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).

Keywords: waste LCDs, hydrometallurgy, indium, ABSs

1. INTRODUCTION

Liquid crystal displays (LCDs) are becoming more and more widespread in electronic TVs and monitors (Dodiba 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 (Figure 1), contains two polarizing films, two glass substrates coated with indium tin

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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_2O_3 and 10-20% SnO_2 (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 to 25 different compounds (Beker et al., 2003; Zhuang et al., 2012).

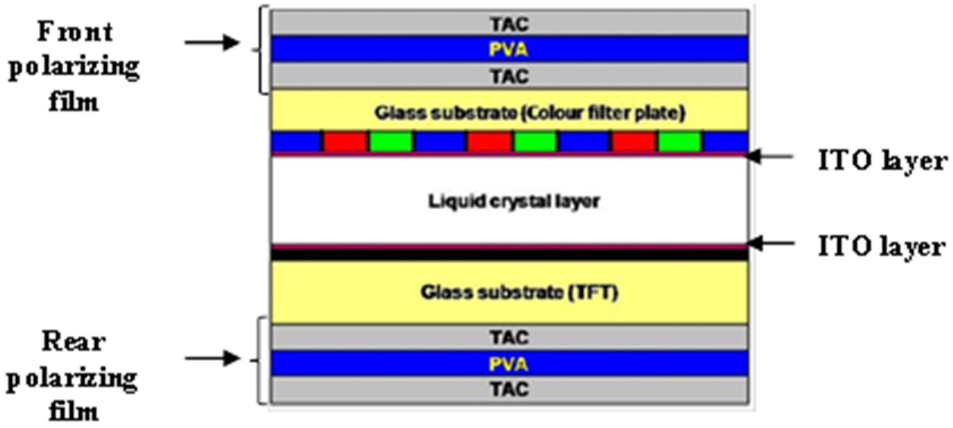


Figure 1. Typical cross-section of a LCD panel (adapted from Dodson et al., 2012).

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) 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=230-240°C the polarizing film can be removed, but only through hard brushing. A shredding step followed by density-based separation was tested by Zhuang at 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 ~6 N to ~10 N; the hydrogen concentration of the leaching agents employed by Ruan et al. (2012) ranges from ~6.5 N to ~18.5 N. Yang et al. (2013) and Virolainen et al. (2011) tested HCl, HNO_3 and H_2SO_4 as leaching agents, fixing the acid concentration in terms of molarity; in this case the comparison is possible only between HCl and HNO_3, since H_2SO_4 has a two-fold 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, toluene etc.) 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 $(NH_4)_2SO_4$, Na_2SO_4, Na_2CO_3, K_2HPO_4, 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 Roger et al. (2005), metal ion extraction in aqueous two-phase PEG-based systems can be classified into three categories: extraction in the PEG-rich phase alone, without an extracting agent (a); extraction of metal ions as chelates using water-soluble

chelating extractants (b); extraction of metal ions as complexes with inorganic anions, such as Cl^-, Br^-, I^- (c). A number of parameters affect metal ion partitioning in an ABS, such as the features of the system (nature and concentration of the inorganic salt, molecular mass and concentration of the polymer), the hydration properties of the solute (Roger et al., 1996), the temperature (Fontana and Ricci, 2000) and the type of extracting agent (Ammar et al., 2013).

In recent years an increasing amount of research has focused on metal extraction by means of aqueous biphasic systems. Ammar et al. (2013) investigated the extraction behaviour of Cd(II), Cu(II), Fe(II) and Zn(II) in an aqueous biphasic system composed of PEG and sodium sulphate in the presence of KI and KSCN as extractants; Cd(II) extraction was investigated by Bulgariu and Bulgariu (2008) in a PEG 1550-$(NH_4)_2SO_4$ system. Dzherayan (2006) studied the extraction of gallium from alkaline carbonate solutions with phenylfluorone in the PEG–sodium carbonate–water system; copper extraction with a PEG 3,350-ammonium sulphate-water system was studied by Fontana and Ricci (2000) in the presence of 1,10 phenanthroline as complexing agent.

In this work, indium recovery from the aqueous phase is investigated through PEG-based ABSs. The system consists of PEG-$(NH_4)_2SO_4$-water, since it has been often employed in the literature for the extraction of several metal ions (Fontana and Ricci, 2000; Bulgariu and Bulgariu, 2008). Indium partitioning in the selected ABS was investigated in the presence of 1,10 phenanthroline, which is a traditional ligand employed in coordination chemistry (Bencini and Lippolis, 2010).

2. MATERIALS AND METHODS

The waste LCD panels were provided by an e-waste treatment plant located in northern Italy (STENA Technoworld srl, Castenedolo, BS); a number of LCD monitors (not dismantled) were also provided by an e-waste collecting platform. All chemicals were used as received and without any further purification: acetone, ethyl acetate, limonene, liquid nitrogen, HCl 37-38% w/w, HNO_3 69.9% w/w, H_2SO_4 96% w/w, indium tin oxide powder (ITO) (325 mesh, ≥99.99% trace metals basis, 90% In_2O_3, 10% SnO_2 Sigma Aldrich), polyethylene-glycol (Sigma Aldrich, MW 3,350 and 10,000), ammonium sulphate and 1,10 phenanthroline.

2.1 Removal of the polarizing film

Infrared spectroscopy (Shimadzu IRAffinity-1) was employed to gather information about the chemical composition of the external side of the polarizing films. Thermal and chemical treatments were then compared in order to evaluate the best treatment option in terms of time required to remove the film from the glass substrate and the quality of the recovered product. Each test was repeated on two LCDs of different sizes and compositions, previously cut into small pieces (5cm x 5cm). Thermal treatments were performed by cooling the waste LCDs with liquid nitrogen (T=-

196°C); the amount of reagent required was ~25 L per kg of waste LCDs. Chemical treatments were performed by soaking the waste LCDs in several organic solvents such as acetone, ethyl acetate and limonene. The liquid/solid ratio was 3 mL/g. In order to maximize contact with the solvent, small cracks were made in the glass (with a mortar) to allow the solvent to reach the inner side of the polarizing film where the acrylic adhesive was present. The experiments were then carried out in glass beakers on a mechanical shaker; the influence of ultrasound treatment (35 kHz) was also tested to evaluate the possibility of reducing the contact time. The removed film was analysed by stereomicroscope (Olympus SZX12) to determine its quality. Scanning electron microscope (ZEISS EVO MA 15) was also employed to examine glass composition; both the thin film transistor and the colour filter layer were analysed.

2.2 Leaching

In order to define the best operative conditions for indium leaching, preliminary tests were performed on ITO powder by varying the leaching agent (HCl, HNO_3, H_2SO_4, HCl-HNO_3 3:1 v/v), the time (t=0-24 h) and the liquid/solid ratio (L/S= 20 mL/g, 100 mL/g, 500 mL/g); acid concentration was 6 N in all the experiments, since this value was suggested by some other authors (Li et al., 2009; Lee et al., 2013; Yang et al., 2013). Indium leaching efficiency (E%) was calculated according to Eq. (1):

$$E(\%) = \frac{M}{M_0} \cdot 100 \quad (1)$$

where:

- M is the amount of indium dissolved (g);
- M_0 is the amount of indium in the initial sample (g).

The best leaching conditions were then applied to leach the glass substrate remaining after the polarizing film removal process (Section 2.1). The leaching tests were carried out at room temperature in glass beakers on a mechanical shaker, with a liquid/solid ratio of 3 mL/g. Metal content was determined through MP-AES (Microwave Plasma-Atomic Emission Spectrometer) Agilent 4100. SEM analyses were also performed on the glass substrate (both TFT and colour filter layer).

2.3 Indium extraction with aqueous biphasic systems (ABSs)

Indium extraction from the aqueous phase was investigated through solvent extraction with aqueous biphasic systems. The system considered consists of polyethylene-glycol (PEG), ammonium sulphate, water and 1,10 phenanthroline (phen) as a ligand.

Indium $5 \cdot 10^{-3}$ M solutions were prepared by dissolving indium (III) nitrate hydrate in distilled water. No information is available in the literature about indium extraction stoichiometry with this ligand. In this work we assumed that three moles of phenanthroline are required to complex one

mole of In(III); in order to guarantee an excess reagent, a molar ratio (r) equal to 5 was employed, as reported in Eq. (2):

$$r = \frac{\text{phen moles}}{\text{In moles}} = 5 \quad (2)$$

From preliminary tests (not reported here) the optimal pH value which could suggest the formation of indium complexes was ~7.5; however, the operative pH was set at ~5.5 in order to avoid indium precipitation (which was observed after few hours of equilibration at pH=7.5). This value is, thus, the nearest to the optimal one which avoids indium precipitation.

Extraction tests were carried out by mixing weighed amounts of PEG and ammonium sulphate with the metal-rich solution in glass-capped tubes on a mechanical shaker; the extraction time was 2h. Samples were then put in a thermostatic bath (T=25°C) and were allowed to settle for 2h.

The extraction tests were carried out as a function of PEG and salt concentrations (PEG concentration ranging from 9 to 25% w/w; $(NH_4)_2SO_4$ concentration ranging from 11 to 25% w/w) in order to evaluate the influence of system composition on indium partitioning. It must be noted that PEG and salt concentrations were varied according to the phase diagram of the system (Fontana and Ricci, 2000), so as to guarantee the formation of two phases. Two types of PEG were employed (PEG 3,350 and PEG 10,000) to check the possible influence of molecular weight. The two phases were separated and analysed by atomic absorption spectrophotometry (AAS Shimadzu 6300). Indium partitioning between the lower and upper phase was calculated according to Eq. (3) and Eq. (4):

$$E(\%)_{bottom} = \frac{M_{bottom}}{M_0} \cdot 100 \quad (3)$$

$$E(\%)_{top} = \frac{M_{top}}{M_0} \cdot 100 \quad (4)$$

where:

- $E(\%)_{bottom}$ is indium extraction efficiency in the bottom phase (% w/w);
- $E(\%)_{top}$ is indium extraction efficiency in the top phase (% w/w);
- M_{bottom} is the amount of indium extracted in the bottom phase (g);
- M_{top} is the amount of indium extracted in the top phase (g);
- M_0 is the amount of indium in the initial aqueous phase (g); $M_0=M_{bottom}+M_{top}$.

All the experiments were performed in duplicate, in order to check the experimental technique and its precision.

3. RESULTS AND DISCUSSION

3.1 Removal of the polarizing film

FTIR analysis showed that the external side of the front polarizing film is composed of epoxy resins, while the rear one is composed of epoxy resins or acetyl cellulose or poly(butylene)terephthalate (PBT).

In Table 1 the time required to obtain complete removal of the polarizing film from the glass substrate is reported.

Table 1. Polarizing film removal time from the glass substrate of the LCD

TREATMENT	**OPERATIVE PARAMETERS**		**TIME**
Thermal	Liquid nitrogen		10-20 min
Chemical	**SOLVENT**	**ULTRASOUND ASSISTED**	
	Limonene	-	not effective within 8 h
		✓	8 h
	Acetone	-	8 h
		✓	4 h
	Ethyl acetate	-	5 h
		✓	2-3 h

Thermal treatment with liquid nitrogen turned out to be the best option for the removal of the polarizing film, since only 10-20 minutes were required, depending on the type of LCD. Among the organic solvents tested, acetone and ethyl acetate are the most effective, since 8h and 5h, respectively, were sufficient for removing the polarizing film in the absence of ultrasound treatment. This result could be probably linked to partial solubilisation of the pressure-sensitive adhesive. Limonene treatment did not permit removal of the film within 8h. The ultrasound treatment reduces the time required for complete removal of polarizing film in all chemical treatments (Table 1); this improvement could be linked to the enhancement of solid/liquid mass transfer and diffusivity due to cavitation. Limonene treatment required 8h, after which the film could be removed with gentle brushing.

Stereomicroscope analyses of the polarizing films are reported in Figure 2.

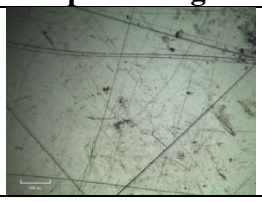
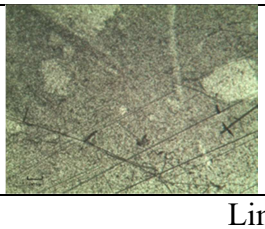
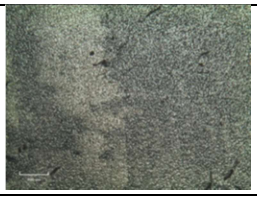
Rear polarizing film	**Front polarizing film**	**Rear polarizing film**	**Front polarizing film**
			
Liquid nitrogen		Acetone	
			
Ethyl acetate		Limonene	

Figure 2. Polarizing film removed after the thermal and chemical treatments - stereomicroscope analysis of the external side. The product obtained following ethyl acetate and acetone treatment results heavily damaged: both films are completely crumpled and grooves are visible, probably due to partial chemical degradation, while limonene treatment leads to some porosity. The polarizing film removed by means of liquid nitrogen does not show significant damage, since only few scratches resulting from sample preparation (manual dismantling, cutting, manual detachment of the polarizing film from the glass substrate) were observed.

It can be concluded that the best technique for removal of polarizing film is thermal treatment with liquid nitrogen, both in terms of time (10-20 minutes) and final product quality.

The polarizing film and the glass substrate were weighed, and it was found that they account for 14% and 86% of the weight of the LCD panel, respectively.

In Figures 3-4, SEM analyses performed on the glass substrate before and after the treatment with liquid nitrogen are reported. The circles (white coloured) identify the X-ray peaks corresponding to the indium element in the EDS* spectrum (characteristic X-rays: Lα 3.286 keV):

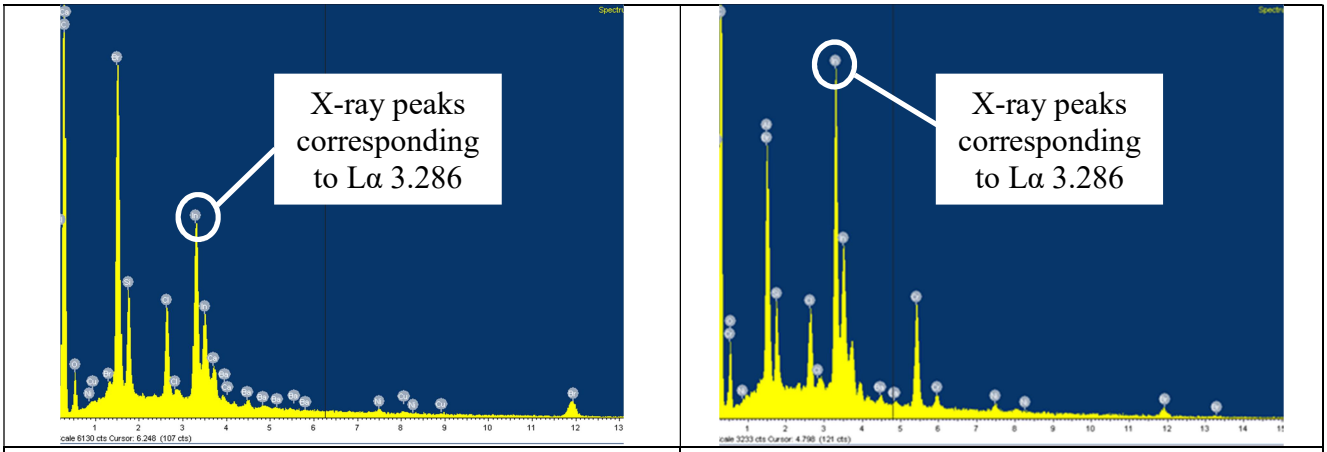


Figure 3. EDS spectrum of the LCD glass substrate (colour filter layer) before (a) and after (b) treatment with liquid nitrogen.

* EDS: Energy Dispersive Spectroscopy

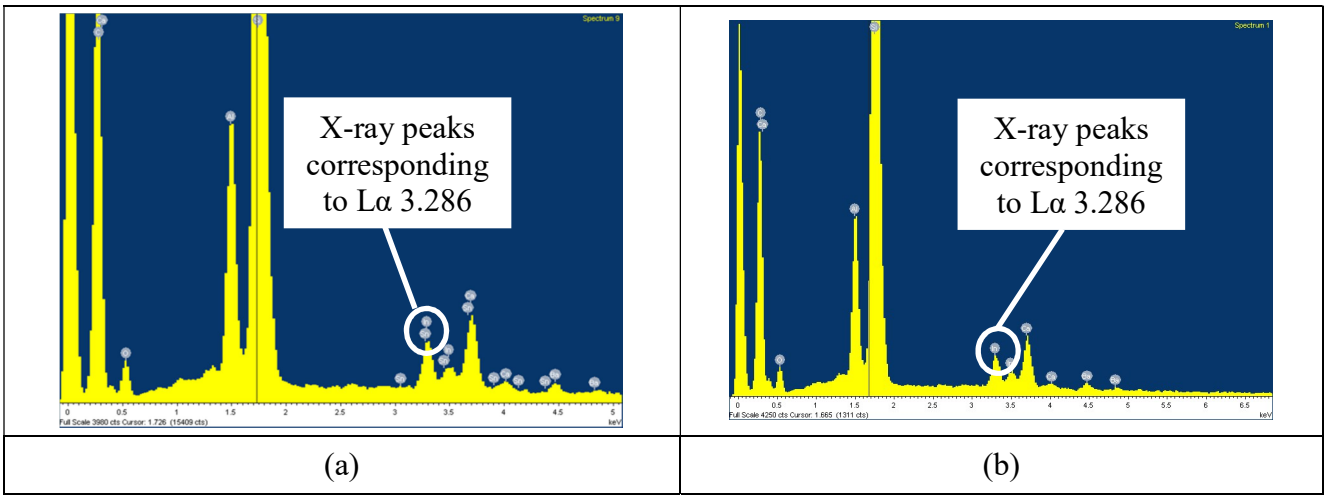


Figure 4. EDS spectrum of the LCD glass substrate (TFT layer) before (a) and after (b) treatment with liquid nitrogen.

It was found that thermal treatment with liquid nitrogen did not remove the ITO layer from the glass substrate, since the EDS spectrum still reveals the presence of indium.

3.2 Leaching

In Figures 5-8 indium leaching efficiency from indium tin oxide powder is reported as a function of time, leaching agent and liquid/solid ratio.

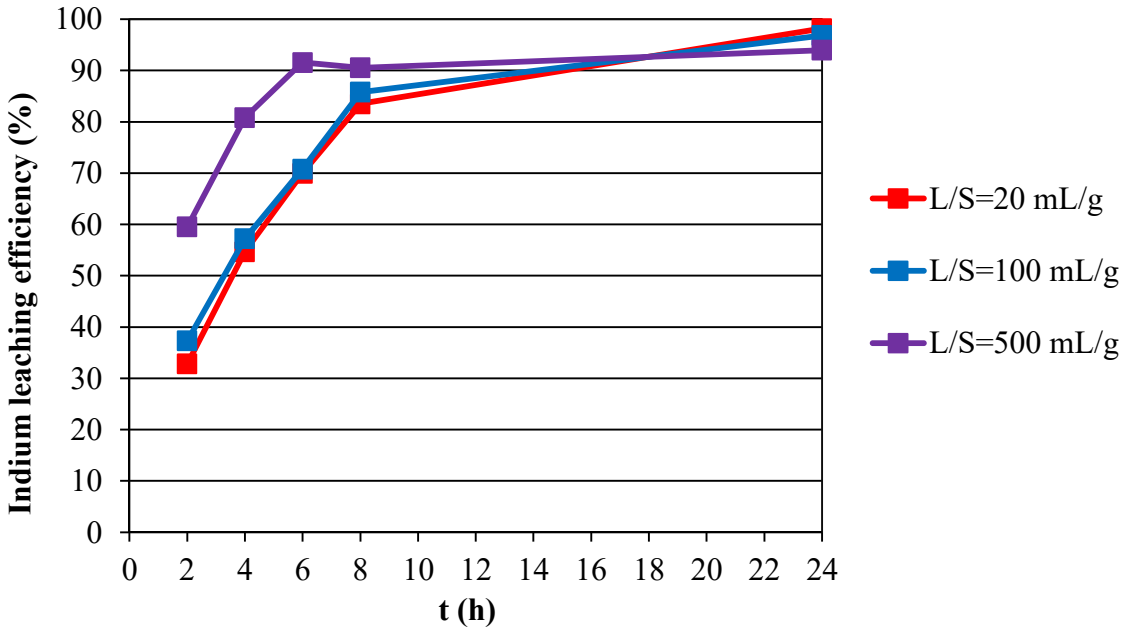


Figure 5. Indium leaching efficiency from indium tin oxide powder (HCl 6 N, T=25°C)

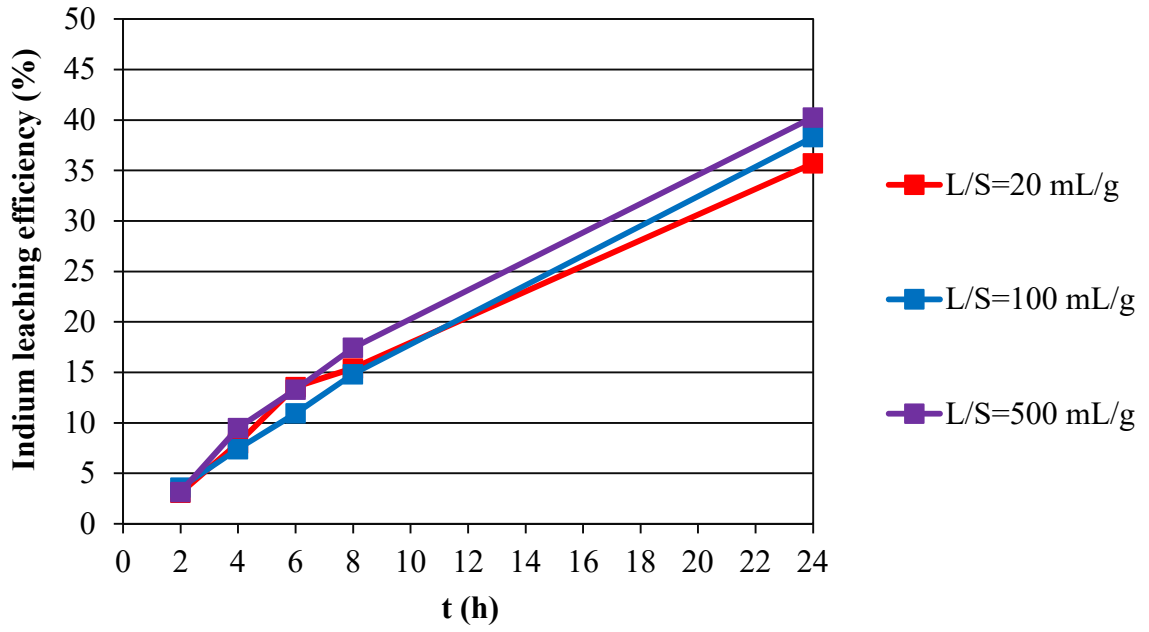


Figure 6. Indium leaching efficiency from indium tin oxide powder (HNO_3 6 N, T=25°C)

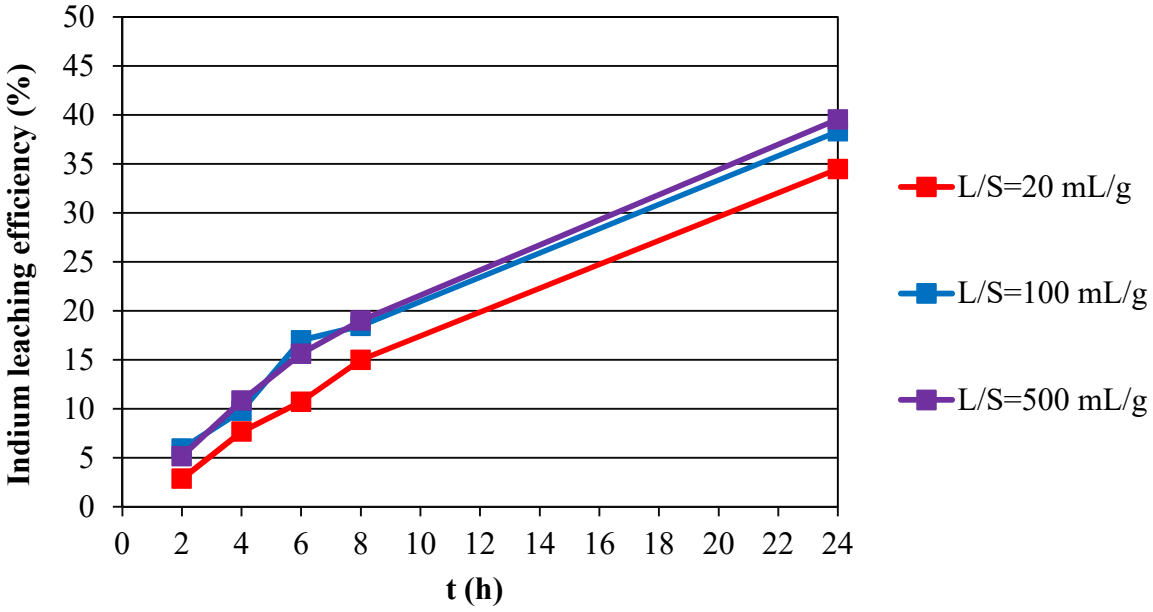


Figure 7. Indium leaching efficiency from indium tin oxide powder (H_2SO_4 6 N, T=25°C)

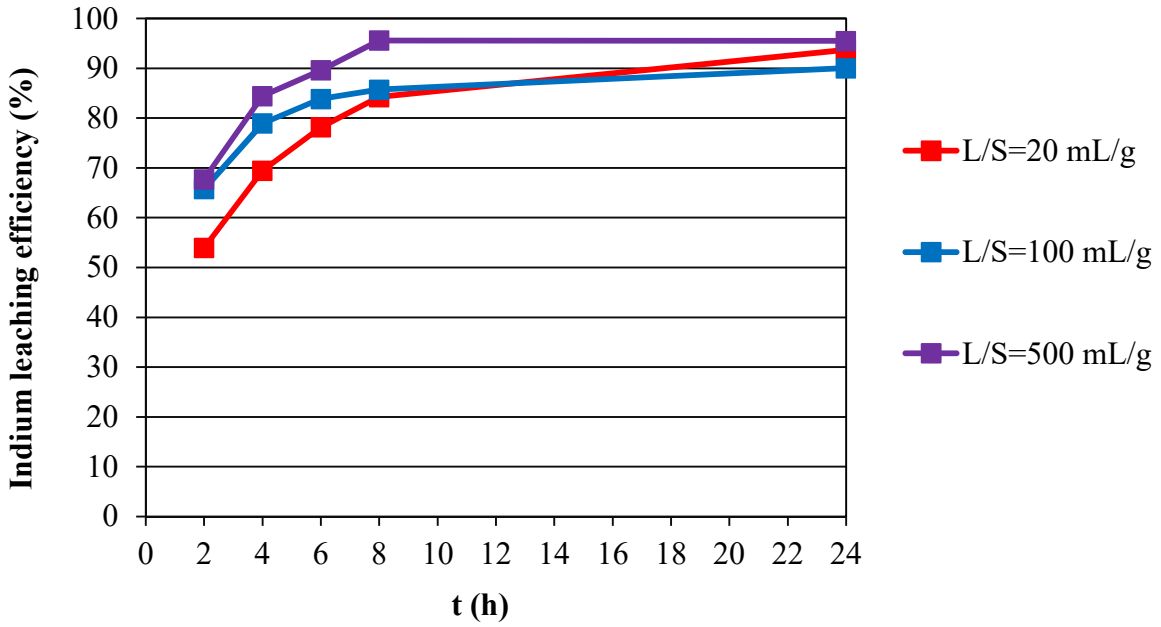


Figure 8. Indium leaching efficiency from indium tin oxide powder (HCl-HNO_3 3:1 v/v 6 N, T=25°C)

It was found that indium leaching efficiency is low if nitric acid and sulphuric acid are employed as leaching agents: as reported in Figures 6-7, only 40% of the indium could be extracted in 24h. Our results confirmed those found in the literature: Virolainen et al. (2011) stated that the rates of the leaching kinetics of ITO powder are in general quite slow, with that of nitric acid the slowest; this result could be explained by the strong oxidizing conditions of nitric acid, which could be responsible for indium precipitation.

A different behaviour was observed by employing a mixture of hydrochloric acid / nitric acid and hydrochloric acid, since approximately 90% of indium was extracted in 6 h employing a liquid/solid ratio of 500 mL/g. Thereafter, only a negligible increase in leaching efficiency is achieved. Our results are comparable to those of Yang et al. (2013), which showed that the dissolution kinetics of indium oxide is the fastest in chloride media. Indium leaching from the glass substrate obtained after removal of the polarizing film with liquid nitrogen was then performed for 6h in HCl solution. It was found that approximately 260 mg In per kg of glass were dissolved with HCl 6 N, which corresponds to a leaching efficiency of 90% w/w. This data is comparable with the figures reported in the literature, where a shredding step is performed prior to leaching. By processing data provided by Li et al. (2009), they succeeded in dissolving less than 125 mg In per kg of glass (which corresponds to a leaching efficiency of 92% w/w) at 60°C and with several acid mixtures, including HCl 6 N, but the leaching was carried out on samples previously shredded to less than 5 mm. Lee et al. (2013) obtained approximately 220 mg In per kg of glass (which corresponds to a 86% recovery efficiency) in 30 minutes, but they crushed the samples down to

micrometric size with a high energy ball milling (HEBM). Yang et al. (2013) found that near-complete leaching of indium can be achieved by using 1 M HCl in less than 8h, on shredded samples. In our case, after the removal of the two polarizing films with liquid nitrogen, two glass substrates were obtained; on each substrate, the ITO layer is only present on one side. For this reason, particle size is not supposed to have any influence on the leaching efficiency since the specific surface area of ITO does not increase with reducing particle size. In Figures 9-10, SEM analyses of the glass substrate before and after leaching with HCl 6 N are reported: no more indium is detected in the EDS spectrum (dashed line), thus confirming the almost complete dissolution of indium oxide.

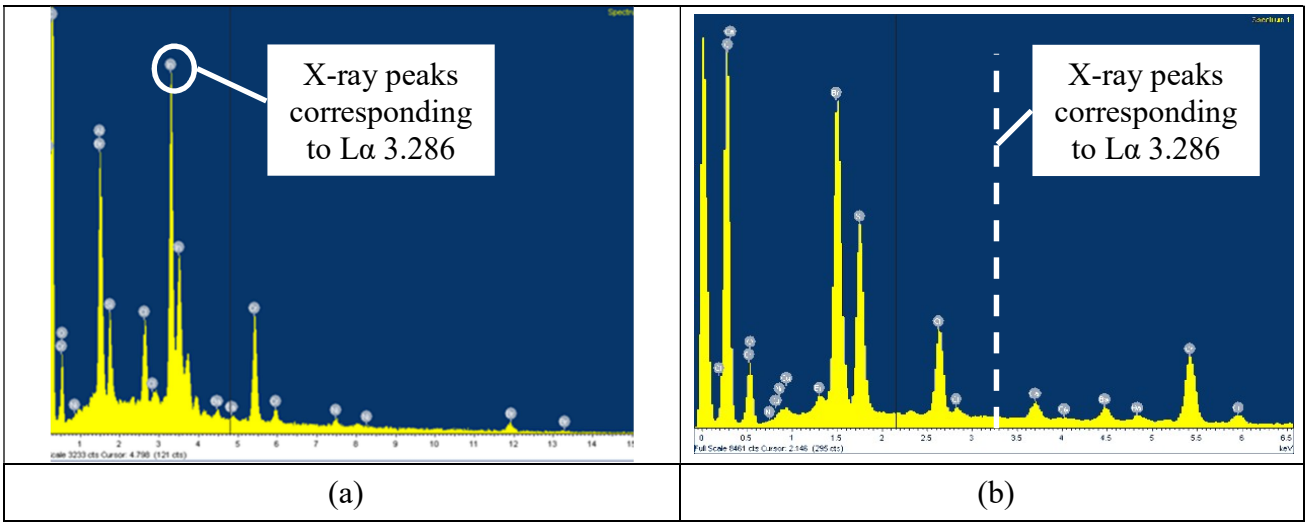


Figure 9. EDS spectrum of the LCD glass substrate (colour filter layer) before (a) and after (b) treatment with HCl 6 N.

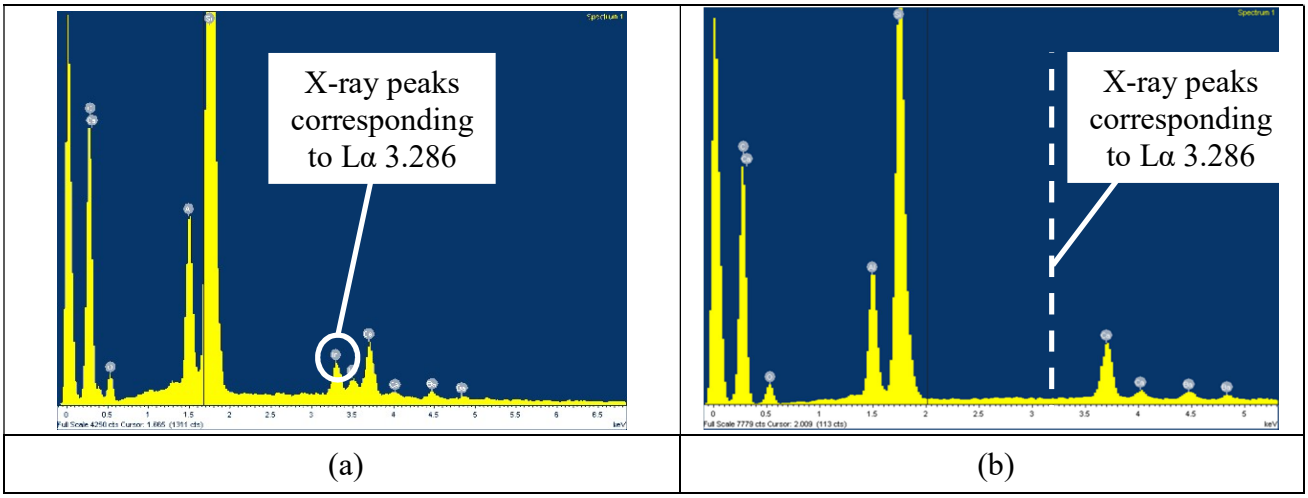


Figure 10. EDS spectrum of the LCD glass substrate (TFT layer) before (a) and after (b) treatment with HCl 6 N.

In Table 2 the composition of the leachate is reported.

307 Table 2. Leachate composition (HCl 6 N leaching, T=25°C, t=6h, L/S=3 mL/g)

	LCD 1	LCD 2
	[ppm]	[ppm]
In	87.54	83.78
Sn	9.48	8.92
Al	7.85	4.92
Cr	2.34	-

308 Tin is of course present as a component of ITO. The presence of aluminium ions could be linked
309 to partial solubilisation of the gate electrode as well as the gate insulator on the TFT layer;
310 chromium traces may be due to the solubilisation of the black matrix on the colour filter layer.
311 Differently from Ruan et al. (2012) and Yang et al. (2013), no iron was found in the leachate. Ruan
312 et al. performed the leaching at high temperature (160 °C), which could have led to an enhancement
313 of the amount of iron dissolved. The presence of iron could be also linked to sample
314 preparation/pretreatment. In the case of Yang et al. (2013), the LCD samples used in the
315 experiments were industrially shredded LCD glass provided by a local recycling company; such
316 LCD glass might have been mixed with other parts of the display or other waste electrical and
317 electronic equipment when shredded, thus leading to contamination.

318 **3.3 Indium extraction with aqueous biphasic systems (ABSs)**

319 In Figures 11-12 indium extraction efficiency in the system PEG-$(NH_4)_2SO_4$-water is reported as
320 a function of PEG concentration and ammonium sulfate concentration, respectively.

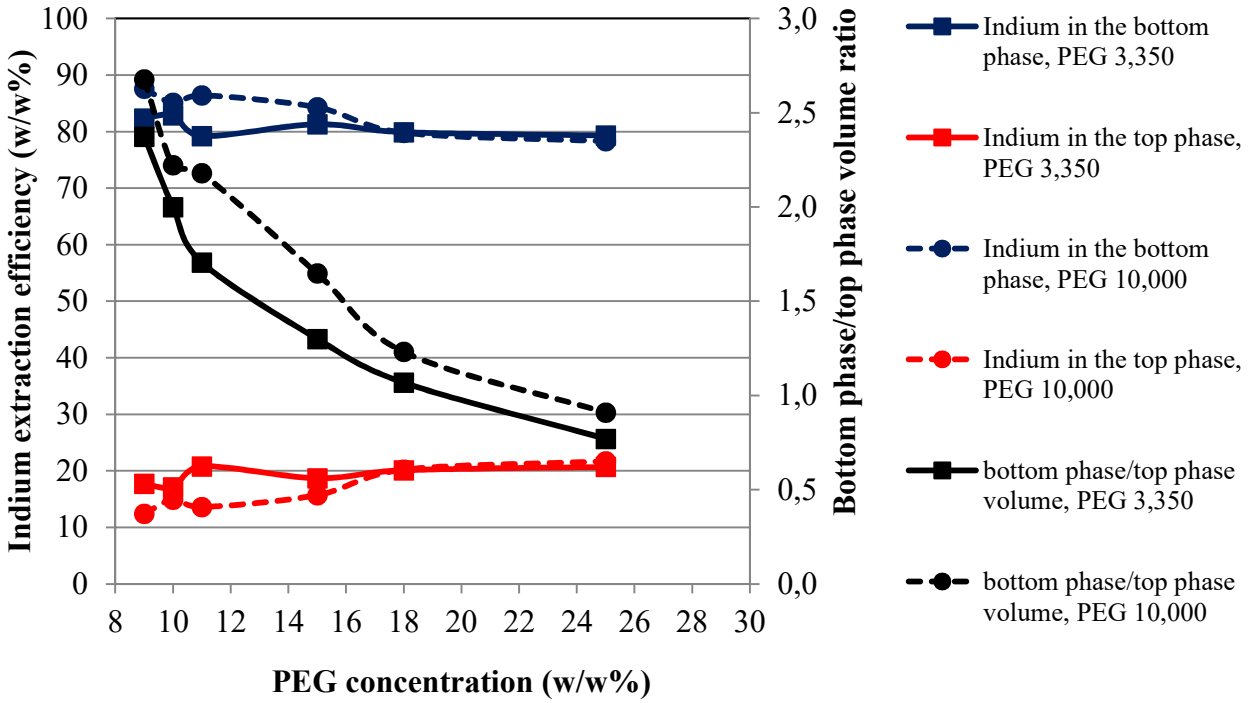


Figure 11. Indium extraction efficiency as a function of PEG concentration ($[(NH_4)_2SO_4]_{ABS}$=12% w/w; pH_{eq}~5.5).

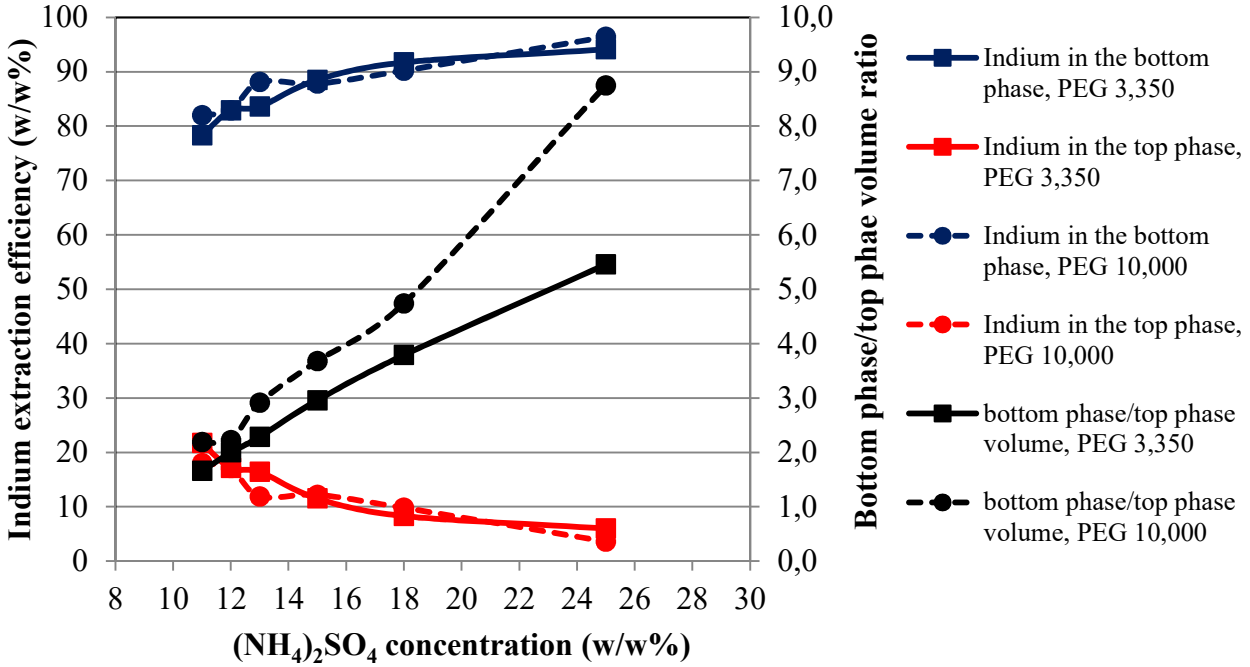
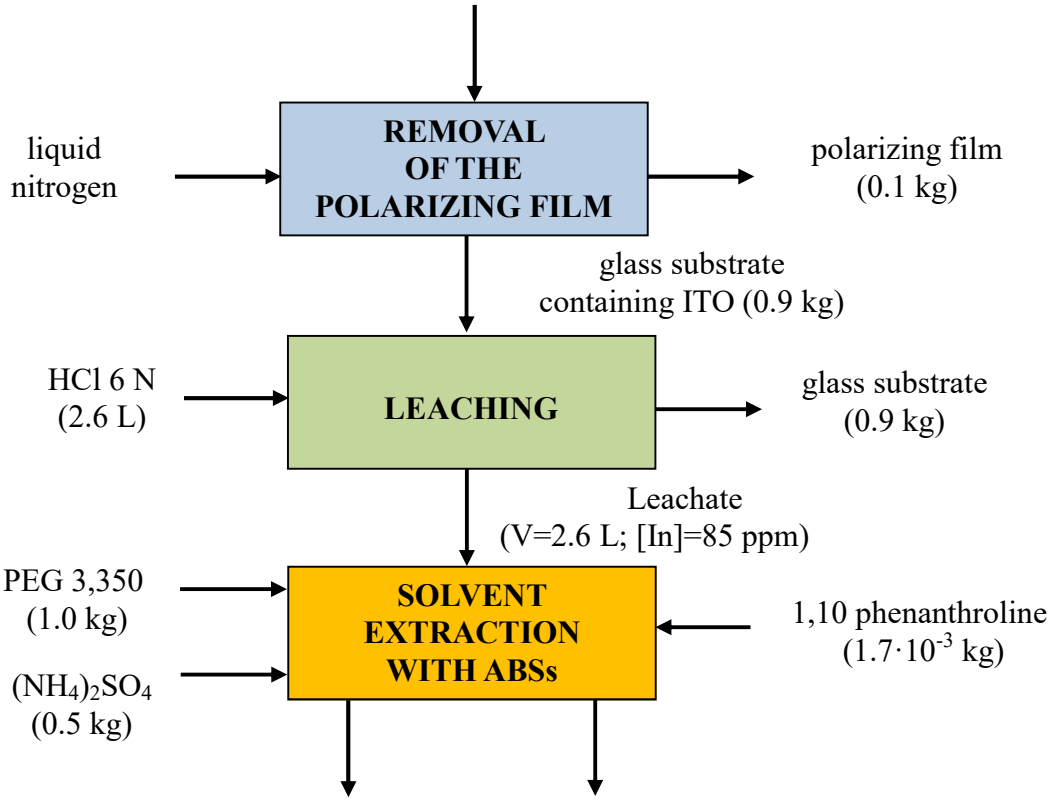


Figure 12. Indium extraction efficiency as a function of $(NH_4)_2SO_4$ concentration ($[PEG]_{ABS}$=10% w/w; pH_{eq}~5.5).It was found that indium partitioning between the bottom and the

top phase is quite independent from system composition, since 80-95% of indium is extracted in the bottom phase and 5-20% in the top phase. According to Huddleston et al. (2003), in a PEG-based ABS the bottom phase corresponds to the salt-rich and the PEG-rich phase, respectively. The fact that indium is mainly extracted in the bottom phase can be explained by the high degree of hydration of indium complexes, which tend to remain in the salt-rich phase of the extraction system, as also reported by Bulgariu and Bulgariu (2007). As shown in Figure 11, if PEG concentration is increased the volume ratio between the bottom and the top phase decreases but, as previously stated, the extraction efficiency of indium ions in both phases is not affected by this variation. For this reason, by working with high PEG concentrations in the selected ABS, it is possible to obtain a higher indium ion concentration in the bottom phase compared to the concentration obtained if lower PEG concentrations are employed. The opposite effect was registered when salt concentration was increased: the volume ratio between the phases increases, thus determining a decrease of indium concentration in the bottom phase. Experimental data demonstrate that indium extraction is quite similar when employing PEG 3,350 as well as PEG 10,000; however, the volume ratio decrease is more significant if PEG 3,350 is employed. It was found that if [PEG 3,350]=25% w/w and [$(NH_4)_2SO_4$]=12%, then the volume ratio between the two phases is equal to 0.8 and indium concentration in the bottom phase is ~30% higher than the initial concentration (before the extraction). The increase is quite small; nevertheless such concentration technique could be helpful to facilitate final recovery processes, in which high metal ions concentrations are usually required. Figure 13 illustrates the entire process in a flow chart. The mass balance is performed on 1 kg of waste LCDs.



Bottom phase (V=1.7 L; [In]=110 ppm)	Top phase (V=2.1 L; [In]=17 ppm)

Figure 13. Flow chart of the waste LCDs recovery process tested in the present work.

As one can see, only a small quantity of chemicals is required (liquid nitrogen, HCl, PEG, ammonium sulphate and a negligible amount of 1,10 phenanthroline). Energy consumption and dust emissions are avoided since no shredding is performed; moreover, leaching is carried out at room temperature, lowering potential hazardous emissions. Solvent extraction is performed through environmentally sound extraction media, since PEG-based ABSs are biodegradable and low-cost.

Two outputs are produced (a glass fraction and the polarizing film), which could be sent to existing treatment plants for material recovery. An indium-rich phase is also obtained, which needs further treatment in order to recover indium ions, for example through precipitation.

4. CONCLUSIONS

In this work, indium recovery from waste LCDs was experimentally investigated in the laboratory using a sequence of different techniques. Thermal and chemical treatments aimed at removing the polarizing film from the glass substrate were for the first time systematically compared and discussed; the best results were obtained with liquid nitrogen, since only 20 minutes were required; moreover, the obtained product did not show substantial degradation, suggesting a better recycling potential. The best operative leaching conditions performed on indium tin oxide powder were then applied for leaching of the glass residue. It was found that, without shredding, HCl 6 N (T=25°C, t=6h, L/S=3 mL/g) leaches approximately 260 mg In per kg of glass at room temperature, with no energy consumption or dust emissions. An attempt was made to extract indium ions through PEG-based aqueous biphasic systems, which are now receiving increasing attention among the scientific community due to their characteristics of low toxicity and low flammability, and which have not been tested for indium recovery yet. It was found that if [PEG 3,350]=25% w/w and [$(NH_4)_2SO_4$]=12%, indium concentration in the bottom phase is ~30% higher than the initial concentration.

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