

1 **Materials recovery from waste liquid crystal displays: a focus on indium**

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

23 **Keywords:** waste LCDs, hydrometallurgy, indium, ABSs

24 **1. INTRODUCTION**

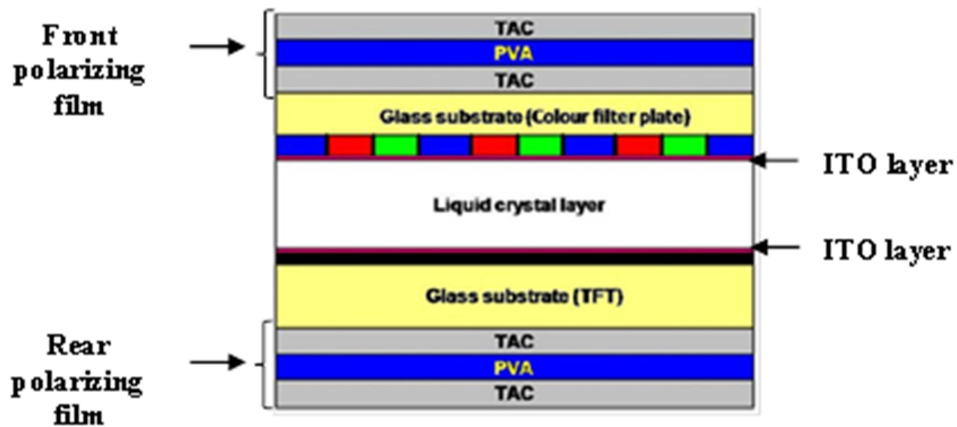
25 Liquid crystal displays (LCDs) are becoming more and more widespread in electronic
26 applications and are definitely replacing the old cathode ray tube devices in TVs and monitors
27 (Dodiba et al., 2012). Since the lifespan of an LCD is typically 3-5 years (Zhuang et al., 2012), the
28 amount of waste LCDs is rapidly increasing, requiring the development of suitable treatment and
29 recovery processes. The LCD module, i.e. the main part of an LCD display after primary
30 dismantling (Figure 1), contains two polarizing films, two glass substrates coated with indium tin

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31 oxide (ITO) film and a liquid crystal layer (Wang et al., 2013; Dodson et al., 2012).

32 Over the front glass substrate is the colour filter layer, consisting of a black matrix, colorants and
33 binders, an overcoat layer and an ITO layer (Yen and Tso, 2004). Over the rear glass substrate is the
34 TFT (thin film transistor) layer, containing three terminals, a gate insulator, a semiconductor, an
35 ohmic contact, a passivation layer and the conductive electrode (Lee and Cooper, 2008). Indium tin
36 oxide is an optoelectronic material with the key features of transparency to visible light, electricity
37 conduction and thermal reflection (Li et al., 2011); it is composed of 80-90% In_2O_3 and 10-20%
38 SnO_2 (Virolainen et al., 2011; Lee et al., 2013). Polarizing films generally consist of a layer of
39 iodine doped-polyvinyl-alcohol (PVA) sandwiched between two protective layers of cellulose
40 triacetate (TAC) (Dodson et al., 2012); they are assembled on the glass substrate using a pressure
41 sensitive adhesive (PSA) composed of acrylic polymers (Nam et al., 2012; Passamani, 2011). Liquid
42 crystals are a mixture of aromatic-based polymers with benzene, cyano-group, fluorine, bromine
43 and chlorine; this mixture typically contains 10 to 25 different compounds (Beker et al., 2003;
44 Zhuang et al., 2012).



45
46 Figure 1. Typical cross-section of a LCD panel (adapted from Dodson et al., 2012).

47 The main driver for waste LCDs treatment is indium recovery. Indium is a rare and valuable
48 metal that has recently been included by the European Commission in a list of critical raw
49 materials, due to its economic importance and the high supply risk that it is subject to, especially
50 because production is concentrated in non-European countries (European Commission, 2014). More
51 than 80% of indium is employed for the production of ITO coatings used in liquid crystal displays
52 (Park et al., 2009). In Europe, LCDs are fed into a separate recycling process after collection
53 (Buchert et al., 2012). The treatment process generally consists of a dismantling step aimed at
54 removing hazardous components (such as the cold cathode fluorescent lamps employed for
55 background illumination) and valuable components (printed circuit boards, cables, plastic and
56 metallic fractions) for further treatment and recovery. The LCD glass panels are currently stocked at
57 the plant or incinerated, since no recycling process is yet available on an industrial scale; this

58 practice obviously leads to a loss of potentially recoverable resources, such as the critical metal
59 indium. Considering the amount of LCD appliances put on the market in Europe 27 in 2011, 6.5
60 tons of indium will become available in the coming years as potential stock (ENEA elaborations
61 from OCSE data, <http://www.oecd.org/>).

62 In the last decade a number of studies have focused on indium recovery from end-of-life LCDs.
63 In most cases thermal treatment at high temperature was employed to remove the polarizing film
64 (Li et al., 2009; Lee et al. 2013), which leads to energy consumption and potentially harmful
65 atmospheric emissions. According to Li et al. (2009), by heating the LCD in a furnace at T=230-
66 240°C the polarizing film can be removed, but only through hard brushing. A shredding step
67 followed by density-based separation was tested by Zhuang et al. (2012). Ruan et al. (2012)
68 employed liquid nitrogen to strip the polarizing film, but no information was provided about the
69 amount of time required and the removal efficiency achieved. Indium recovery from the glass
70 substrate is generally performed using hydrometallurgical techniques, consisting of a leaching step
71 aimed at dissolving the metals of interest, followed by a separation step.

72 Leaching is often carried out employing several acids and acid mixtures; however, the hydrogen
73 concentration of such mixtures is not always kept constant so that comparison of lixiviants (in terms
74 of leaching efficiency) is not straightforward.

75 Li et al. (2009) and Lee et al. (2013) tested several acid mixtures with acid concentrations
76 ranging from ~6 N to ~10 N; the hydrogen concentration of the leaching agents employed by Ruan
77 et al. (2012) ranges from ~6.5 N to ~18.5 N. Yang et al. (2013) and Virolainen et al. (2011) tested
78 HCl, HNO₃ and H₂SO₄ as leaching agents, fixing the acid concentration in terms of molarity; in this
79 case the comparison is possible only between HCl and HNO₃, since H₂SO₄ has a two-fold hydrogen
80 concentration.

81 Moreover, a shredding step is often performed prior to leaching; in some cases it is carried out
82 on the glass substrate obtained after the removal of the polarizing film (Li et al., 2009; Lee et al.,
83 2013), and in other cases on the entire LCD module (Yang et al., 2013).

84 Due to the low concentration of indium in the leachate, concentration techniques are strongly
85 required; for this purpose, Rocchetti et al. (2015) applied six steps of leaching to increase indium
86 concentration which was about 35 mg/L after the first step, almost 2-fold at the second step and
87 about 3-fold at the fifth step.

88 Indium recovery from the aqueous phase is then generally performed through solvent extraction.
89 Organic solvent extraction (or liquid-liquid extraction) has been widely used in the past as a
90 concentration and separation technique due to its characteristics of high selectivity and high
91 recovery efficiency. However, organic extractants such as D2EHPA (Yang et al., 2013), TBP

92 (Virolainen et al., 2011), Cyanex 272 and Cyanex 923 (Yang et al., 2013) diluted in organic
93 diluents (such as kerosene, toluene etc.) are often employed, which are potentially hazardous for
94 human health and the environment due to emissions of Volatile Organic Compounds (VOC) into
95 the atmosphere.

96 Recently, an electrochemical method followed by acid treatment was proposed by Choi et al.
97 (2014), aimed at recovering the indium tin oxide layer as well as the glass plate.

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

106 Differently from what is commonly found in the available literature, samples were not shredded
107 before the leaching, since particle size is not supposed to have any influence on leaching efficiency
108 (the ITO layer is only present on one side of the glass substrate),

109 Indium recovery from the aqueous phase was then investigated through solvent extraction with
110 aqueous biphasic systems (ABSs): due to their characteristics of low cost, reduced flammability and
111 reduced toxicity, ABSs are gradually emerging as a more sustainable alternative to the traditional
112 oil-water extraction systems (Rogers et al., 2005). They are formed when a water-soluble polymer
113 (e.g. PEG, polyethylene glycol) is mixed with certain inorganic salts (such as $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_4 ,
114 Na_2CO_3 , K_2HPO_4 , KCl) at a suitable concentration (da Silva et al., 1997; Mishima et al., 1998; Wu
115 et al., 1999). The formation of an aqueous two-phase system can be explained on the basis of
116 competition for hydration between the polymer and the salt phase (Cabezas, 1996); the addition of
117 an inorganic salt increases the dehydration of the polymer chains, due to the salting-out effect and
118 phase separation, and two immiscible aqueous phases are obtained. In such a system, metal ions are
119 partitioned between the phases according to a certain distribution coefficient, defined as the solute
120 concentration in the upper phase divided by the solute concentration in the lower phase (Fontana
121 and Ricci, 2000). Several water-soluble polymers may be utilized to form aqueous two-phase
122 systems; polyethylene glycol (PEG) is often employed because it is non-toxic, non-flammable and
123 non-volatile (Visser et al., 2000). According to Roger et al. (2005), metal ion extraction in aqueous
124 two-phase PEG-based systems can be classified into three categories: extraction in the PEG-rich
125 phase alone, without an extracting agent (a); extraction of metal ions as chelates using water-soluble

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

131 In recent years an increasing amount of research has focused on metal extraction by means of
132 aqueous biphasic systems. Ammar et al. (2013) investigated the extraction behaviour of Cd(II) ,
133 Cu(II) , Fe(II) and Zn(II) in an aqueous biphasic system composed of PEG and sodium sulphate in
134 the presence of KI and KSCN as extractants; Cd(II) extraction was investigated by Bulgariu and
135 Bulgariu (2008) in a PEG 1550- $(\text{NH}_4)_2\text{SO}_4$ system. Dzherayan (2006) studied the extraction of
136 gallium from alkaline carbonate solutions with phenylfluorone in the PEG–sodium carbonate–water
137 system; copper extraction with a PEG 3,350-ammonium sulphate-water system was studied by
138 Fontana and Ricci (2000) in the presence of 1,10 phenanthroline as complexing agent.

139 In this work, indium recovery from the aqueous phase is investigated through PEG-based ABSs.
140 The system consists of PEG- $(\text{NH}_4)_2\text{SO}_4$ -water, since it has been often employed in the literature for
141 the extraction of several metal ions (Fontana and Ricci, 2000; Bulgariu and Bulgariu, 2008). Indium
142 partitioning in the selected ABS was investigated in the presence of 1,10 phenanthroline, which is a
143 traditional ligand employed in coordination chemistry (Bencini and Lippolis, 2010).

144 2. MATERIALS AND METHODS

145 The waste LCD panels were provided by an e-waste treatment plant located in northern Italy
146 (STENA Technoworld srl, Castenedolo, BS); a number of LCD monitors (not dismantled) were
147 also provided by an e-waste collecting platform. All chemicals were used as received and without
148 any further purification: acetone, ethyl acetate, limonene, liquid nitrogen, HCl 37-38% w/w, HNO_3
149 69.9% w/w, H_2SO_4 96% w/w, indium tin oxide powder (ITO) (325 mesh, $\geq 99.99\%$ trace metals
150 basis, 90% In_2O_3 , 10% SnO_2 Sigma Aldrich), polyethylene-glycol (Sigma Aldrich, MW 3,350 and
151 10,000), ammonium sulphate and 1,10 phenanthroline.

152 2.1 Removal of the polarizing film

153 Infrared spectroscopy (Shimadzu IRAffinity-1) was employed to gather information about the
154 chemical composition of the external side of the polarizing films. Thermal and chemical treatments
155 were then compared in order to evaluate the best treatment option in terms of time required to
156 remove the film from the glass substrate and the quality of the recovered product. Each test was
157 repeated on two LCDs of different sizes and compositions, previously cut into small pieces (5cm x
158 5cm). Thermal treatments were performed by cooling the waste LCDs with liquid nitrogen ($T=-$

159 196°C); the amount of reagent required was ~25 L per kg of waste LCDs. Chemical treatments
160 were performed by soaking the waste LCDs in several organic solvents such as acetone, ethyl
161 acetate and limonene. The liquid/solid ratio was 3 mL/g. In order to maximize contact with the
162 solvent, small cracks were made in the glass (with a mortar) to allow the solvent to reach the inner
163 side of the polarizing film where the acrylic adhesive was present. The experiments were then
164 carried out in glass beakers on a mechanical shaker; the influence of ultrasound treatment (35 kHz)
165 was also tested to evaluate the possibility of reducing the contact time. The removed film was
166 analysed by stereomicroscope (Olympus SZX12) to determine its quality. Scanning electron
167 microscope (ZEISS EVO MA 15) was also employed to examine glass composition; both the thin
168 film transistor and the colour filter layer were analysed.

169 **2.2 Leaching**

170 In order to define the best operative conditions for indium leaching, preliminary tests were
171 performed on ITO powder by varying the leaching agent (HCl, HNO₃, H₂SO₄, HCl-HNO₃ 3:1 v/v),
172 the time (t=0-24 h) and the liquid/solid ratio (L/S= 20 mL/g, 100 mL/g, 500 mL/g); acid
173 concentration was 6 N in all the experiments, since this value was suggested by some other authors
174 (Li et al., 2009; Lee et al., 2013; Yang et al., 2013). Indium leaching efficiency (E%) was calculated
175 according to Eq. (1):

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

176 where:

- 177 - M is the amount of indium dissolved (g);
- 178 - M₀ is the amount of indium in the initial sample (g).

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

185 **2.3 Indium extraction with aqueous biphasic systems (ABSs)**

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

189 Indium 5·10⁻³ M solutions were prepared by dissolving indium (III) nitrate hydrate in distilled
190 water. No information is available in the literature about indium extraction stoichiometry with this
191 ligand. In this work we assumed that three moles of phenanthroline are required to complex one

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

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

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

198 Extraction tests were carried out by mixing weighed amounts of PEG and ammonium sulphate
199 with the metal-rich solution in glass-capped tubes on a mechanical shaker; the extraction time was
200 2h. Samples were then put in a thermostatic bath ($T=25^\circ\text{C}$) and were allowed to settle for 2h.

201 The extraction tests were carried out as a function of PEG and salt concentrations (PEG
202 concentration ranging from 9 to 25% w/w; $(\text{NH}_4)_2\text{SO}_4$ concentration ranging from 11 to 25% w/w)
203 in order to evaluate the influence of system composition on indium partitioning. It must be noted
204 that PEG and salt concentrations were varied according to the phase diagram of the system (Fontana
205 and Ricci, 2000), so as to guarantee the formation of two phases. Two types of PEG were employed
206 (PEG 3,350 and PEG 10,000) to check the possible influence of molecular weight. The two phases
207 were separated and analysed by atomic absorption spectrophotometry (AAS Shimadzu 6300).
208 Indium partitioning between the lower and upper phase was calculated according to Eq. (3) and Eq.
209 (4):

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

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

210 where:

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

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

218 3. RESULTS AND DISCUSSION

219 3.1 Removal of the polarizing film

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

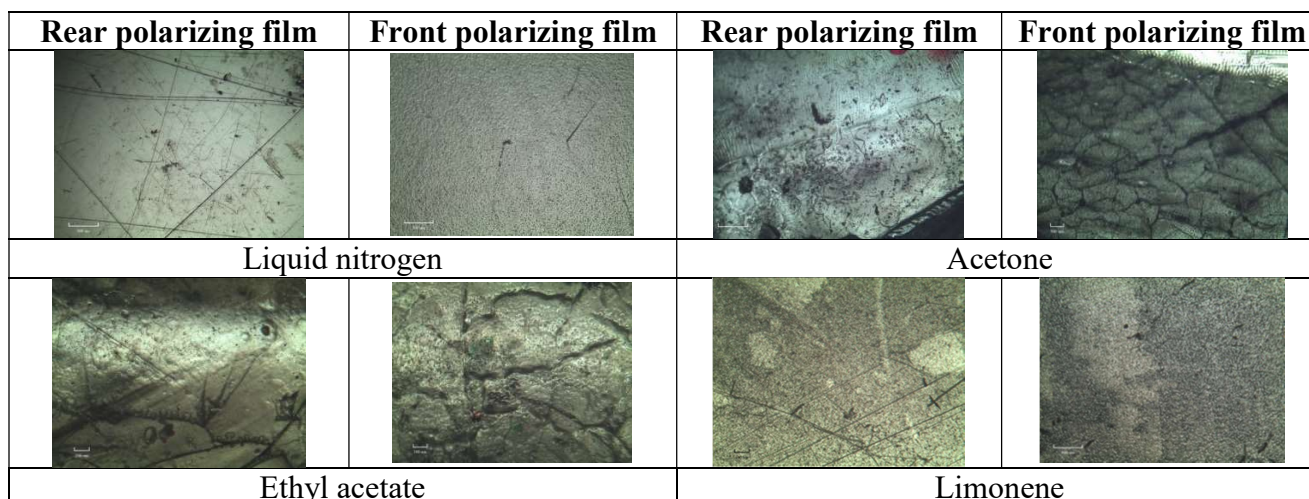
223 In Table 1 the time required to obtain complete removal of the polarizing film from the glass
 224 substrate is reported.

225 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	

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

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



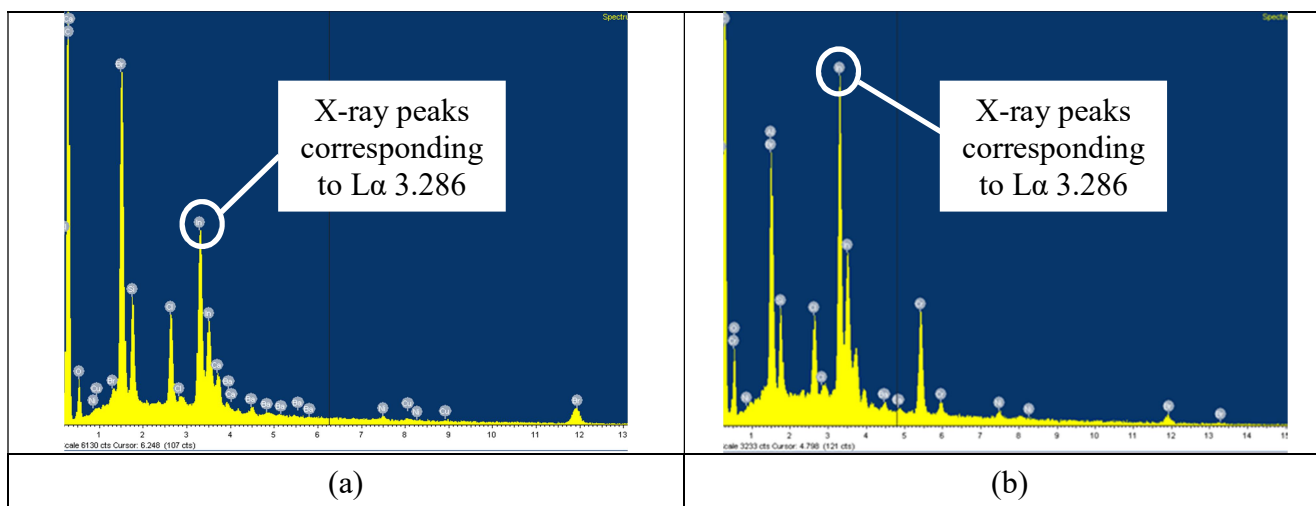
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238 Figure 2. Polarizing film removed after the thermal and chemical treatments - stereomicroscope
239 analysis of the external side. The product obtained following ethyl acetate and acetone treatment
240 results heavily damaged: both films are completely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

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

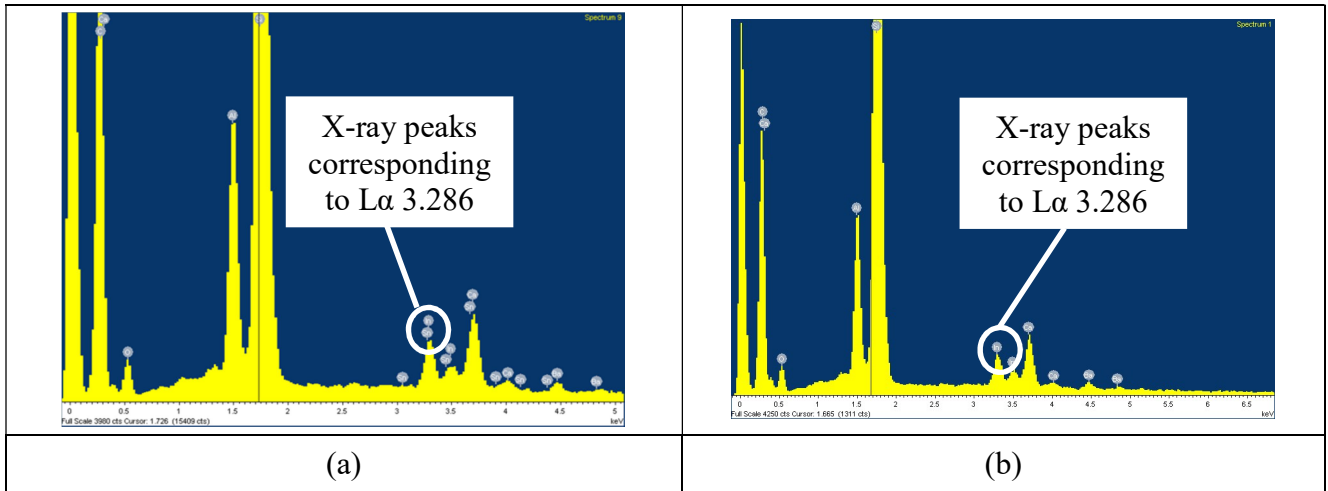
247 The polarizing film and the glass substrate were weighed, and it was found that they account for
248 14% and 86% of the weight of the LCD panel, respectively.

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



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

* EDS: Energy Dispersive Spectroscopy

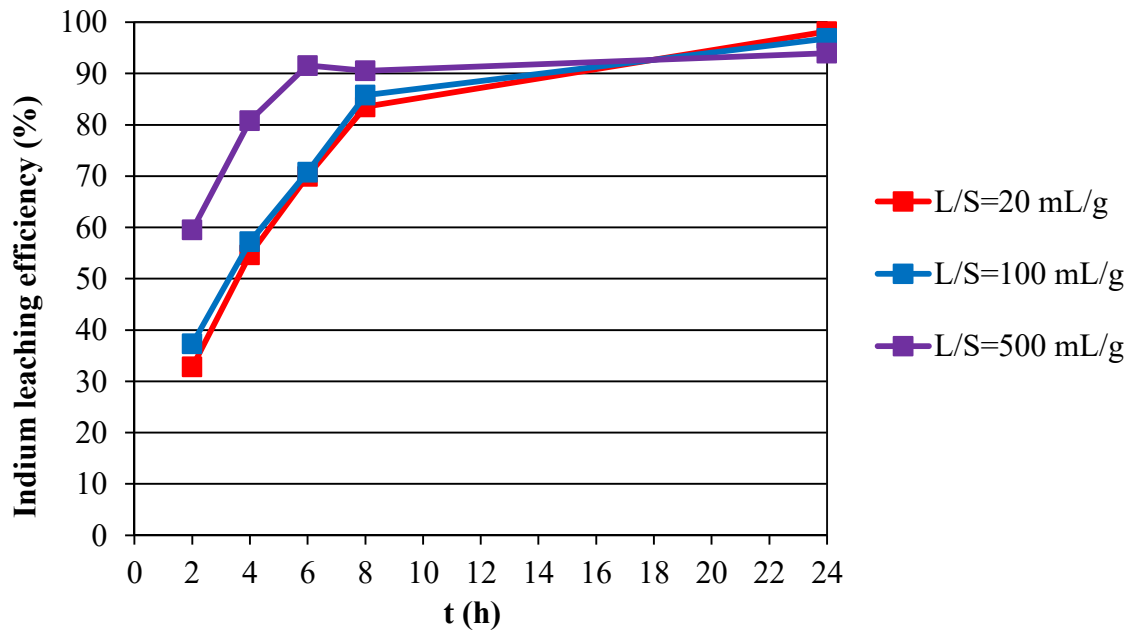


254 Figure 4. EDS spectrum of the LCD glass substrate (TFT layer) before (a) and after (b) treatment
 255 with liquid nitrogen.

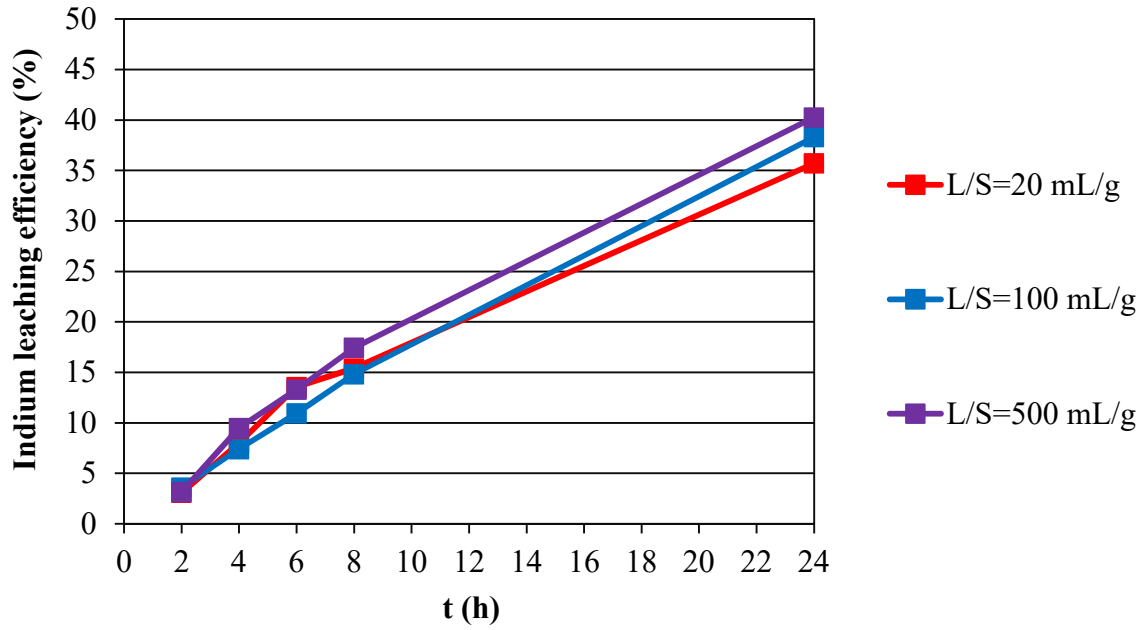
256 It was found that thermal treatment with liquid nitrogen did not remove the ITO layer from the
 257 glass substrate, since the EDS spectrum still reveals the presence of indium.

258 3.2 Leaching

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



261
 262 Figure 5. Indium leaching efficiency from indium tin oxide powder (HCl 6 N, T=25°C)
 263

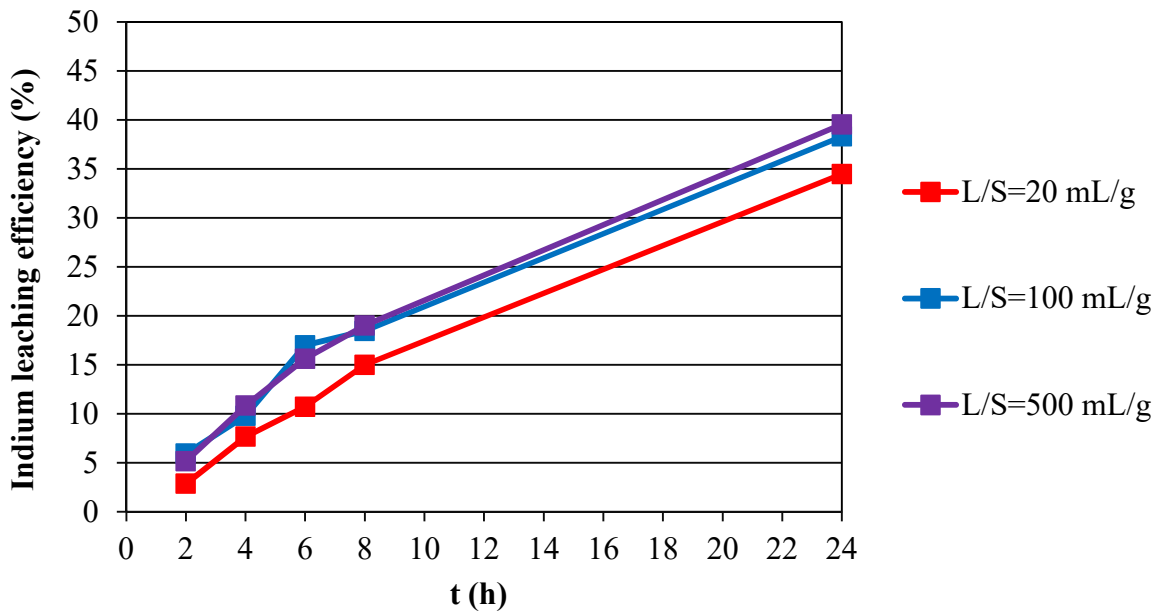


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Figure 6. Indium leaching efficiency from indium tin oxide powder (HNO₃ 6 N, T=25°C)

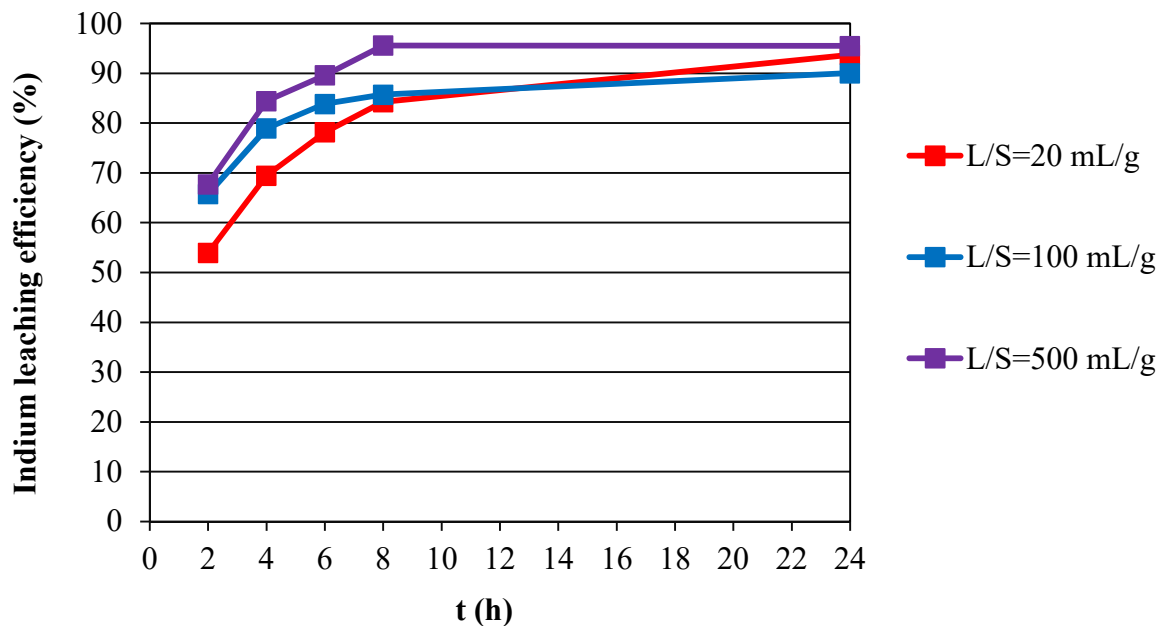
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Figure 7. Indium leaching efficiency from indium tin oxide powder (H₂SO₄ 6 N, T=25°C)



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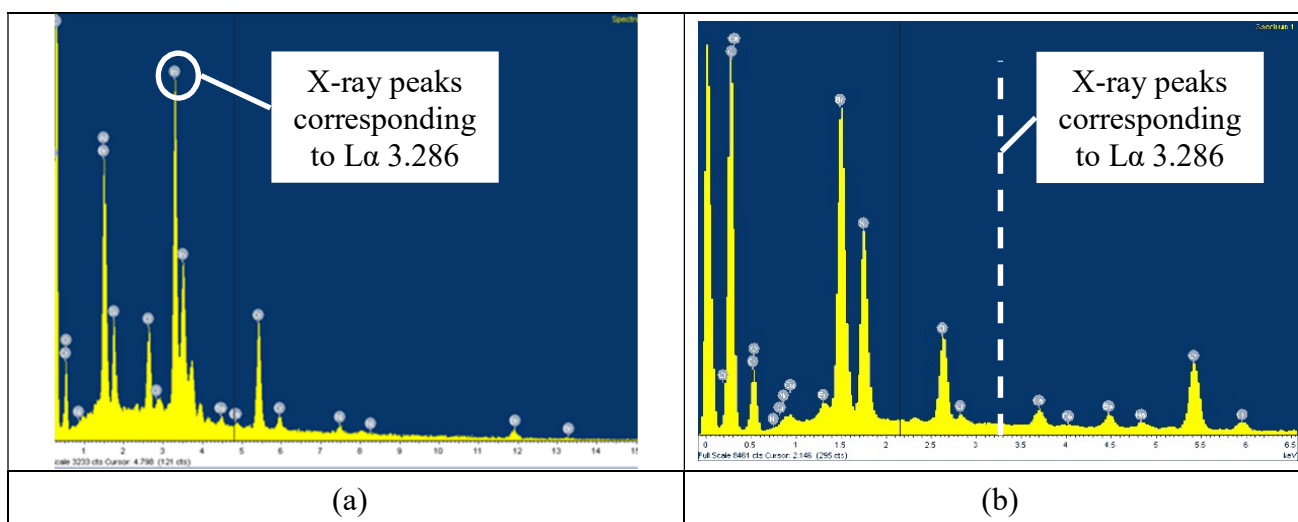
270 Figure 8. Indium leaching efficiency from indium tin oxide powder (HCl-HNO₃ 3:1 v/v 6 N,
271 T=25°C)

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

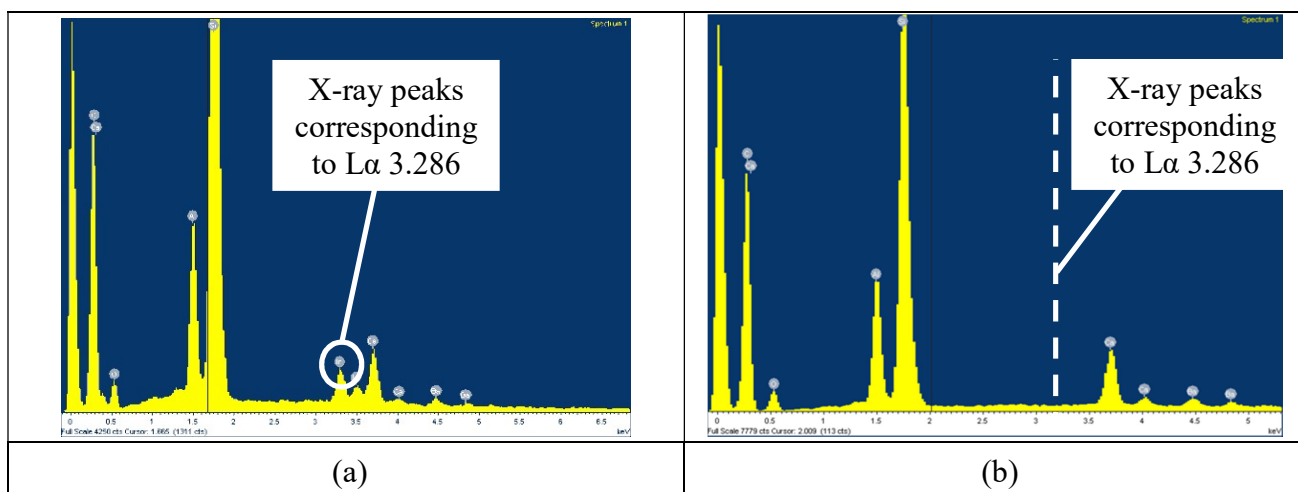
278 A different behaviour was observed by employing a mixture of hydrochloric acid / nitric acid
279 and hydrochloric acid, since approximately 90% of indium was extracted in 6 h employing a
280 liquid/solid ratio of 500 mL/g. Thereafter, only a negligible increase in leaching efficiency is
281 achieved. Our results are comparable to those of Yang et al. (2013), which showed that the
282 dissolution kinetics of indium oxide is the fastest in chloride media. Indium leaching from the glass
283 substrate obtained after removal of the polarizing film with liquid nitrogen was then performed for
284 6h in HCl solution. It was found that approximately 260 mg In per kg of glass were dissolved with
285 HCl 6 N, which corresponds to a leaching efficiency of 90% w/w. This data is comparable with the
286 figures reported in the literature, where a shredding step is performed prior to leaching. By
287 processing data provided by Li et al. (2009), they succeeded in dissolving less than 125 mg In per
288 kg of glass (which corresponds to a leaching efficiency of 92% w/w) at 60°C and with several acid
289 mixtures, including HCl 6 N, but the leaching was carried out on samples previously shredded to
290 less than 5 mm. Lee et al. (2013) obtained approximately 220 mg In per kg of glass (which
291 corresponds to a 86% recovery efficiency) in 30 minutes, but they crushed the samples down to

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

301



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



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

306 In Table 2 the composition of the leachate is reported.

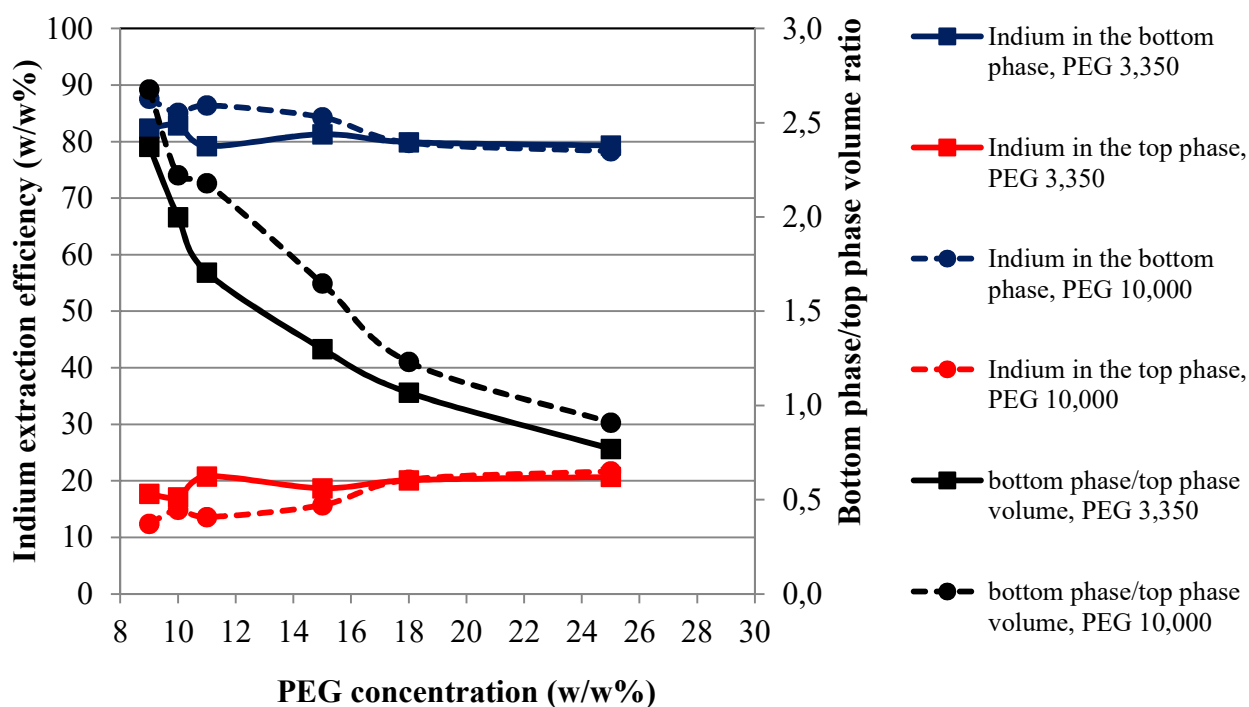
307 Table 2. Leachate composition (HCl 6 N leaching, T=25°C, t=6h, L/S=3 mL/g)

	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-(NH₄)₂SO₄-water is reported as
 320 a function of PEG concentration and ammonium sulfate concentration, respectively.



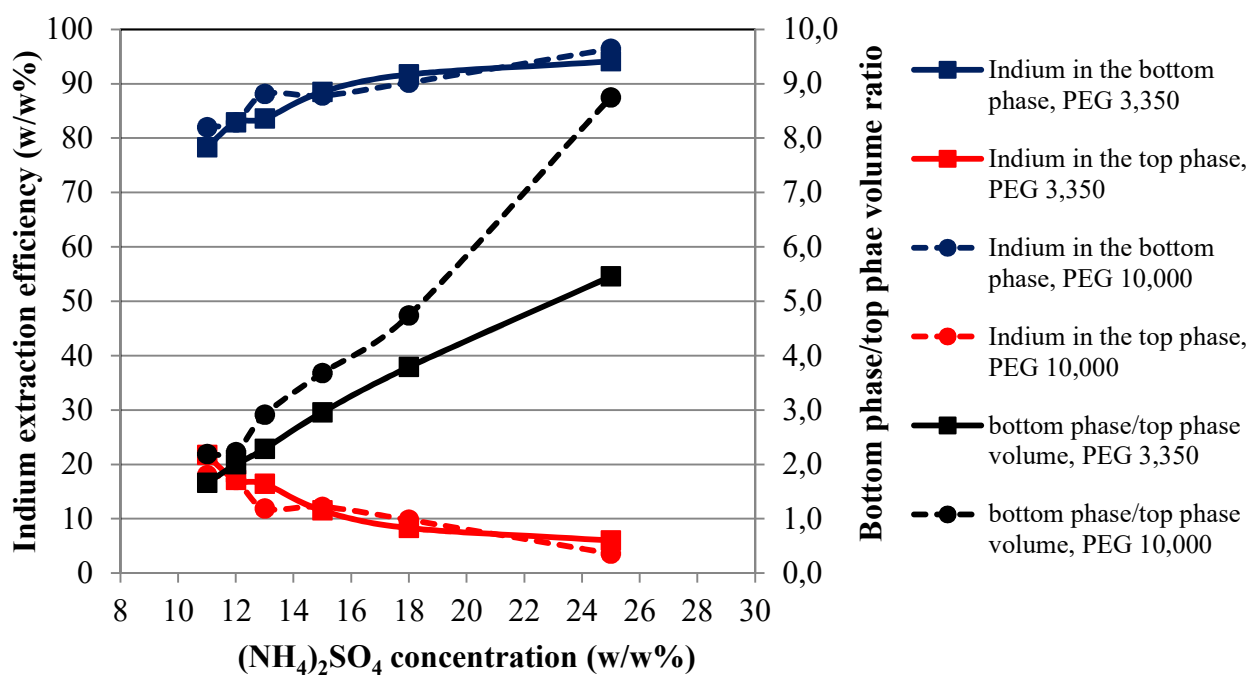
321
322

323 Figure 11. Indium extraction efficiency as a function of PEG concentration ($[(\text{NH}_4)_2\text{SO}_4]_{\text{ABS}}=12\%$
324 w/w; $\text{pH}_{\text{eq}}\sim 5.5$).

325

326

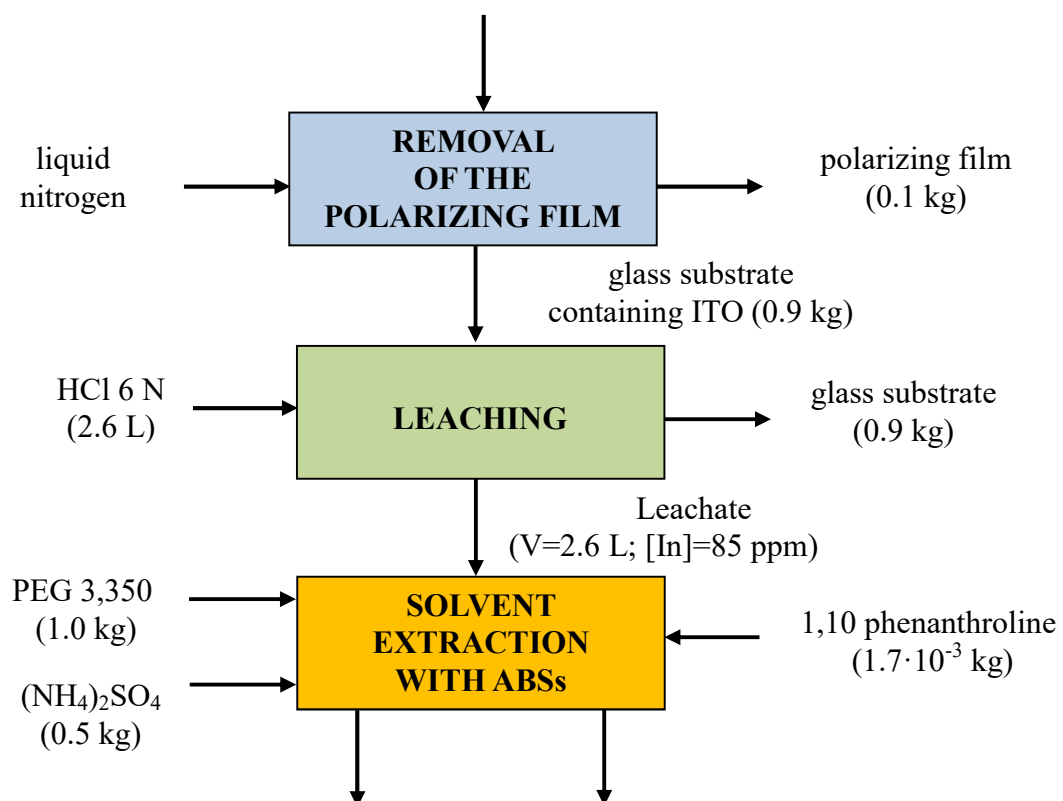
327



328

329 Figure 12. Indium extraction efficiency as a function of $(\text{NH}_4)_2\text{SO}_4$ concentration
330 ($[\text{PEG}]_{\text{ABS}}=10\%$ w/w; $\text{pH}_{\text{eq}}\sim 5.5$). It was found that indium partitioning between the bottom and the

331 top phase is quite independent from system composition, since 80-95% of indium is extracted in the
 332 bottom phase and 5-20% in the top phase. According to Huddleston et al. (2003), in a PEG-based
 333 ABS the bottom phase waste LCDs correspond to the salt-rich and the PEG-rich phase,
 334 respectively. The fact that (1.0 kg) indium is extracted in the bottom phase can be explained
 335 by the high degree of hydration of indium complexes, which tend to remain in the salt-rich phase of
 336 the extraction system, as also reported by Bulgariu and Bulgariu (2007). As shown in Figure 11, if
 337 PEG concentration is increased the volume ratio between the bottom and the top phase decreases
 338 but, as previously stated, the extraction efficiency of indium ions in both phases is not affected by
 339 this variation. For this reason, by working with high PEG concentrations in the selected ABS, it is
 340 possible to obtain a higher indium ion concentration in the bottom phase compared to the
 341 concentration obtained if lower PEG concentrations are employed. The opposite effect was
 342 registered when salt concentration was increased: the volume ratio between the phases increases,
 343 thus determining a decrease of indium concentration in the bottom phase. Experimental data
 344 demonstrate that indium extraction is quite similar when employing PEG 3,350 as well as PEG
 345 10,000; however, the volume ratio decrease is more significant if PEG 3,350 is employed. It was
 346 found that if [PEG 3,350]=25% w/w and $[(\text{NH}_4)_2\text{SO}_4]=12\%$, then the volume ratio between the two
 347 phases is equal to 0.8 and indium concentration in the bottom phase is ~30% higher than the initial
 348 concentration (before the extraction). The increase is quite small; nevertheless such concentration
 349 technique could be helpful to facilitate final recovery processes, in which high metal ions
 350 concentrations are usually required. Figure 13 illustrates the entire process in a flow chart. The mass
 351 balance is performed on 1 kg of waste LCDs.



364

365

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

366

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

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

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

376

377 4. CONCLUSIONS

378 In this work, indium recovery from waste LCDs was experimentally investigated in the
379 laboratory using a sequence of different techniques. Thermal and chemical treatments aimed at
380 removing the polarizing film from the glass substrate were for the first time systematically
381 compared and discussed; the best results were obtained with liquid nitrogen, since only 20 minutes
382 were required; moreover, the obtained product did not show substantial degradation, suggesting a
383 better recycling potential. The best operative leaching conditions performed on indium tin oxide
384 powder were then applied for leaching of the glass residue. It was found that, without shredding,
385 HCl 6 N (T=25°C, t=6h, L/S=3 mL/g) leaches approximately 260 mg In per kg of glass at room
386 temperature, with no energy consumption or dust emissions. An attempt was made to extract
387 indium ions through PEG-based aqueous biphasic systems, which are now receiving increasing
388 attention among the scientific community due to their characteristics of low toxicity and low
389 flammability, and which have not been tested for indium recovery yet. It was found that if [PEG
390 3,350]=25% w/w and [(NH₄)₂SO₄]=12%, indium concentration in the bottom phase is ~30% higher
391 than the initial concentration.

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