Facile method for the selective recovery of Gd and Pr from LCD screen wastes using ultrasound-assisted leaching

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Abstract

Rare earth elements (REE) are essential for the production of technological devices. However, their high demand and low availability, together with an increase in electronic waste generation, compel the development of efficient, economic and green methods for recovering these elements from electronic waste. In this work, a facile method for selective recovering of REE from Liquid Crystal Display (LCD) screen wastes, employing ultrasound assisted leaching is presented. The screen wastes were milled and sieved to pass through a -325 mesh sieve (44 µm). The milled powder was subjected to ultrasound-assisted leaching in an aqueous medium, at room temperature (25 °C) and pH 6 for 60 min. Subsequently, a magnetic separation was applied to the leach residue. Inductively coupled plasma was employed to quantitatively analyze the composition of the LCD powders and determine the effectiveness of the extraction process. Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy allowed qualitative chemical analysis of the solid materials. The results show that the LCD screen wastes are formed, mainly, by amorphous oxides of Si, Fe, In, Sn and REE. The amount of Gadolinium (Gd) and Praseodymium (Pr) in the wastes were 93 and 24 mg kg\(^{-1}\), respectively, which justifies their recovery. X-ray diffraction analysis of the magnetic portion of the leached residue, confirmed the presence of an amorphous phase together with crystalline metallic iron alloy. The magnetic behavior, obtained by Vibration Sample Magnetometry, helped to understand the nature of the residues. The formation of this metallic alloy is attributed to the effect of high power ultrasonic during the leach. It was confirmed that the magnetic residue concentrates and recovers 87 wt% of Gd and 85 wt% of Pr contained in the original material. Therefore, ultrasound-assisted leaching is a selective and facile method for recovering Gd and Pr from waste LCD.

1. Introduction

Currently, electronic waste has become one of the major contributors to environmental pollution, mainly due to the politics of programmed obsolescence of many electronic devices over the past 20 yr [1]. Nowadays, the average life of a computer or a mobile phone is between 4 and 5 yr [2], considerably increasing the amount of electronic waste generated [3]. Since the end of the 20th century, Liquid Crystal Display (LCD) screens have been used in various electronic products due to the advantages of light quality, small volume and low energy consumption; therefore, more than 700 million LCD panels have been produced worldwide in recent years. Considering the average lifespan of 3–8 yr of these panels, large quantities of LCD panels will be reaching their end-of-life in the coming years, tremendously contributing to the generation of electronic waste [4]. Despite the many disadvantages, these wastes contain important amounts of different elements with high commercial value [5, 6]. Among these, the rare earth elements (REE) [7] are considered critical raw materials [8], due to the difficulty of their separation, acquisition and the uncertainty of their disposition [9]. Recent studies have shown the quantities of REE in LCD screens are economically attractive for recovery, however, the proposed methods have focused mainly on the backlight or light-emitting diodes of the LCD screens [10, 11]. In contrast, this investigation studies the recovery of Gadolinium (Gd) and Praseodymium (Pr), among others, contained in the LCD
panels, a subject that has not been reported. Furthermore, the importance of the recovery these REEs is implicit not only in their use in new technologies, but also in their current high prices, which are among the REEs with the greatest economic value [12].

The development of REE recovery strategies has been trending in recent years; most of the proposed processes employ inorganic acids such as HCl, H$_2$SO$_4$ or HNO$_3$ for leaching [13-15], which can damage the environment and human health, if they are not adequately controlled. Additionally, more environmentally friendly reagents, such as sulfate-roasting followed by water leaching [16] and ionic liquids [17] have also been studied, to leach the REE. However, the chemicals and conditions employed in both proposals are costly and involve complicated downstream separation processes.

In the present investigation, the pyrophosphate ion (PPi) is used as a less hazardous alternative to inorganic acids since it has been employed as a selective ligand for the REE ions in other studies [18]. It is also employed in the preparation of medicines and the preservation of different foods, proving to be safe for the environment and for humans [19, 20]. A thermodynamic study, in the form of species distribution diagrams using the Hydra-Medusa software suite [21] was performed to determine the appropriate leaching conditions. In addition, ultrasound was employed as an enhancement method during the leach, since recent studies have shown that the use of ultrasound accelerates the dissolution of metals [22] and REEs, achieving nearly 100% in 1 to 3 h [23-25]. In sonochemistry, molecules undergo chemical reactions promoted by the application of ultrasound radiation (20 kHz–10 MHz) in solid–liquid systems; ultrasound enhances the diffusion of soluble species in the liquid phase and increases the rate of penetration into the solid principally by the cavitation effect, which leads to the creation of many microcracks on the solid surface. Furthermore, if the raw material is a powder, ultrasound energy can cause particle rupture, with a consequent increase in surface area available for reaction [26].

Hence, the present study explores the recovery of the REE compounds (Pr and Gd) from waste LCD screens by ultrasound-assisted leaching, using PPi. This proposal introduces a quick, easy and inexpensive method to recover these valuable elements from wastes.

**Materials And Methods**

The LCD screens were collected from electronic wastes (televisions, cell phones, electronic tablets, laptops and cameras). The total weight of a waste LCD screen was not determined, since it varies according to the type of electronic device. The LCD screens were cleaned by separating components that were not required, such as polarized, adhesives, connectors, diffusive sheets, reflective sheet and, the plastic frame. Subsequently, the LCD were subjected to the leaching assisted by ultrasound process or sono-leaching, followed by a magnetic separation shown in Fig. 1.

First, 500 g of LCD screen wastes were milled for 30 min, using an automatic mortar grinder. The milled powder was sieved to pass through -325 mesh sieve (44 µm), since the largest quantity of RE elements is recovered by leaching at this particle size [27]. The milling process to obtain the fine particle sizes
consumes extra time and energy in the process; however, the use of inexpensive and safe reagents, compensate this expenditure, rendering the process economically feasible.

Subsequently, representative samples of 3 g were taken from the milled and screened powder, using the quartering method. The powder obtained was characterized by X-ray diffraction, XRD, (Equinox 2000 diffractometer), scanning electron microscopy with Energy-dispersive X-ray spectroscopy (SEM-EDS-Jeol, model IT 300) and, by vibration sample magnetometry, VSM (MicroSense EV7) at room temperature (20 °C) and a maximum magnetic field of ± 18 kOe.

In order to quantify the chemical composition of the raw materials, 3 g sample of LCD powders was digested in aqua regia (HCl:HNO$_3$, 3:1) at 90 °C for 2 h. The obtained liquor was filtered. Aliquot of 1.5 mL of the liquor were diluted to 30 mL with deionized water, for their analysis by inductively coupled plasma (ICP-OES, Perkin Elmer, Optima 3000 XL). This process was performed on three different samples of the same material, in order to ensure the repetitively of the data obtained.

For the leaching tests, 3 g of the milled and sieved powder were immersed in a beaker with 150 mL of the solution of 0.05 M PPi ($P_2O_7^{4-}$) as leaching agent, using a liquid-to-solid ratio of 20 g L$^{-1}$. The solution pH was adjusted and maintained at 6, using 1 M sulfuric acid. These experimental conditions were selected in accordance with the results of previous studies [18]. The leaching solution was sonicated during the leaching time, using an Ultrasonic Homogenizer 300VT, equipped with a piezoelectric transducer at a frequency of 90 kHz and a solid titanium tip of 9.5 mm. The experiments were performed at a sonication output power of 120 W. The beaker was placed into an ice bucket, to guarantee that the temperature of the solution in all cases did not exceed room temperature (25 °C). The ultrasound was used to promote the exposure of the rare elements to the leaching agent, through the rupture of the particles, and to increase the rate of penetration into the solid by the cavitation effect [26]. The leaching solution was filtered, obtaining a liquor and a solid phase (leach residue). The leach liquor was characterized by ICP. The solid residue was magnetically separated, into non-magnetic and magnetic powders, after having been air-dried at 80 °C for 15 min. The magnetic and non-magnetic residues were characterized by XRD, SEM-EDS, VSM and ICP. The digestion procedures of the solid residues, for ICP analysis, is the same as that previously described for LCD powders.

**Results And Discussion**

Due to technological limitations, the Results and Discussion section can only be accessed as a download in the supplementary files section.

**Conclusions**

LCD screen wastes were found to contain 93 and 24 mg kg$^{-1}$ of Gd and Pr, respectively. To retrieve these REEs, a facile method for selective concentrating of some REEs is proposed. In particular, Gd and Pr from LCD screen wastes can be effectively recovered by ultrasonic-assisted leaching, using pyrophosphate ion
as complexing ligand. A retrieval of 85 and 87 wt% of Gd and Pr, respectively, was achieved, using an ultrasound-assisted leaching for 60 min at room temperature. The combination of ultrasound and leaching at room temperature showed positive impacts on enhancing the separation of REEs; substantial physicochemical changes occurred during the leaching assisted with ultrasound, including structural transformations, chemical radical formation, chemical reduction, and even, compound decomposition. Structural analysis and chemical decomposition, promoted by the formation of water radicals, could explain the effectiveness of the ultrasound leaching in improving the recovery of Gd and Pr from LCD screen waste. However, other valuable REEs, such as In and Er, remain in the non-magnetic solid residue.

**Declarations**

**Availability of data and materials**

All data generated or analyzed during this study will be made available on request.

**Competing interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Authors’ contributions**

Conceptualization, G.T.L.L. and A.M.B.M.; methodology, A.D.T.P. and A.M.B.M.; software, A.D.T.P. and G.T.L.L.; validation, A.M.B.M., F.S.D. and G.T.L.L.; formal analysis, A.M.B.M. and G.T.L.L.; investigation, A.D.T.P.; resources, G.T.L.L. and A.M.B.M.; data curation, A.D.T.P.; writing original draft preparation, A.D.T.P. and A.M.B.M.; writing review and editing, A.M.B.M., G.T.L.L., F.S.D. and A.D.T.P.; visualization, A.D.T.P. and A.M.B.M.; supervision, G.T.L.L.; project administration, G.T.L.L. and A.M.B.M.; funding acquisition, G.T.L.L. and A.M.B.M. All authors have read and agreed to the published version of the manuscript. All authors read and approved the final manuscript.

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Tables

**Table 1** Results of the ICP analysis of the leach liquor, the magnetic and non-magnetic residues

| Element | Non-magnetic residue | Magnetic residue | Leached liquor |
|---------|----------------------|------------------|---------------|
|         | mg kg\(^{-1}\) % remaining | mg kg\(^{-1}\) % recovery | mg kg\(^{-1}\) % leached |
| Pr      | 3 13 | 21 87 | 0 0 |
| Gd      | 2 2  | 78 85 | 11 12 |
| Er      | 449 84 | 20 4 | 64 12 |
| In      | 1749 99 | 0 0 | 25 1 |
| Sn      | 542 74 | 11 2 | 180 25 |
| Fe      | 84 4 | 2089 94 | 37 2 |
| Zn      | 2 9 | 0 0 | 19 91 |

Figures

**Figure 1**
Figure 2

XRD patterns of the milled LCD screen waste
Figure 3

Elemental mapping at the microstructural level by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS) of milled LCD screen powder.
Figure 4

Specie distribution diagram of Gd3+ as a function of pH in the (P2O7)4- system at 25 °C.
Figure 5

XRD of different residues: (a) combined leached residue of LCD screen powder, submitted to ultrasonic-assisted leaching for 60 min in 0.05 M pyrophosphate solution using ultrasonic energy (US) at pH 6, (b) non-magnetic leach residue and (c) magnetic leach residue
Figure 6

Magnetic hysteresis loops of the different residues: combined residue of screen wastes leached for 60 min in pyrophosphate solution with ultrasonic energy (US) at pH 6, as well as the non-magnetic and the magnetic residues.
Figure 7

Elemental mapping at the microstructural level by scanning electron microscopy with energy dispersive X-ray spectrometry of the magnetic residue

Supplementary Files

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