A truly circular process for recycling all main raw materials of waste of LCDs screens of smartphones

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Abstract A liquid-crystal display (LCD) screen is composed by two transparent glasses coated with indium-tin oxide (ITO) on it and crystal liquids (LCs) sandwiched between them. The current implemented recycling process usually adopts mechanical crushing or pyrolysis as the primary LCDs screens treatment step. However, the toxic (LCs) and valuable recyclable (Indium, In) materials are treated together and the In recovery rate is low. Furthermore, in a circular economy perspective, the recovery of glass and plastics from the LCD screens should be targeted too, to close the loop of the recycling chain. Here, we propose a hybrid (physical plus chemical steps) method that removes the polymeric film (PF) attached to the ITO glass to recover the highest amount of In and also to recover the plastic fraction and the glass substrate. For that, the cut LCDs pieces were put in a water and ethyl acetate (1:5) mixture in a low-pressure reactor (1 hour at 180 °C) for detaching the PF, separate it and dissolve the LCs in the solvent. Subsequently, a high In recovery yield (99.0%) was achieved from the ITO glass under microwave-assisted soft acid leaching conditions followed by continuous column ion-exchange technology (IET) to purify In from other metals impurities.

Keywords: Indium, Critical Raw Material, LCD screens recycling

1. Introduction

A smartphone is composed by several fractions (Figure 1.A) being the screen a valuable fraction to recover due to the presence of indium (In). A LCD screen (Figure 1.B) typically has a sandwich structure composed of two different kinds of glass substrate covered with the ITO substrate within the liquid crystal (LC) between the glass and the polymeric film (PF). ITO is a mixture of In(III) oxide (In2O3) and tin(IV) oxide (SnO2), with 80–90% by weight of In2O3, and 10 – 20% by weight of SnO2 [1]. In addition to ITO, LCD screens include LCs, glass and polymers (polymethyl methacrylate, PMMA, and polycarbonate, PC) in their composition, which can be also recovered and incorporated in a composite [2] (Figure 1.B).

Figure 1: A) Schematic representation of a dismantled smartphone: including the LCD screen. B) Schematic representation of the ITO substrate, the color filters, and the PF.

The waste of the screens is valuable because of (i) resource of In; (ii) recycling of glass substrates; (iii) potential recycling of organic materials, such as LCs. On the other hand, the pollution of LCs in the treatment of screen of smartphones is a serious and worrying problem because it contains large amounts of organic matters, such as polycyclic aromatic hydrocarbons. Regrettably, up to now, the studies about separation and recovery of LCs from LCD panels are scarce [3] and incineration or landfill are the main treatment and disposal of waste LCs. Although the amount of In available in smartphone screens is about 102 mg/kg, it can increase up to 1400 mg/kg per screen [4], if the PF attached to the LCD substrate is previously removed. An effective liberation and size-reduction method of ITO glass is an important pre-treatment step that involves removing the PF and dissolution of LCs, aiming to obtain the ITO-glass for subsequent recycling of In. Furthermore, removing and separation of LCs is also a crucial step because it is also a disadvantage for recycling In since LCs and ITO substrate are closely linked together.

The current recycling process usually adopts mechanical crushing or pyrolysis [4], [5] as the primary step for the treatment. However, the toxic materials (LCs) and recyclable materials (In) are treated together and the recovery rate of In is low. To overcome these problems, a hybrid (physical plus chemical steps) method is proposed that recycles all the main raw materials (In with high purity, plastic fraction and the glass substrate). The pre-
treatment proposed here consists on using a suitable polar solvent in order to remove the PF coated on the ITO substrate and facilitate the subsequent leaching of In. Several polar solvents will be tested for their efficient removal of PF and dissolution of LCs. Some studies using baths of LCD screen in acetone showed good separation between PF and ITO [6]; additionally, acetone can be used as a suitable solvent for the dissolution of the LCs, but the time of the reaction is up to 4h. Furthermore, the precipitation process of In took 24h, potentially limiting its industrial applicability [6]. So, an alternative microwave pre-treatment, which offers the appropriate heating and pressure, will be considered as it can significantly reduce the time and increase the efficiency. After efficient separation of PF and immobilization of LCs in an appropriate solvent, In will be leached from ITO-glass using hydrochloric acid (HCl) under microwave-assisted conditions. This acid is an appropriate choice since chilo complexes of In are formed in a wider pH range, which will be advantageous for its subsequent purification by ion-exchange technology (IET) after previous precipitation of metals impurities.

2. Materials and Methods

2.1. Materials

Various brands and models of smartphones were collected from local collectors. After collection, the smartphones were manually dismantled to remove the screens from the other constitutive components by mean of specifics designed screwdrivers for that purpose available in the market. All reagents used were of analytical grade and used without any further treatment.

2.2. Methods

Separation of the layers that constitute the LCDs screens: The screens were cut with dimensions ranging from 21.0 to 38.5 cm², by mean of a guillotine. The metal characterization of the different LCDs screens under study were performed by acid digestion with aqua regia (ratio 1:3 of HNO₃/HCl) to the cut pieces. Then, the cut pieces were put into a sealed reactor (5100 Parr Reactor), into an appropriate aqueous solution of ethyl acetate (99.9%, purchased from AnalaR NORMAPUR) and ultra-pure water (in a proportion of 1:5), with a solid/liquid (S/L) ratio of 70 g/L, at 180 °C for 1h. After the reaction, all the detached layers from the screens were then filtrated and dried for 8h in a drying oven. The remaining aqueous solutions were analyzed by UV-visible spectroscopy (UV-Visible spectrophotometer - UV-6300PC double beam) to confirm the dissolution of the LCs in the solution. The appearance of a new band at 325 nm in the aqueous solution at the end of each trial confirmed the dissolution of the LCs in the aqueous media. To separate the dried layers containing mainly the ITO substrate from the other’s layers (polymeric film, cover glass and anti-reflecting layer) a wet density separation process was performed using water and the pure densities of each layer determined as described somewhere else [7].

Leaching assays of the ITO substrate to recover Indium: The recovery of indium from the ITO substrate was performed by microwave-assisted acid leaching. Several concentrations of HCl (0.25, 0.5, 1.0, 2.0 and 2.5 M) were prepared from the concentrated acid (HCl ≥ 37%, purchased from Honeywell) to evaluate the indium extraction efficiency versus acid concentration. The ITO substrate (touch screen and glass substrate) pieces were cut with an area of 4 cm² and put inside 23 mL polytetrafluoroethylene vessels with a S/L ratio of 1/5, during 3 cycles of microwave of 30 seconds each with a power of 840 W.

Indium purification process by continuous mode adsorption-elution assays: Indium recovery from HCl leachates was performed using DOWEX M4195 (referred as M4195), which is a weakly basic bispicolylamine chelating resin purchased from Sigma Aldrich. Synthetic leachates, containing In(III), Al(III), Fe(III), Cu(II), Zn(II) and Sn(II), which mimicked the composition of the real leachate, were prepared by solubilizing a suitable amount of each metal’s salt (InCl₃, AlCl₃, FeCl₃·6H₂O, Cu(NO₃)₂·3H₂O, ZnCl₂ and SnCl₂·2H₂O) in a 0.5 mol/L HCl solution. The initial pH of the synthetic leachate was adjusted to 2+0.1 using concentrated solution of NaOH and measured by Crison Instruments SA MicropH. This chloride multi-metal synthetic leachates contained the subsequent metal concentrations (mmol/L) of 0.435 In, 2.59 Al, 0.0895 Fe, 0.0472 Cu, 0.0153 Zn, and 0.0421 Sn. The synthetic leachates were used as inlet solutions for continuous mode adsorption assays in a glass chromatographic column (d = 6.6 mm, h = 100 mm) filled with a packed bed of M4195 resin (0.75 g) and a volume of 0.845 mL. The flow rate was controlled using a peristaltic pump from MS-Reglo (Ismatec, Switzerland), which was maintained at 0.5 mL/min (i.e., 35.5 BV/h) for both adsorption and elution assays. Air pockets were removed from the packed bed by passing through deionised water, simultaneously washing the resin, before introduction of the synthetic leachate. Between adsorption and elution steps, the resin was washed with 30 mL deionized water. Samples were collected from the outlet solution at different intervals of time to measure metals concentration and two final assays without collecting any sample during adsorption and elution stage were performed. Elution of indium was performed using 0.25 mol/L of H₂SO₄ at room temperature.

At the several stages, the analysis of the metal concentrations (namely, Ag, Al, Au, As, Ba, Cr, Cu, Fe, Ga, In, Ni, Pb, Sn, Sr and Zn) was performed by inductively coupled plasma optical emission spectrometry (ICP-OES) using a ICAP 7400 THERMO spectrophotometer (Waltham, MA, United States) equipped with a nebulizing system.

3. Results and Discussion

The first step of our studies was to determine all the metal constitution of the several layers that constitute the smartphones screens. The results presented in Table 1
summarizes the metal constitution of the smartphones screen.

Table 1. Metal composition, expressed in mg of metal per gram of the smartphones screen and in percentage in weight (% wt.) for each metal.

<table>
<thead>
<tr>
<th>Metal</th>
<th>mg/g of LCD screen</th>
<th>% wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>9.83x10^{-5}</td>
<td>0.39</td>
</tr>
<tr>
<td>Al</td>
<td>3.25x10^{-4}</td>
<td>0.17</td>
</tr>
<tr>
<td>Au</td>
<td>4.17x10^{-7}</td>
<td>0.03</td>
</tr>
<tr>
<td>Ba</td>
<td>4.34x10^{-6}</td>
<td>0.43</td>
</tr>
<tr>
<td>Cr</td>
<td>4.01x10^{-6}</td>
<td>0.52</td>
</tr>
<tr>
<td>Cu</td>
<td>4.04x10^{-6}</td>
<td>5.40</td>
</tr>
<tr>
<td>Fe</td>
<td>8.60x10^{-5}</td>
<td>4.96</td>
</tr>
<tr>
<td>In</td>
<td>3.19x10^{-4}</td>
<td>43.31</td>
</tr>
<tr>
<td>Pb</td>
<td>4.82x10^{-6}</td>
<td>0.74</td>
</tr>
<tr>
<td>Sn</td>
<td>3.14x10^{-5}</td>
<td>4.17</td>
</tr>
<tr>
<td>Sr</td>
<td>3.27x10^{-5}</td>
<td>1.34</td>
</tr>
<tr>
<td>Zn</td>
<td>3.39x10^{-5}</td>
<td>4.53</td>
</tr>
<tr>
<td>Others</td>
<td>--------------------</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

The LCD screen is majority constituted by In (43 % wt.), Al (34 % wt.), Cu (5 % wt.), Fe (5 % wt.) and Zn (5 % wt.). These values are in accordance with others published in the literature [8].

At this stage, one of the major challenges to overcome is to properly separate the glass substrate that contains the In from the polymeric films of the screens and, additionally, to isolate the toxic LCs. As mentioned in the literature, LCs can be dissolved in solvents, namely in acetone [6] or in toluene [9]. Here, we tested several polar solvents for their efficient removal of the polymeric films and the dissolution of LCs with several techniques (thermal bath, low-pressure reactor and microwave). The polar solvents under studied were acetone, ethyl acetate and ultra-pure water. From the results obtained, visually, our best experimental conditions to detach all the layers were obtained using a low-pressure reactor in a solution of 1.5 ethyl acetate and water as it is shown in Figure 2. The experiments were carried out at 180 °C for 1h with a S/L ratio of 70g/L and dimensions ranging from 21 to 42 cm² of the smartphone’s screens. To verify the dissolution of the LCs in the aqueous media, emission spectra were performed confirming the emission in the UV-visible of the electromagnetic spectra (data not shown). Additionally, by wet density, it was possible to separate all the plastic components that constitutes the smartphones, namely the color filters, PF and other plastics. The ITO substrate recovered without the polymeric film is mainly constituted by Al (37.9 % wt.), In (22.9 % wt.), Cu (4.9 % wt.), Fe (4.3 % wt.), Sn (2.2 % wt.) and Zn (2.1 % wt.) being 25% wt. of other metals (such as, Ag, Au, Ba, Sr).

Therefore, at this stage, a chemical process should be employed if the aim is to recover In at high purity from the glass substrate. For that purpose, In was extracted from the glass substrate using HCl as leaching agent. The extraction of In was performed in a microwave-assisted leaching, which proved to be more efficient in terms of time and energy consumption over the traditional method [10]. After optimization of the various experimental parameters (S/L ratio, pH, concentration of the acid and time), our best experimental conditions were: S/L of 1:5, during 3 cycles of microwave of 30 seconds each with a power of 840 W using 0.50M of HCl. Under these conditions, 99 % of the total amount of In was extracted from the ITO substrate but the purity of the In (54.0%) was not satisfactory being Al (33.5 %), Fe (5.2 %), Sn (0.9 %), Zn (4.0 %) and Cu (2.4 %) the main contaminants (Figure 3: Inlet solution). To increase the purity of the extracted In, a weakly basic bispicolylamine chelating resin was selected. This resin presents the following order of affinity: Cu(II) > In(III) > Zn(II) > Fe(II) ≈ Al(III) [11]. Using a flow rate of 0.5 min./L, the breakthrough capacity of the resin for In was achieved after 540 minutes. After elution for 100 minutes (flow rate 0.5 min./l) with 0.25M of H2SO4, an eluate containing In with a purity of 92% was achieved (Figure 3: Eluted solution). This technology proved to be very efficient and fast to increase the purity of the recovered In.

4. Conclusions

The combination of physical and chemical methodologies demonstrated to recover efficiently all the fractions that constitute the LCD screen from smartphones waste. The hybrid methodology developed allowed to recover In,
the toxic substance (LC), plastics and glass substrate in an eco-friendly way without generating any tertiary effluent (dusts or wastewaters). Additionally, the toxic substances (LC) were recovered and isolated from the ecosystem in a safer approach when compared to the implemented technologies that generally overlook them. After testing several polar solvents to detach all the layers, the total separation was achieved in an aqueous media mixed with ethyl acetate in a proportion of 1:5 respectively. This allows to recover all the plastic fraction separated from the ITO substrate that contained the higher amount of In to be recovered subsequently. Our targeted metal, In, was extracted with a high recovery yield (99%) using microwave-assisted acid leaching. This technique showed to be very efficient and rapid. In a way to increase the purity of the extracted In, a chelating bispycylamine resin was used. This resin showed a good selectivity to In over the other base metals, namely, for Al, Fe, and Sn. The high affinity of the resin to In results in an increase of the purity of In up to 92%. Globally, all these achievements demonstrated a faster and efficient process to recover all the layers of the LCDs screens, minimizing the production of dusts, toxic fumes and wastewater for the subsequent recovery of the In and potentially scale-up for industrial practices.

Acknowledgments

This work is financially supported by national funds through the FCT/MCTES (PIDDAC), under the project PTDC/CTA-AMB/3489/2021. This work was also financially supported by: the Base Funding UIDB/50006/2020 and UIDB/00511/2020 of the Associated Laboratory for Green Chemistry - Clean Technologies and Processes, LAQV-REQUIMTE and the Laboratory for Process Engineering, Environment, Biotechnology and Energy (LEPABE), respectively, both funded by national funds through the FCT/MCTES and the Project 2SMART - engineered Smart materials for Smart citizens, with reference NORTE-01-0145-FEDER-000054, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

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