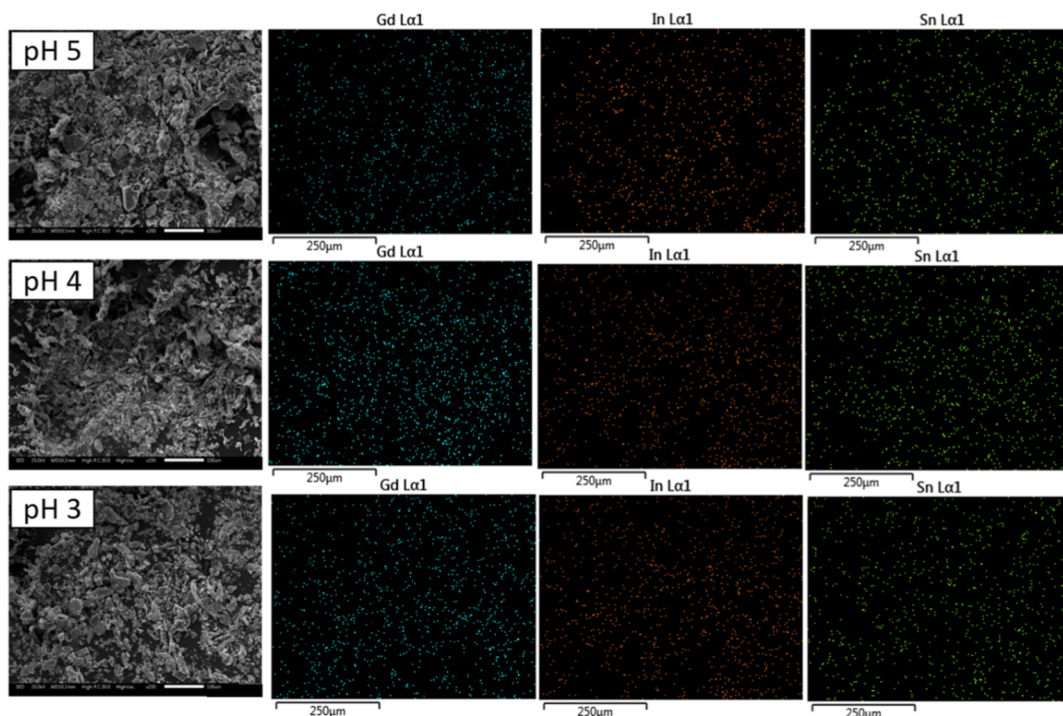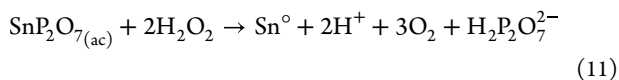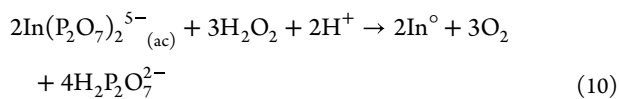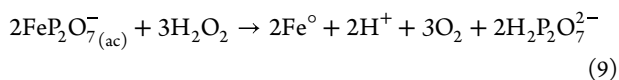

Figure 6. Representative SE micrographs and multi-elemental EDS mapping images of magnetic residue after sono-leaching for 2 h using 0.05 M of PPi, H_2O_2 (3% v/v) at room temperature (25 °C).

contrast, the residue obtained without US is formed by large polyhedral particles, denoting the mechanical effect of the US on the particles.

3.4. Effect of pH. The effect of pH was analyzed in experiments under controlled conditions of sono-leaching for 1 h using 0.05 M of [PPi] and 3% H_2O_2 at room temperature (25 °C); the pH was varied from 3 to 6. The results are presented in Figure 4.

According to species distribution diagrams (Figure 2), under these pH conditions, an enhancement in the dissolution of the elements under study was expected. As can be appreciated in Figure 4, Gd, Sn, and In did not report to the leach solution but were recovered in the magnetic residue. Almost 48% of Er is leached at pH 3, and this percentage decreases as pH is increased, down to 10% at pH 6; this may be explained by the fact that Er is present in the form of oxides in the original material and therefore is more easily attacked under stronger acid conditions, in addition, according to the species distribution diagrams in Figure 2, Er can be as a complex with PPi. A similar behavior is presented by Fe, which shows a 65% dissolution at pH 3 and drops to approximately 7% at pH 6. However, the difference in these percentages is balanced by the amount of iron reporting to the magnetic residue, implying that the iron leached is later reduced and basically constitutes the magnetic residue. With respect to Sn and In, the relatively small amount recovered from the starting material, more favored at lower pH values, is almost completely incorporated into the magnetic residue. Their presence in the magnetic residue could be expected since their reduction potential is similar to that of iron (Pourbaix-type diagrams in Appendix A, Figure A1). Moreover, this would be the result of the combination of the use of the ultrasonic probe, the H_2O_2, and the PPi that promote the reduction of the elements. The proposed reactions for magnetic residue formation are as follows for iron, indium, and tin

$$2FeP_2O_{7\,(ac)}^- + 3H_2O_2 \rightarrow 2Fe^\circ + 2H^+ + 3O_2 + 2H_2P_2O_7^{2-}$$

(9)

$$2In(P_2O_7)_2^{5-}{}_{(ac)} + 3H_2O_2 + 2H^+ \rightarrow 2In^\circ + 3O_2$$
$$+ 4H_2P_2O_7^{2-}$$

(10)

$$SnP_2O_{7(ac)} + 2H_2O_2 \rightarrow Sn^\circ + 2H^+ + 3O_2 + H_2P_2O_7^-$$

(11)

Gd shows low levels of dissolution in the leaching liquor (1−14%), especially at low pH, although it achieves high recoveries in the magnetic residue, almost 98% at pH 3; a slight decrease in the recovery is observed at higher pH values. The explanation of the quantitative recovery of Gd in the magnetic residue requires further investigation, although it can be speculated that Gd is incorporated as an alloy with the iron since, unlike In and Sn, Gd has a very negative reduction potential.

3.5. Influence of Time on Different pH Values. The effect of the leaching time may be appreciated by comparing Figures 4 and 5 under the same experimental conditions, with different leaching times of 1 and 2 h, respectively. The dissolution of Er at pH 3 improves considerably with the longer leaching time from 48% (at pH 3) to 93% when the sono-leaching was varied from 1 to 2 h, respectively. Iron shows a similar behavior since its dissolution increases with leaching time. In contrast, Gd is not affected by the leaching time, as is observed in Figure 5; Gd shows 83% of recovery at pH 6 and 97% at pH 3 for sono-leaching for 2 h, which is very close to that

observed in the leaching process for 1 h (Figure 4). The behavior of the In is radically different; when the sono-leaching time is increased from 1 to 2 h, the recovery in the magnetic residue at pH 3 is favored, increasing from 27% to nearly 100%. Furthermore, the recovery of In is greater than 95% in the pH range of 3 to 5, when the sono-leaching is applied for 2 h (considering that the objective of the study is to find an effective, simple, and, at the same time, less harmful method for the environment by obtaining good results in 2 h of leaching with small proportions of solid to liquid, there was no need to carry out tests for longer times). Similar recovery behavior was observed for Sn (at pH 3, 46.8% Sn and 71.9% Sn were recuperated in the magnetic residue for 1 and 2 h, respectively). In this case, the leaching time is an important factor in the process. This is due to longer contact time between the LCD powder and the leaching solution and because US has a greater opportunity to generate free radicals (OH$^\bullet$ and H$^\bullet$) and bubbles or cavities with implosive collapses,[44] which altogether improves the leaching and recovery efficiency of the elements of interest. This also implies that the ITO phase is, in general, more refractory compared to the rare earth oxides.

Secondary electron (SE) micrographs of representative magnetic residue after applying the sono-leaching to the LCD powder for 2 h at different pHs are shown in Figure 6. As may be appreciated, the powders consist of irregular and rounded particles, with a size less than 44 μm (−325 mesh). No apparent difference can be noted in the particle size or morphology for the different pH values. Multi-elemental EDS mapping images are included in the same Figure 6, which allows the visualization, through colors, of the elemental distribution; as can be seen, the amount of In and Sn contained in the magnetic residue increased with decreasing pH value (pH 3), and gadolinium shows a similar trend. It is important to note that the indium, contained in LCD screens, is in the form of ITO, which explains the similarity in its leaching and recovery behaviors (In and Sn); the ITO phase is possibly more refractory requiring different, more extreme redox conditions.[44] Moreover, the composition of ITO in LCD screens is very complex since these screens are made up of various layers of different materials.[15]

Finally, using the optimal experimental conditions of the leaching process (pH 3, H_2O_2 3% v/v, 0.05 M PPi, 25 °C), complementary tests were carried out using higher solid to liquid ratios (6 and 12 g in 150 mL), keeping constant the conditions mentioned for 3 h (90 kHz with 120 W). After leaching, the solids were filtered and air-dried, after which the magnetic residue was separated. For each case, the amount of magnetic residue was 0.149 g and 0.201 g for the initial 6 and 12 g of LCD powder, respectively, thus representing a concentration factor of 40 and 60 in each case, with similar REE, indium, and tin recoveries compared to the lower S/L ratio (data not shown here).

4. CONCLUSIONS

Erbium was selectively leached and gadolinium, tin, and indium were (overall) selectively recovered from LCD screen waste powder by sono-leaching, followed by magnetic separation. The LCD screen waste contains values of Er (477 mg·kg^{-1}), Gd (93 mg·kg^{-1}), Sn (835 mg·kg^{-1}), and In (2422 mg·kg^{-1}), which have potential commercial interest. The PPi allows the formation of complexes with Er, which leads to the selective separation from other elements, Gd, and In. The elemental dissolution is enhanced with the sono-leaching time. Moreover, the use of low pH values (<4) favored the selective dissolution of Er in the
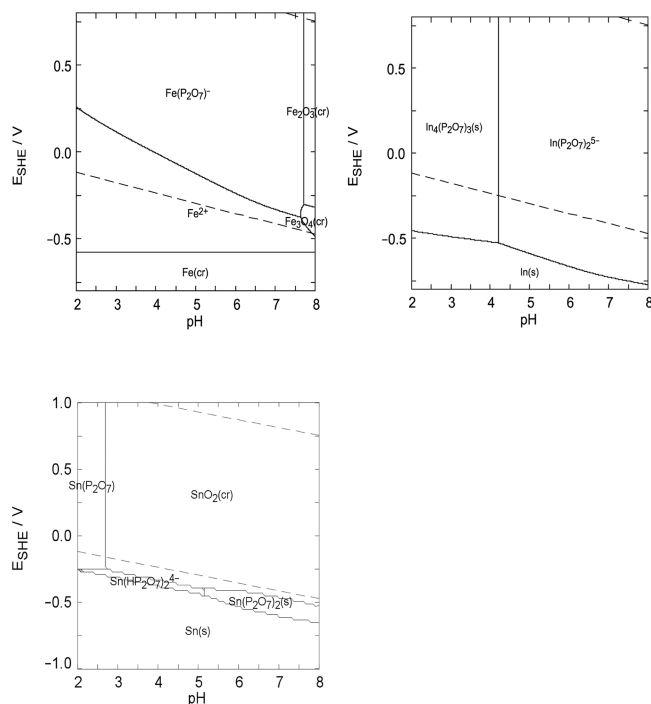
Figure A1. Pourbaix-type diagrams for iron, indium, and tin, employing the concentrations that would be present if these were completely dissolved at the *S/L* ratio employed in this study (0.35 mM Fe, 0.7 mM In, and 0.5 mM Sn for 3 g LCD powder in 150 mL of 0.1 M sodium pyrophosphate solutions).
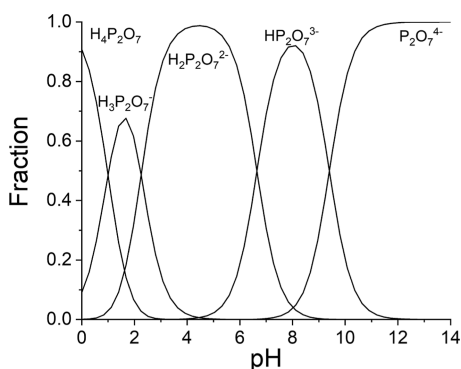

Figure A2. Species distribution diagram for $P_2O_7^{4-}$ (0.1 M) (0.35 mM Fe, 0.7 mM In, and 0.5 mM Sn for 3 g LCD powder in 150 mL of 0.1 M sodium pyrophosphate solutions).

leaching liquor and the recuperation of Gd, Sn, and In into the magnetic residue. Maximum recoveries of 93% of Er, 99% of Gd, 72% of Sn, and 97% of In were achieved, with respect to the initial content of these elements in the raw material, which are appreciably higher than those reported by other methods. Therefore, this method to selectively recover REE, Sn, and In is, without doubt, a novel, low-cost (considering the selectivity of pyrophosphate/US combination for separating metal ions in the +III and +IV oxidation state from others present in the material), nontoxic, and, above all, environmentally friendly alternative to the conventional procedures currently employed. Finally, for future studies, the possibility of recirculating the liquors obtained from the sono-leaching after the recovery of the Er ions contained in the solution has been considered.

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A.D.T.-P., G.T.L., and A.M.B.-M.: conceptualization of the research idea, data curation, investigation, writing- original draft preparation, editing, and data analysis; A.D.T.-P. and G.T.L.: data analysis (species distribution diagrams); A.M.B.-M., G.T.L., F.S.D., and A.D.T.-P.: visualization; A.D.T.-P. and A.M.B.-M.: supervision; G.T.L.; project administration; G.T.L. and A.M.B.-M.; funding acquisition. All authors have read and agreed to the published version of the manuscript. All authors read and approved the final manuscript.

Notes

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