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## Materials recovery from waste liquid crystal displays: A focus on indium

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## ABSTRACT

In the present work the recovery of indium and of the polarizing film from waste liquid crystal displays was experimentally investigated in the laboratory. First of all, the polarizing film was removed by employing a number of different techniques, including thermal and chemical treatments. Leaching of indium was then performed with HCl 6 N, which allowed solubilisation of approximately 90% In (i.e. 260 mg In per kg of glass) at room temperature, without shredding. Indium recovery from the aqueous phase was then investigated through solvent extraction with polyethylene glycol (PEG)-based aqueous biphasic systems. Indium extraction tests through the PEG–ammonium sulphate–water system were conducted as a function of PEG concentration, salt concentration and molecular weight of PEG, using 1,10 phenanthroline as a ligand. The experimental results demonstrated that indium partitioning between the bottom (salt-rich) and the top (PEG-rich) phase is quite independent on the composition of the system, since 80–95% indium is extracted in the bottom phase and 5–20% in the top phase; it was also found that when PEG concentration is increased, the ratio between the bottom and the upper phase volumes decreases, resulting in an increase of indium concentration in the bottom phase (at [PEG] = 25% w/w, indium concentration in the bottom phase is ~30% higher than the initial concentration before the extraction).

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## 1. Introduction

Liquid crystal displays (LCDs) are becoming more and more widespread in electronic applications and are definitely replacing the old cathode ray tube devices in TVs and monitors (Dodbiba et al., 2012). Since the lifespan of an LCD is typically 3–5 years (Zhuang et al., 2012), the amount of waste LCDs is rapidly increasing, requiring the development of suitable treatment and recovery processes. The LCD module, i.e. the main part of an LCD display after primary dismantling (Fig. 1), contains two polarizing films, two glass substrates coated with indium tin oxide (ITO) film and a liquid crystal layer (Wang et al., 2013; Dodson et al., 2012).

Over the front glass substrate is the colour filter layer, consisting of a black matrix, colorants and binders, an overcoat layer and an ITO layer (Yen and Tso, 2004). Over the rear glass substrate is the TFT (thin film transistor) layer, containing three terminals, a gate insulator, a semiconductor, an ohmic contact, a passivation layer and the conductive electrode (Lee and Cooper, 2008). Indium tin oxide is an optoelectronic material with the key features of transparency to visible light, electricity conduction

and thermal reflection (Li et al., 2011); it is composed of 80–90% In<sub>2</sub>O<sub>3</sub> and 10–20% SnO<sub>2</sub> (Virolainen et al., 2011; Lee et al., 2013). Polarizing films generally consist of a layer of iodine doped-polyvinyl-alcohol (PVA) sandwiched between two protective layers of cellulose triacetate (TAC) (Dodson et al., 2012); they are assembled on the glass substrate using a pressure sensitive adhesive (PSA) composed of acrylic polymers (Nam et al., 2012; Passamani, 2011). Liquid crystals are a mixture of aromatic-based polymers with benzene, cyano-group, fluorine, bromine and chlorine; this mixture typically contains 10–25 different compounds (Becker et al., 2003; Zhuang et al., 2012).

The main driver for waste LCDs treatment is indium recovery. Indium is a rare and valuable metal that has recently been included by the European Commission in a list of critical raw materials, due to its economic importance and the high supply risk that it is subject to, especially because production is concentrated in non-European countries (European Commission, 2014). More than 80% of indium is employed for the production of ITO coatings used in liquid crystal displays (Park et al., 2009). In Europe, LCDs are fed into a separate recycling process after collection (Buchert et al., 2012). The treatment process generally consists of a dismantling step aimed at removing hazardous components (such as the cold cathode fluorescent lamps employed for background illumination)

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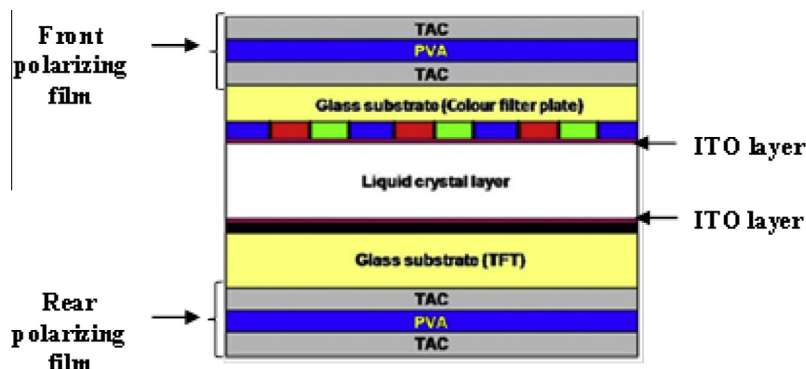


Fig. 1. Typical cross-section of a LCD panel (adapted from Dodson et al., 2012).

and valuable components (printed circuit boards, cables, plastic and metallic fractions) for further treatment and recovery. The LCD glass panels are currently stocked at the plant or incinerated, since no recycling process is yet available on an industrial scale; this practice obviously leads to a loss of potentially recoverable resources, such as the critical metal indium. Considering the amount of LCD appliances put on the market in Europe 27 in 2011, 6.5 tons of indium will become available in the coming years as potential stock (ENEA elaborations from OCSE data, <http://www.oecd.org/>).

In the last decade a number of studies have focused on indium recovery from end-of-life LCDs. In most cases thermal treatment at high temperature was employed to remove the polarizing film (Li et al., 2009; Lee et al., 2013), which leads to energy consumption and potentially harmful atmospheric emissions. According to Li et al. (2009), by heating the LCD in a furnace at  $T = 230\text{--}240\text{ }^{\circ}\text{C}$  the polarizing film can be removed, but only through hard brushing. A shredding step followed by density-based separation was tested by Zhuang et al. (2012). Ruan et al. (2012) employed liquid nitrogen to strip the polarizing film, but no information was provided about the amount of time required and the removal efficiency achieved. Indium recovery from the glass substrate is generally performed using hydrometallurgical techniques, consisting of a leaching step aimed at dissolving the metals of interest, followed by a separation step.

Leaching is often carried out employing several acids and acid mixtures; however, the hydrogen concentration of such mixtures is not always kept constant so that comparison of lixiviants (in terms of leaching efficiency) is not straightforward. Li et al. (2009) and Lee et al. (2013) tested several acid mixtures with acid concentrations ranging from  $\sim 6\text{ N}$  to  $\sim 10\text{ N}$ ; the hydrogen concentration of the leaching agents employed by Ruan et al. (2012) ranges from  $\sim 6.5\text{ N}$  to  $\sim 18.5\text{ N}$ . Yang et al. (2013) and Virolainen et al. (2011) tested HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> as leaching agents, fixing the acid concentration in terms of molarity; in this case the comparison is possible only between HCl and HNO<sub>3</sub>, since H<sub>2</sub>SO<sub>4</sub> has a twofold hydrogen concentration. Moreover, a shredding step is often performed prior to leaching; in some cases it is carried out on the glass substrate obtained after the removal of the polarizing film (Li et al., 2009; Lee et al., 2013), and in other cases on the entire LCD module (Yang et al., 2013). Due to the low concentration of indium in the leachate, concentration techniques are strongly required; for this purpose, Rocchetti et al. (2015) applied six steps of leaching to increase indium concentration which was about 35 mg/L after the first step, almost 2-fold at the second step and about 3-fold at the fifth step. Indium recovery from the aqueous phase is then generally performed through solvent extraction. Organic solvent extraction (or liquid–liquid extraction) has been widely used in the past as a concentration and separation

technique due to its characteristics of high selectivity and high recovery efficiency. However, organic extractants such as D2EHPA (Yang et al., 2013), TBP (Virolainen et al., 2011), Cyanex 272 and Cyanex 923 (Yang et al., 2013) diluted in organic diluents (such as kerosene and toluene) are often employed, which are potentially hazardous for human health and the environment due to emissions of Volatile Organic Compounds (VOC) into the atmosphere. Recently, an electrochemical method followed by acid treatment was proposed by Choi et al. (2014), aimed at recovering the indium tin oxide layer as well as the glass plate.

In the present work indium recovery from waste LCDs was investigated at laboratory scale. The first step in the process proposed here aims to remove the polarizing film from the glass substrate by thermal and chemical treatments. The product removed with such techniques was then analysed through stereomicroscope to determine its quality. Indium recovery from the solid residue was investigated through leaching and solvent extraction. Preliminary leaching tests were carried out on synthetic indium tin oxide powder in order to define the best operative conditions; acid concentration was fixed in terms of normality to permit comparison.

Indium leaching from the glass substrate was then performed. Differently from what is commonly found in the available literature, samples were not shredded before the leaching, since particle size is not supposed to have any influence on leaching efficiency (the ITO layer is only present on one side of the glass substrate). Indium recovery from the aqueous phase was then investigated through solvent extraction with aqueous biphasic systems (ABSs): due to their characteristics of low cost, reduced flammability and reduced toxicity, ABSs are gradually emerging as a more sustainable alternative to the traditional oil–water extraction systems (Rogers et al., 2005). They are formed when a water-soluble polymer (e.g. PEG, polyethylene glycol) is mixed with certain inorganic salts (such as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>HPO<sub>4</sub>, KCl) at a suitable concentration (da Silva et al., 1997; Mishima et al., 1998; Wu et al., 1999). The formation of an aqueous two-phase system can be explained on the basis of competition for hydration between the polymer and the salt phase (Cabezas, 1996); the addition of an inorganic salt increases the dehydration of the polymer chains, due to the salting-out effect and phase separation, and two immiscible aqueous phases are obtained. In such a system, metal ions are partitioned between the phases according to a certain distribution coefficient, defined as the solute concentration in the upper phase divided by the solute concentration in the lower phase (Fontana and Ricci, 2000). Several water-soluble polymers may be utilized to form aqueous two-phase systems; polyethylene glycol (PEG) is often employed because it is non-toxic, non-flammable and non-volatile (Visser et al., 2000). According to Rogers et al. (2005), metal ion extraction in aqueous

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