Investigation of indium and other valuable metals leaching from unground waste LCD screens by organic and inorganic acid leaching

Citation for the original published paper (version of record):
Schuster, J., Ebin, B. (2021). Investigation of indium and other valuable metals leaching from unground waste LCD screens by
organic and inorganic acid leaching. Separation and Purification Technology, 279.
http://dx.doi.org/10.1016/j.seppur.2021.119659

(article starts on next page)

Separation and Purification Technology 279 (2021) 119659

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Investigation of indium and other valuable metals leaching from unground waste LCD screens by organic and inorganic acid leaching

Jonas Schuster, Burçak Ebin [*]

Nuclear Chemistry and Industrial Material Recycling, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg S-412 96, Sweden

ARTICLE INFO

Keywords:
Indium
Waste LCD screen
Recovery
Leaching
Inorganic acids
Organic acids

ABSTRACT

Indium (In) is the indispensable part of liquid crystal display (LCD) screen which is applied as a thin semiconductor layer on the surface mainly in the form of indium tin oxide (ITO), and feasible end-of-life recycling of indium from this electronic devices is technologically challenging. The present study investigates the recovery of indium from spent untreated liquid crystal display (LCD) screen by inorganic and organic leaching. Critical process parameters such as effects of different acids, leaching duration, reusability of acidic solution and both sides of the organic layers on the LCD were studied to optimize the indium leaching from the waste screen. The efficiencies of inorganic acids (nitric and sulfuric) and organic acids (citric, glycolic, L-ascorbic, maleic and DL-tartaric) to leach metals on LCD were investigated in different leaching duration from 3 to 168 h. Extracted metal concentrations and dissolved organics are characterized by inductively coupled plasma with mass spectrometry and total organic carbon analyser, respectively. The results indicate that over 90% extraction of indium and the lowest amount of other impurities can be achieved using 1 M H_2SO_4 for a leaching period of 48 h. Moreover, similar results could reach with 1 M HNO_3, while organic acids were less successful under these conditions. Overall, the indium amount could reach up to 69 mg/kg$_{\text{ITO glass}}$ for the front and 31 mg/kg$_{\text{ITO glass}}$ for the back side glass. However, relatively high amount of organic layer from LCD screen dissolves in nitric acid solution up to 4000 mg$_{\text{TOC}}$/l, which can affect the further stages of a recycling process. Besides, aluminium, zinc and tin were identified as the elements with the highest amount with indium in the leachate. All these elements were found in both, glass and organic layer of the LCD screen. Although metals from LCD screen have limited solubility in organic acids, specifically tartaric acid has a selective extraction behaviour for molybdenum. By reusing the leachate for further leaching processes, the concentration of indium could be increased constantly up to five times, which indicates that it is possible to increase the indium concentration to the industrially processable amount.

1. Introduction

Over the past few years, electronic waste has been identified as an actual global problem, which has been continuously increasing [1]. A significant amount of electronic waste contains liquid crystal displays (LCD), which are used in a lot of different monitor applications, such as laptops, tablets, mobile phones, and televisions [2]. Besides developing new materials for screen technologies, the recycling of used LCD panels has become a research focus during the past decades [3]. LCD applications usually contain indium, which is part of a transparent semiconductor electrode material in terms of indium-tin-oxide layer (ITO). In general, ITO is coated onto the LCD glass and consists of a solid mixture of indium (III) oxide (In_2O_3), with an amount of 90 – 95 wt%, and tin (IV) oxide (SnO_2), with an amount of 5 – 10 wt% [4].

By the European commission, indium is identified as one of the most critical raw material for diverse reasons [5]. The main reasons are the importance of the electronics industry and abundancy factors since indium is a minor component of the earth's crust with a concentration of 0.45 nmol g^{-1}[6]. Around 70 % of the worldwide indium reserves distributes to China, while other countries with the resources have noteworthy amounts up to ~ 3 % [7]. Besides, there are difficulties in primary indium production, because it is mainly obtained as a by-

---

[*] Corresponding author at: Nuclear Chemistry and Industrial Material Recycling, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Kemivägen 4, Gothenburg S-412 96, Sweden.

E-mail address: burcak@chalmers.se (B. Ebin).

https://doi.org/10.1016/j.seppur.2021.119659
Received 3 May 2021; Received in revised form 31 August 2021; Accepted 1 September 2021
Available online 4 September 2021

product of zinc mining, specifically from zinc sulfide ores [8]. The indium concentration of zinc deposits which can be recovered should be at least 50 g per ton (ppm – part per million), and it can be range from 10 to 100 ppm [9–11]. It is also significant to state that this value is directly dependent on the extraction technology. This condition can be challenging for the timely supply as the demand increases [12]. On the other hand, the indium amount in the LCD screens is more than 200 ppm [11,13] which is several times higher than the average of a primary source. Based on the named reasons, it becomes more and more important to investigate different recycling methods from secondary resources of indium.

Recently, hydrometallurgical methods for the recovery of indium from production waste and end-of-life products were investigated due to the advantage of their lower energy consumptions compared to pyrometallurgical methods. The hydrometallurgical treatment of scrap ITO targets was the most promising approach for indium recycling for years. Han et al. [14] identified an indium purity of more than 99.99 % for the recovery from scrap ITO target. In recent years, the recovery of indium from end-of-life LCD screens became more significant due to the increasing amount of its waste. Generally, pure strong inorganic acids as sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3) could be identified as successful leaching agents for indium by different studies [4,15,16]. One of the main challenges about the indium recovery is the small amount of ITO layer on the screen around 0.37 wt% of the total panel weight, which can vary between different manufacturers and LCD applications [17].

Therefore, the pretreatment of the LCD screen took an appropriate role in several studies to liberate the indium in the form of the ITO layer. Generally accepted pretreatment methods are shredding or milling before the leaching stage. Silveria et al. [18] investigated in different milling equipment, named knife mill, hammer mill and ball mill, and identified ball mill as the best pretreatment process. Lee et al [19] successfully used the high energy ball milling (HEBM) as a pretreatment technique. In addition to the type of milling, the milling time has pointed out as a parameter which influences the particle size significantly and thus the recovery rate as well [18–21]. This investigation showed that optimum particle size related to a maximum recovery rate of indium in a further leaching process could slightly vary between 7.5 μm and 5 mm. Despite the requirement for very fine particles to improve the leaching behaviour, pretreatments as shredding and/or milling can have some drawbacks. On the one hand, Rocchetti and Beolchini [22] reported an indium loss, which can be observed by excessive grinding. Moreover, Yang et al. [15] mentioned that other materials can contaminate the particles during the shredding or milling process by mixing with different segments of the display or other waste electrical and electronic equipment.

The development of an environmental and feasible indium recovery must be one of the main goals for actual and future work for a sustainable electronic industry. Although the crushing of the glass as a pretreatment was generally suggested as an initial processing stage, it can cause a drawback to the following leaching stage. After leaching the valuable metals, filtering the fine glass powders should be an additional treatment step in this approach, increasing the processing cost. It can be way easier for industrial applications to simplify the entire process by eliminating the pretreatment step. Only a limited number of research were conducted on this purpose. Fontana et al. [23] showed the possibility of leaching 90 % of the indium from untreated LCD panel with high concentrated hydrochloric acid (HCl 6 M). Zhang et al. [24] applied ultrasonic waves to the leaching process with low concentrated (0.8 M) HCl without extra heating to the non-crushed samples. The suggested method was able to increase the leaching efficiency up to 98.8 %. A similar approach, using high concentrated sulfuric acid (9 – 18 M) as leaching agent was investigated bySouada et al. [25]. The nearly quantitative yield of indium could reach after 3 – 4 min by 18 M sulfuric acid and simultaneous use of ultrasonication and heating up to 60 °C. Without ultrasound application, the maximum efficiency was reduced down to 70% under the same circumstances where the remaining parameters were same. Indium leaching from crushed LCD by nitric acid and other inorganic acids were studied by Yang et al. [15]. Their results showed that at high acidic concentration, indium dissolution is faster in HCl solution. On the other hand, leaching by H_2SO_4 solution is more effective when low acid concentration was used. Furthermore, innovative and effective recycling methods for indium like novel mechanical pre-treatment methods [26] or supercritical CO_2 for extraction [27] were investigated and discussed recently.

Considering an environmental solution for developing a leaching process, the use of organic acids became a practical method for leaching hazardous and rare-earth elements (REE) [28,29]. Currently, there is no research known about the indium recovery from untreated LCD panels by using organic acids. Although in other fields, such as the recovery of REEs from neodynum magnet waste, maleic, glycolic and ascorbic acid show selective leaching behaviour for the elements Nd, Pr and Dy [30]. Furthermore, citric and tartaric acid showed some achievement by leaching the metals Co, Ni, Mn, Fe, Cu, Zn and Li from used battery materials [31–33].

The paper aims a selective leaching method for indium without shredding or other mechanical treatment of the LCD screen and other kinds of pretreatment respectively. For environmental reasons, the use of organic acids besides the known inorganic acids were investigated. Moreover, different parameters that influence the indium leaching, such as leaching time and influence of the organic layer on the top of the LCD screen, were studied to optimize the indium extraction. Furthermore, this study present results on the reusability of leachate solution, and increasing the indium concentration in the leachate by circulating the solution in order to perform a more environmentally recovery process.

2. Experimental

2.1. Materials

All experiments were performed with an LCD television screen from LG Electronics. The electronic waste is industrially dismantled, such as removing all the electronic components and the liquid crystal. The research was performed using both front and back side of the LCD panel, separately. Image of both sides is shown in Fig. 1.

There is an additional organic layer on top of the glass which invisible in the picture given in Fig. 1. The screen was cut small pieces by hand glass cutter, and the organic layer was removed by hand from some samples. In the experimental procedure, three different samples were studied for the leaching experiments: (i) only organic layer, (ii) organic layer removed LCD glass (Fig. 1b), which is called ITO glass through the rest of the text and (iii) organic layer together with LCD glass (Fig. 1a), which is called LCD screen through rest of the text.

Experiments with LCD screen were performed with small glass pieces around 4.8 cm^2 (±0.2 cm^2), which means an approximate weight of 0.8 g (±0.1 g). By removing the organic layer from the LCD screen, the glass was broken into smaller pieces. For ITO glass experiments, samples of broken glass pieces with the same weight were prepared. A general overview of the material used in this work, as well as the entire experimental procedure is illustrared in in Fig. 2.

2.2. Leaching experiments

The leaching experiments were carried out using different inorganic and organic acids; sulfuric- (H_2SO_4), nitric- (HNO_3), citric- ($C_6H_8O_7$), glycolic- ($C_2H_4O_3$), L-ascorbic- ($C_6H_8O_6$), maleic- ($C_4H_4O_4$) and DL-tartaric acid ($C_4H_6O_6$). All acids were supplied from SIGMA-ALDRICH®, except for nitric acid, which was provided from Emsure®. The acids concentration was set at 1 M for the leaching experiments. The acid solutions were prepared by diluting the concentrated acids and dissolution of the organic acid powder with the appropriate amount of Mili-Q water (18.2 MΩ* cm at 25 °C ± 2 °C). The experiments were

Fig. 1. Front and back side of the LCD before (a) and after (b) the removing of the organic layer. Dark: front side, bright: back side.

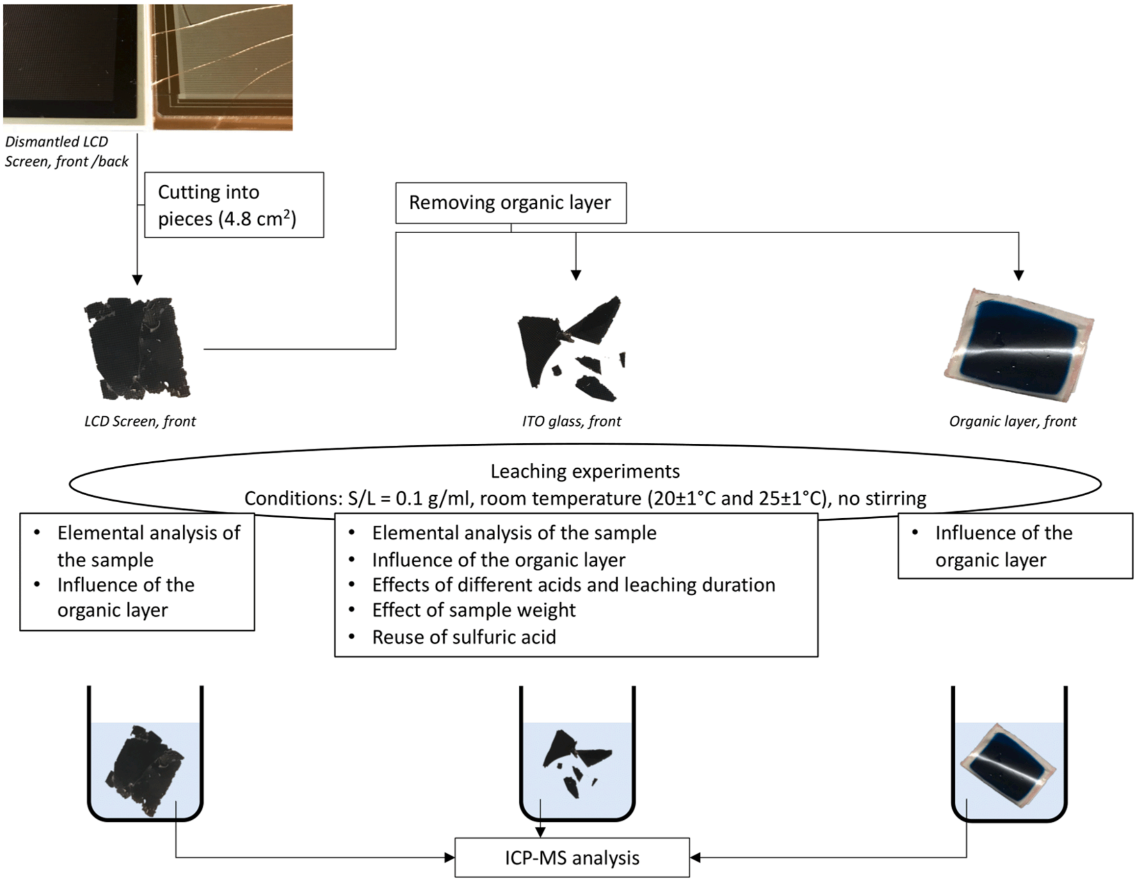

Fig. 2. Overview of the materials and their procedures investigated in this work.

performed using 0.1 g_{LCD}/ml_{acid} solid–liquid ratio (S/L) at room temperature without stirring, and all experiments were performed under the given condition. After the leaching duration, the samples were removed from the solution, and the leachates were taken with syringes and corresponding 0.45 μm filters.

The leaching experiments focused on detecting recoverable metal amounts from the LCD sample, understanding the influence of the organic layer, effects of the different acids, sample weight, and reusability of the acidic solution. LCD screen and ITO glass samples were leached by aqua regia at room temperature for 48 h to determine the total soluble metal amount and the experiments were triplicated.

2.2.1. *Influence of the organic layer*

The influence of the organic layer was investigated by leaching front and back side samples with and without organic layer by 1 M sulfuric and nitric acid for 168 h at room temperature. Besides, only the organic layer without any LCD glass parts was leached using the same conditions. The weight of the organic layer from both sides was 0.4 g in the leaching experiments, which is different than the LCD leaching set but the S/L was the same. Dissolution of the organic layer was specifically controlled by total organic carbon (TOC) in leachate in this set.

2.2.2. *Effect of different acids and leaching duration*

The possibility for selective leaching of indium with the mentioned 1 M organic and inorganic acid solutions from ITO glass were investigated in a first screening experimental set. Therefore, the front and back side of the ITO glass samples were leached by each acid for 168 h at room temperature. According to the results, nitric-, sulfuric-, glycolic- and maleic acid were chosen to go on for time dependent leaching behaviour studies. Leaching of the metals from ITO glass samples was studied using the chosen acidic solutions at room temperature for 3, 8, 24, 48, 72 and 168 h. Different samples and new experimental set were used for each time points to collect the leachates, and all experiments were triplicated to obtain statistically accurate results for the time dependent leaching behaviour study.

2.2.3. *Effect of sample weight*

In the experiment set, different weights of ITO glass front and back side, approximately 0.6, 1.2 and 2.4 g, were kept in sulfuric acid in 0.1 S/L ratio for 48 h at room temperature to investigate the effect of the process size on metal leachabilities. All experiments in this set were triplicated.

2.2.4. *Reuse of sulfuric acid*

The front and back side of the ITO glass with a weight of approximately 1 g were placed in 1 M sulfuric acid solution for 48 h at room temperature. After the leaching period, the ITO glass sample was removed and leachate was reused for the following leaching experiment with new ITO glass pieces. This procedure was repeated up to five times to determine the cyclability of the sulfuric acid solution in the recovery process. S/L ratio was kept at 0.1 for each leaching step.

2.3. *Characterization*

The metals concentrations in each leachate were measured by an inductively coupled plasma with mass spectrometry (ICP-MS, iCAP^{TM} RQ by Thermo Fischer). This equipment allows reliable measurements with the expected low concentrations of metals in LCD leachate due to the low detection limit less than parts per billion (ppb = µg/L). The leachates were diluted 100 times by 0.5 M nitric acid solution.

Total organic carbon (TOC-5050A) analyser in combination with the autosampler ASI-5000A (both by Shimadzu) was used to identify the TOC in leachate. The calibration was done with 1000 parts per million (ppm) carbon solution, prepared of potassium phthalate and Mili-Q water. Standard samples were diluted within the selected range 5, 10, 20, 40 and 100 ppm to obtain a fine calibration curve.

3. Results and discussion

3.1. *Elemental analysis of the sample*

Dissolution in aqua regia was performed for the LCD samples with and without organic layer to screen the elemental composition of the sample. The results are shown in Table 1.

The results give a first impression of the possible concentration range in the leachate of each element. It needs to be considered, that values can significantly affect by different acids for further experiments. Meanwhile, this first screening shows that indium concentration is the highest for the front side. The In/Sn ratio for this particular LCD screen can be identified as approximately 10 wt% for the front and the back side, respectively. However, several significant impurities as aluminium, molybdenum, copper, arsenic and iron, besides the indium were observed. Furthermore, iron concentration shows a comparatively wide deviation between different measurements. This can be caused by a known ICP-MS issue that is related to several polyatomic interferences. May and Wiedmeyer [34] published a table of polyatomic interferences for ICP-MS which shows some argon complex interferences for the investigated iron isotope ^{57}Fe, such as $^{40}Ar^{16}O^{1}H^{+}$, $^{40}Ar^{17}O^{+}$ or $^{38}Ar^{18}O^{1}H^{+}$. A source for the interferences can be found in the provided plasma gas argon in combination with possible entrained atmospheric oxygen. However, to have appropriate and reliable iron concentrations, characterization can be performed by different equipment such as optical emission spectroscopy (OES).

Table 1
Metal concentration in aqua regia leaching, front and back side, organic layer removed (ITO glass) and LCD screen (see Fig. 2 for detailed explanation), 48 h, S/L = 0.1 g/ml,room temperature (25 ± 1 °C), no stirring.

Element	Front side ITO glass mg/kg$_{\text{ITO glass}}$	Back side ITO glass mg/kg$_{\text{ITO glass}}$	Front side LCD screen mg/kg$_{\text{LCDScreen}}$	Back side LCD screen mg/kg$_{\text{LCDScreen}}$
Al	12.3 ± 0.4	93.0 ± 2.1	14.3 ± 2.2	78.5 ± 3.0
Zn	1.4 ± 0.2	1.0 ± 0.2	2.0 ± 0.3	1.3 ± 0.3
Cu	5.7 ± 0.0	3.7 ± 0.8	12.6 ± 0.5	13.9 ± 1.6
As	9.3 ± 0.2	9.8 ± 0.1	9.0 ± 0.5	10.6 ± 0.1
Mo	0.2 ± 0.1	122.4 ± 0.9	0.0 ± 0.0	101.6 ± 1.7
Ag	0.6 ± 0.0	0.6 ± 0.0	1.0 ± 0.1	0.9 ± 0.2
In	91.6 ± 2.3	36.9 ± 0.5	86.7 ± 3.3	28.7 ± 0.6
Sn	9.0 ± 0.2	3.9 ± 0.1	10.0 ± 0.4	7.2 ± 0.9
Fe	20.9 ± 6.8	14.1 ± 6.8	3.8 ± 1.0	7.2 ± 3.2

3.2. *Influence of the organic layer*

The first leaching experiments designed to investigate the influence of the organic layer and possibility of selective indium leaching. Fig. 3 (a) shows the distinction for the sulfuric acid leaching for front and back side, while Fig. 3 (b) shows the same for nitric acid. The measuring of the iron concentration was not performed.

Indium dissolution can reach the concentration of 66 and 68 mg/kg$_{\text{ITO glass}}$ for the front side with sulfuric and nitric acid for 168 h leaching duration, respectively. For the back side, both acids show the same maximum concentration at 30 mg/kg$_{\text{ITO glass}}$. Considering the aqua regia results, it is not possible to leach the entire amount of indium with both inorganic acids in given conditions.

The organic layer affects the indium leaching in sulfuric acid for both sides, which is shown in a higher concentration for samples without organic layer. According to visual observations, sulfuric acid does not dissolve the organic layer, which hinders the leaching of the ITO layer below. Furthermore, nitric acid showed a partial dissolution of the organic layer after a period between one and two days, which might be the reason for the same indium concentration for the front side with and without organic layer.

Regarding further elements compared to the elemental analyses of the ITO glass, aluminium can be confirmed as the main impurity for sulfuric and nitric acid leaching. Moreover, the higher zinc concentration for sulfuric acid detected by ICP-MS can likely be caused by potential polyamotic interferences from sulfur complexes with oxygen or argon such as $^{36}S^{16}O_2^{+}$ or $^{36}Ar^{32}S^{+}$ for the measured isotope ^{68}Zn [34]. Although a relatively high amount of molybdenum is dissolved in aqua regia, 129.2 ± 3.9 mg/kg$_{\text{ITO glass}}$ from back side, it is amount sharply decreased to 21 mg/kg$_{\text{ITO glass}}$ by leaching in nitric acid for 168 h, and also the dissolution of the molybdenum in sulfuric acid is in negligible amount. From various studies of the recovery of molybdenum from spent catalysts performed by Medvedev and Aleksandrov [35] and Vemic [36], it is well known that a selective molybdenum leaching by sulfuric acid is increasing with higher temperatures. Meanwhile, the extraction of molybdenum can be achieved by high concentrated nitric acid at lower temperature because of its behaviour as a strong oxidizing agent. However, a mixture of different inorganic acids, such as aqua regia, shows a notable advancement in leaching efficiency for molybdenum [36].

During the removal of the organic layer, metal-based components can remain on both glass and organic surfaces, and thus the dissolution of the metals from organic layers was studied. Fig. 4 shows the metal concentrations after leaching only the organic layer from both sides using 1 M sulfuric and nitric acid solutions for 168 h at room temperature. Results indicate that a significant amount of indium remained on the front side organic layer, which are 13 and 18 mg/kg$_{\text{Organic layer}}$ for sulfuric and nitric acid leaching, respectively. Meanwhile, indium amount in the back side is limited, which were detected as 1 and 2 mg/kg$_{\text{Organic layer}}$ for sulfuric and nitric acid leaching, respectively. The standard deviations are caused by the remaining residues of fine ITO glass pieces or particles that still stick on the organic layer.

The possible dissolution of the organic layer in the acid solutions were identified by measuring TOC in the leachates for the LCD screen samples. The results are given in the Table 2. The visually observation showed that nitric acid starts dissolving the organic layer after one day,

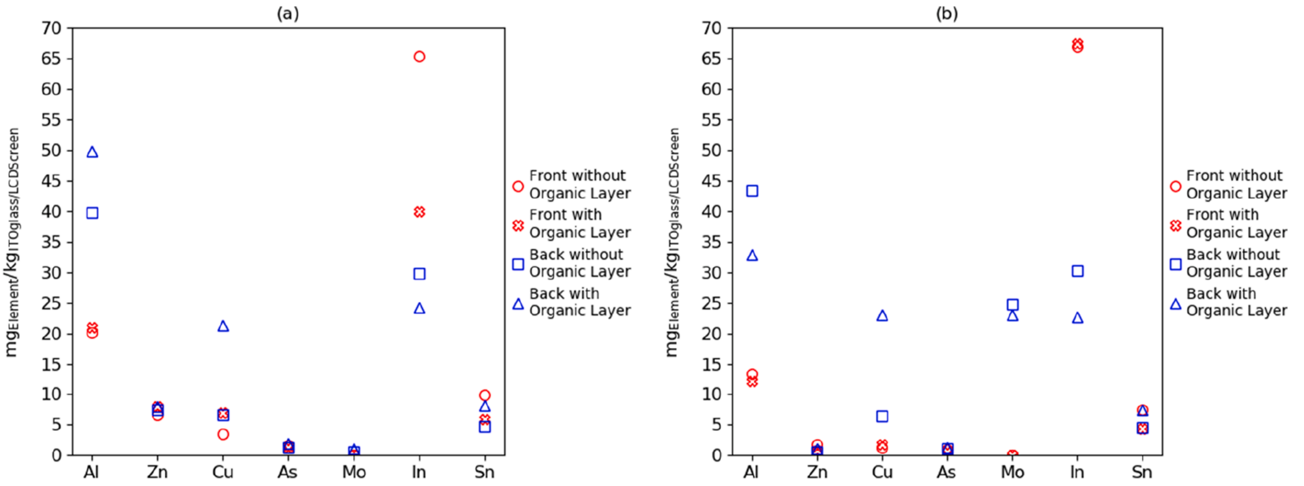

Fig. 3. Influence of the organic with 1 M sulfuric (a) and nitric (b) acid leaching, front and back side, 168 h, S/L = 0.1, room temperature (20 ± 1 °C).

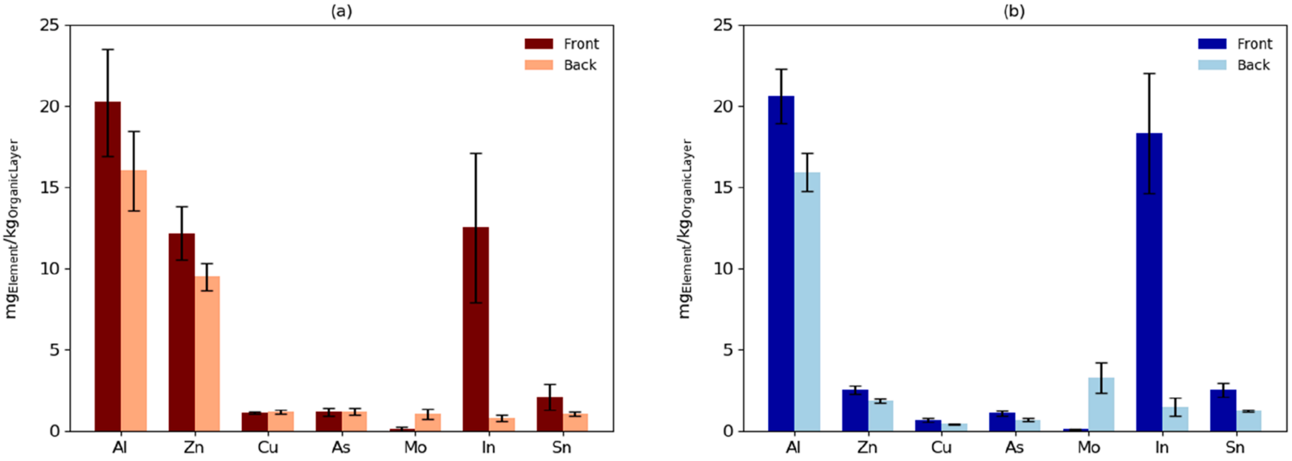

Fig. 4. Organic layer only, with 1 M sulfuric (a) and nitric acid (b), 168 h, S/L = 0.1, room temperature (20 ± 1 °C).

Table2
TOC value for leaching the LCD screen (Fig. 2) in 1 M sulfuric and nitric acid, 168 h, S/L = 0.1, room temperature (20 ± 1 °C).

Acid	Front/Back	TOC mg_{TOC}/l
Sulfuric acid	Front	131 ± 26
	Back	168 ± 5
Nitric acid	Front	4004 ± 90
	Back	3458 ± 91

while the organic layer dissolution in sulfuric acid is limited during the entire leaching period. After 168 h, the TOC amount in the leachate of nitric acid is significantly higher for both sides, than in the leachate from sulfuric acid. These results confirm the visually observations about a partially dissolving by nitric acid during the leaching process.

Considering a further separation step by solvent extraction, investigations from [15,37] show the feasibility of extract indium over 99% with DEHPA and Cyanex 923 as extractants and kerosene as a diluent in artificial solutions. For the transformation of this cognition to real solution, it is necessary to keep impurities in the leachate such as TOC, as low as possible. On the other hand, limited organic dissolution by the sulfuric acid leaching makes its usage more favourable considering a possible following solvent extraction step to obtain pure metals.

According to the obtained maximum indium concentrations, experiments continued further stages using only ITO glass (without organic layer) samples.

3.3. Effects of different acids on leaching

Different inorganic and organic acid solutions were used to investigate the selective leaching of indium from ITO glass sample with 0.1 S/L ratio for 168 h at room temperature. The applied acids are sulfuric-, nitric-, DL-tartaric-, maleic-, L-ascorbic-, glycolic- and citric acids, and 1 M solutions of them were used in the experiments. The recovered element amounts per ITO glass, are shown in Fig. 5, were detected from leachates after the 168 h leaching time at room temperature. Besides the already given concentration of indium for sulfuric and nitric acid, maleic and glycolic acid leaching reach an indium concentration of 44 and 50 mg/kgITO glass, respectively. According to results, indium extraction efficiencies from ITO glass front side are 72% and 74% for sulfuric and nitric acid, as well as, 48% and 55% for maleic and glycolic acids. This particular feasibility of selective indium leaching with organic acids is on hand caused by their different strength.

The strength of an acid can be represented by the dissociation constant K_a which can be described as in equations (2) and (3). Both formula are based on the general expression of equation (1) [38].

$$HA(aq) \rightleftharpoons H^{+}(aq) + A^{-}(aq) \quad (1)$$

$$K_a = [A^{-}][H^{+}]/[HA] \quad (2)$$

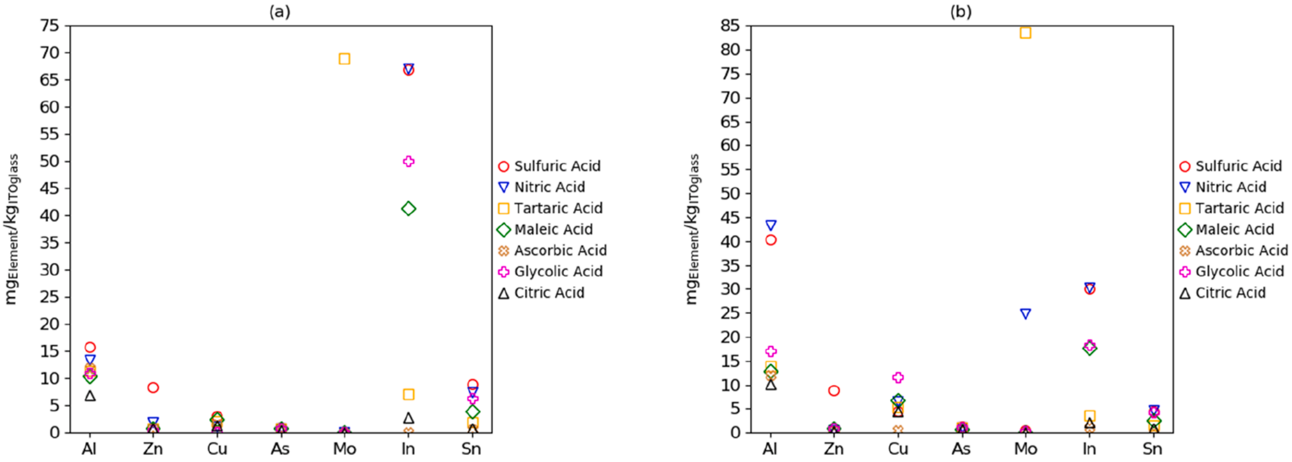

Fig. 5. Effect of different acids (1 M), front (a) and back (b) side, organic layer removed (ITO glass), 168 h, S/L = 0.1, room temperature (20 ± 1 °C).

$$pK_a = -log_{10}K_a \tag{3}$$

HA – Acid, in [] the respective concentration in mol/l

H^+ – Hydrogen ion from dissociated acid, in [] the respective concentration in mol/l

A^- – Conjugated base from dissociated acid, in [] the respective concentration in mol/l

K_a – Acid dissociation constant

pK_a – Logarithmic acid dissociation constant

If Ka is large (small pKa), the acid is mostly dissociated, which signifies a strong acid whereas if Ka is small (large pKa), the acid is slightly dissociated, which belongs to weak acids. In general terms, strong acids show pKa less than around −2 and weak acids between −2 and 12. Due to prepared leaching solutions of 1 M the initial pH as well as K_a and pK_a vary for respective solutions. Regarding the acids used in this work, nitric and sulfuric acid can be considered as strong acids. At the current concentration (1 M), these inorganic acids are fully dissociated. Thus, pH was not measured. Their respective K_a and pK_a values are $3*10^4 -4*10^8$ / −4.5 – −8.6 (sulfuric acid) and 35.5 / −1.55 (nitric acid) , according to the literature [38,39]. For the organic acids used in the experiments, K_a and pK_a were calculated by measured pH. Table 3 shows the particular values for initial dissociation step.

Considering a further separation step by solvent extraction, investigations from

Based on K_a values in the given table, the strength of the organic acids can be sorted as follows: maleic > DL- tartaric > citric > glycolic > L-ascorbic. Moreover, the absence of an oxidizing or reducing agent, such as hydrogen peroxide (H_2O_2) has an impact on the feasibility of organic acid metal leaching. Gergoric et al. [30] showed selective leaching on rare earth metals by using maleic and glycolic acid without any oxidizing or reducing agents. Meanwhile, Chen et al. [31], He et al. [33] and Ma et al. [32] showed a selective metal leaching from spent batteries in combination with oxidizing/reducing agents only for tartaric and citric acid.

Table 3
Measured pH, and calculated/literature based K_a and pK_a values of initial 1 M acid solution, room temperature (20 ± 1 °C).

Acid	pH	K_a	pK_a
Sulfuric acid	–	$3*10^4 -4*10^8$ [38]	−4.5 – -8.6 [38]
Nitric acid	–	35.5 [37]	−1.55 [37]
DL-tartaric acid	1.30	$2.6*10^{-3}$	2.58
Maleic acid	0.95	$1.4*10^{-2}$	1.85
L-ascorbic acid	2.35	$2.0*10^{-5}$	4.70
Glycolic acid	1.90	$1.6*10^{-4}$	3.79
Citric acid	1.39	$1.7*10^{-3}$	2.76

The leaching results of the back side (Fig. 5b) show nearly similar dissolution values, though lower indium amounts are observed than the front panel as expected. It is clear that selective dissolution of indium in sulfuric and nitric acid solution is relatively more favourable comparing to organic acids. In an indium focus recycling process point, the lower removal amount of the other elements from the ITO glass, in other words, their lower concentration is a significant advantage to reduce purification stages to obtain pure indium.

3.4. *Time dependent leaching behaviour*

The two inorganic acids, and two organic acids, glycolic- and maleic-acids, were chosen for the time depending leaching behaviour investigation due to acceptable leaching of indium from ITO glass sample. 1 M solutions were used to investigate the leaching behaviour of the metal dissolution from both front and back sides of the ITO glass samples for different durations (3, 8, 24, 48, 72 and 168 h) at room temperature. Metal recovery results from ITO glass by sulfuric acid as a function of time are given in Fig. 6 for high metal amounts and inside of the graph low metal amounts. After 72 h, the indium reached equilibrium at 68 $mg/kg_{ITO\ glass}$ and remained high and almost unchanged afterwards. A similar curve progression is observed for tin, while aluminium shows a linear increase. Furthermore, there is a very low amount of copper and arsenic visible for long leaching periods, meanwhile, the zinc amount stays almost constant at a mid-low level.

There are similar trends for indium and tin curves in the extraction of the metals from the back side using sulfuric acid unless with lower concentrations (around 30 $mg_{Indium}/kg_{ITO\ glass}$). However, aluminium becomes the element with the highest amount after long leaching periods. In summary, it can be claimed that the peak leaching amounts of indium and tin are almost reached after 48 h. Additionally, the concentrations of impurities are as less as possible in this period.

Fig. 7 shows the time dependent leaching behaviour results for the dissolution in 1 M nitric acid solution. Indium and tin curves for both sides are almost similar to the sulfuric acid curves, including nearly identical maximum concentration (69 $mg_{Indium}/kg_{ITO\ glass}$ for the front side). However, indium leaching starts way slower at the beginning up to 72 h. However, for the front side, aluminium shows a more constantly behaviour, compared to sulfuric acid results. For the back side, aluminium increases linearly from the start and is detected with the highest concentration at the end. Also, there can be observed a higher molybdenum amount after 168 h. The nitric acid leaching process should be terminated before 72 h for optimal selective indium leaching.

Time dependent leaching behaviour using maleic acid from LCD glass sides without organic layer are presented in Fig. 8. In comparison

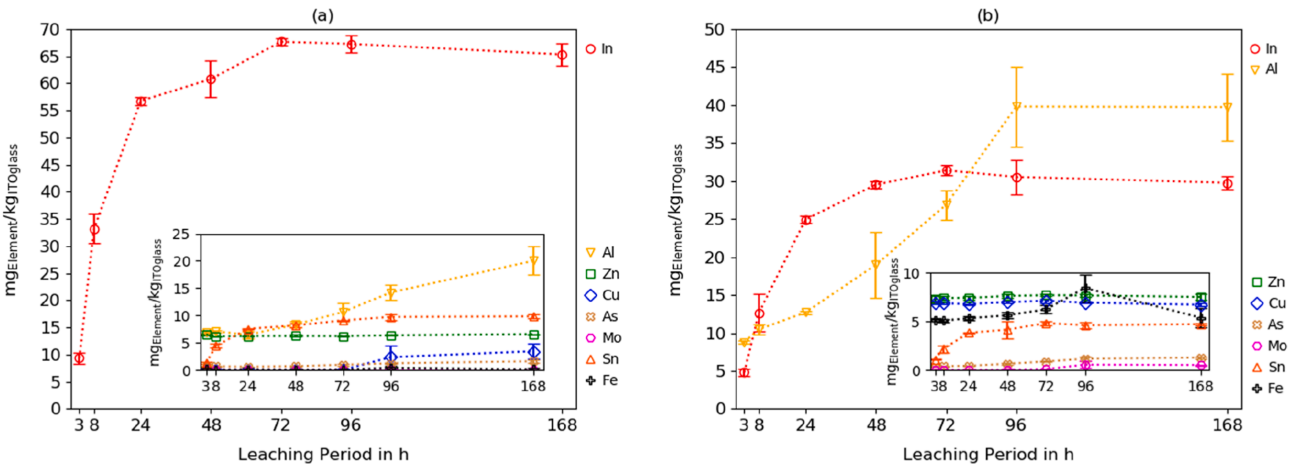

Fig. 6. Time dependent leaching behaviour with 1 M sulfuric acid, front (a) and back (b) side, organic layer removed (ITO glass), S/L = 0.1, room temperature (20 ± 1 °C).

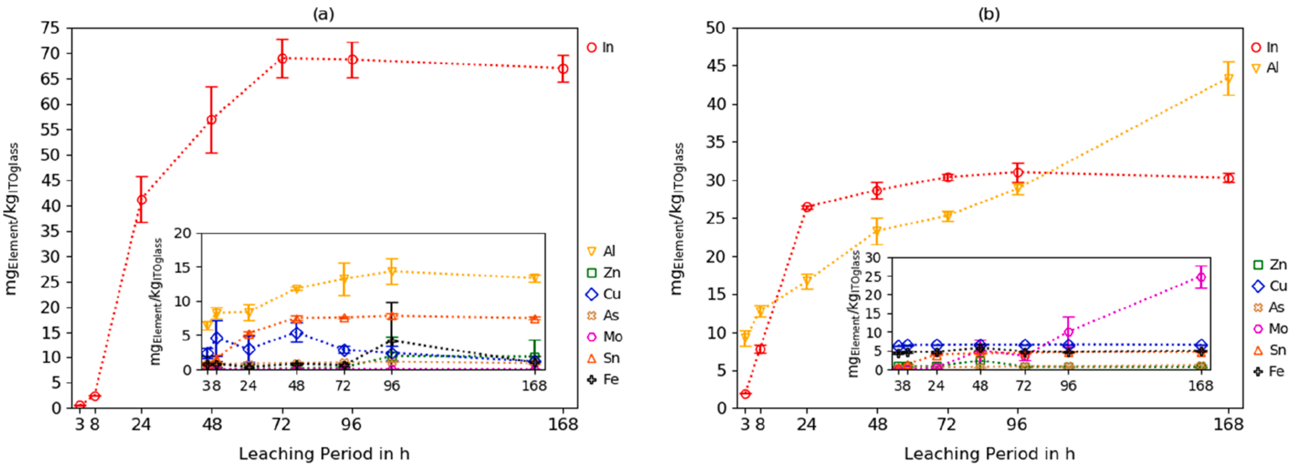

Fig. 7. Time dependent leaching behaviour with 1 M nitric acid, front (a) and back (b) side, organic layer removed (ITO glass), S/L = 0.1, room temperature (20 ± 1 °C).

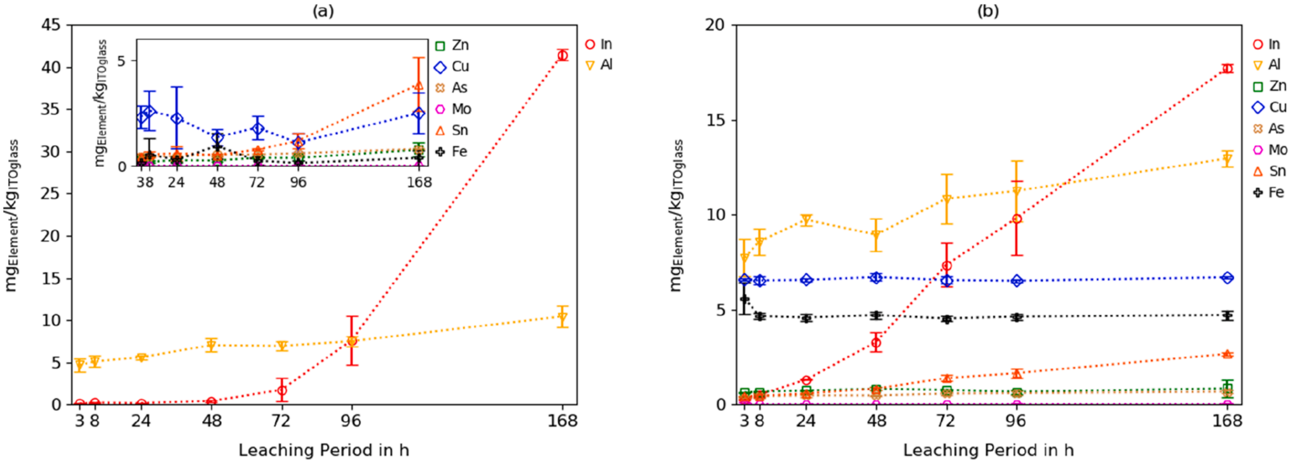

Fig. 8. Time dependent leaching behaviour with 1 M maleic acid, front (a) and back (b) side, organic layer removed (ITO glass), S/L = 0.1, room temperature (20 ± 1 °C).

to inorganic acids, the indium dissolution is lower and exhibits a different trend. After 72 h, the recovered indium amount starts increasing in a sharp linear inclination up to 44 mg/kg$_{ITO\ glass}$. The same curve progression is observed for tin concentration. For the back side, indium and tin concentrations curves behave similarly. Besides the lower indium concentration in the maximum point, compared to the inorganic acids, the long leaching period is a limiting factor for future investigations.

The results of the metal recovery from the organic layer removed LCD screens sides by glycolic acid leaching for different times are given in Fig. 9. The graphs indicate a similar dissolution characteristic for indium, tin and aluminium as observed in maleic acid. In glycolic acid leaching, maximum indium recovery from the front side is attained around 50 mg/kg$_{\mathrm{ITO\ glass}}$ for 168 h leaching duration. However, the amounts start to increase significantly after 48 h.

Based on the time dependent leaching behaviour results, sulfuric and nitric acid show the best leachate composition, after a period of 48 h and 72 h, respectively, to continue further purification for indium preferably by solvent extraction processes. Among the other acids, 1 M sulfuric acid for 48 h leaching duration at room temperature is the optimal condition for partly selective indium extraction. In this point, the indium concentration is 61 mg/kg$_{\mathrm{ITO\ glass}}$ for the front side and 30 mg/kg$_{\mathrm{ITO\ glass}}$ for the back side, respectively. Significantly, the aluminium concentration, which is the challenging impurity, can be kept at lower values. Concerning the selective indium leaching behaviour in relation to the leaching period and maximum concentration, organic acids were not feasible for effective extraction and thus were not used for further investigations.

To summarize the significant results, an overview of the maximum recovery efficiencies of indium together with other metals are given in Table 4. For this overview, indium concentration was leached with the highest efficiency. Therefore, the maximum leached amount of each metal after the particular leaching period is divided by the respective metal amount detected using aqua regia leachate (Table 1).

3.5. *Leaching of different sample weight*

Concerning the effects of the growing volumes in a process on the leaching yield, an experimental set was designed to analyse this phenomenon in a laboratory scale. Leaching experiments were performed by different sample weights but same S/L ratio at optimal leaching conditions for indium recovery, which is dissolution in 1 M sulfuric acid for 48 h using 0.1 S/L ratio. The results of these experiments presented in Fig. 10 show that the recovery of indium and other metal amounts are nearly stable during variation of the sample weight. However, the higher total concentration of indium compared to the time depedent leaching behaviour studies might occur because of leaching temperature which was at 25 °C (slight changes at the room temperature during summer period). The values can be found in a similar range as the results from aqua regia leaching experiments, shown in Table 1.

Table 4
Recovery efficiency of leaching over time, calculated by the concentration of each metal in ITO glass leachate (Figs. 6 – 9) divided by the concentration of the respective metal in aqua regiaITO glass leachate (Table 1). Leaching time was chosen depending on the highest amount of indium in the leachate. Results are shown for front and back side of ITO glass.

Acid	Time hours	Al %	Zn %	Cu %	As %	Mo %	In %	Sn %	Fe %
Front									
Sulfuric acid	72	86	100	0	10	4	74	100	0
Nitric acid	72	100	18	50	11	28	75	84	3
Maleic acid	168	85	55	44	9	6	48	43	2
Glycolic acid	168	89	30	0	9	2	55	70	5
Back									
Sulfuric acid	72	29	100	100	9	0	85	100	44
Nitric acid	72	27	65	100	8	3	82	100	34
Maleic acid	168	14	85	100	7	0	48	68	33
Glycolic acid	168	18	85	100	11	0	50	100	33

3.6. *Reuse of sulfuric acid*

In this subtitle, different units is used to share the leaching results to explain the reusability of the acidic solution clearly. We reached the indium concentration in the leachate approximately 8.7 mg/l (87 mg/kg$_{\mathrm{ITO\ glass}}$) and 3.3 mg/l (33 mg/kg$_{\mathrm{ITO\ glass}}$) for the front and back side, respectively, when 1 M sulfuric acid leaching was applied for 48 h leaching duration. This concentration is far low to design an economically feasible indium recovery process. Moreover, the mass of needed sulfuric acid is immense, which leads to a low efficient process. The investigation focuses on reusing the leachate up to five times by removing the sample from the leachate and placing a new sample after each leaching step. The results of the development of the element concentrations in solution are shown in Fig. 11.

The indium concentration increases constantly up to 43.6 mg/l for the front side and to 17.0 mg/l for the back side, respectively. Consequently, an indium amount approximately five times higher than after the first leaching step can be detected. Considering the pH of the leachate solution after each leaching round, it showed no significant change and remained at similar ranges between 0 and 1. Due to this observation, sulfuric acid is not losing the acidic strength up to the five leaching steps. Moreover, a slight increase of the correlated tin concentration can be observed. However, observation from the recent results confirms aluminium as the main impurity up to five leaching steps. It is clear that leachate can be recirculated to increase the indium concentration to the much higher values that can make the indium recycling feasible.

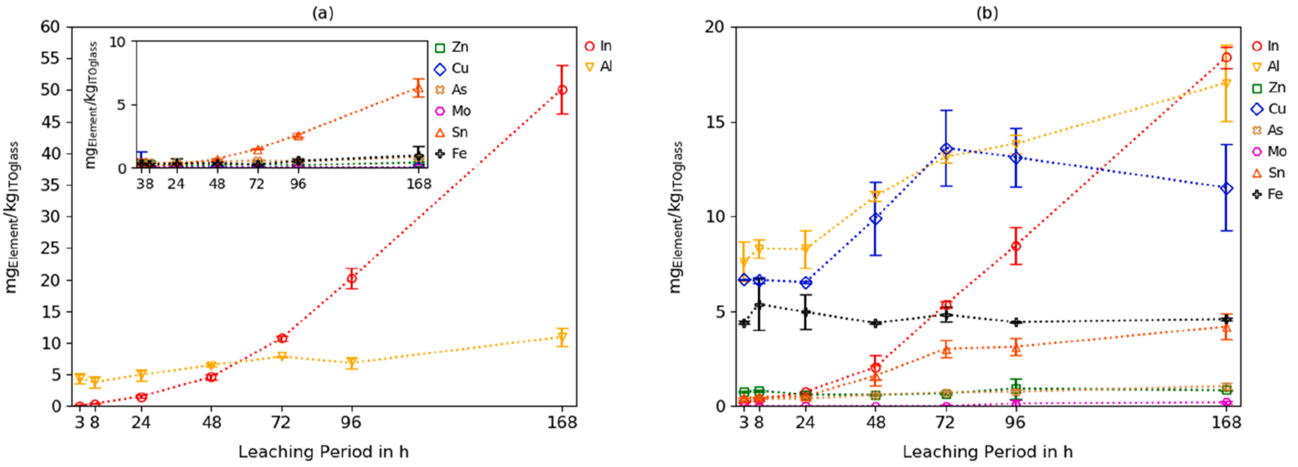

Fig. 9. Time dependent leaching behaviour with 1 M glycolic acid, front (a) and back (b) side, organic layer removed (ITO glass), S/L = 0.1, room temperature (20 ± 1 °C).

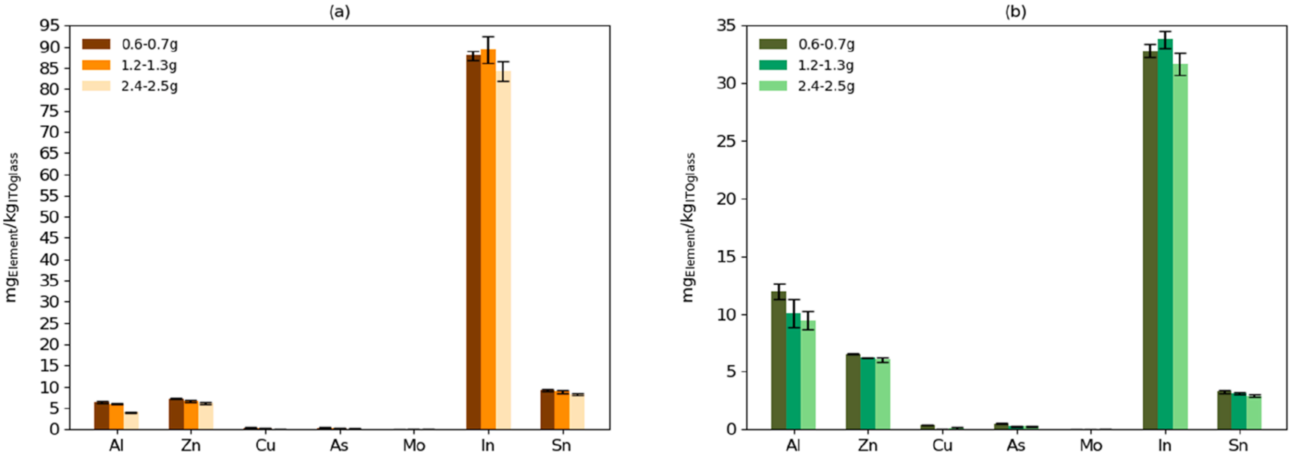

Fig. 10. Leaching of different sample weight with 1 M sulfuric acid, front (a) and back (b) side, organic layer removed, 48 h, S/L = 0.1, room temperature (25 ± 1 °C).

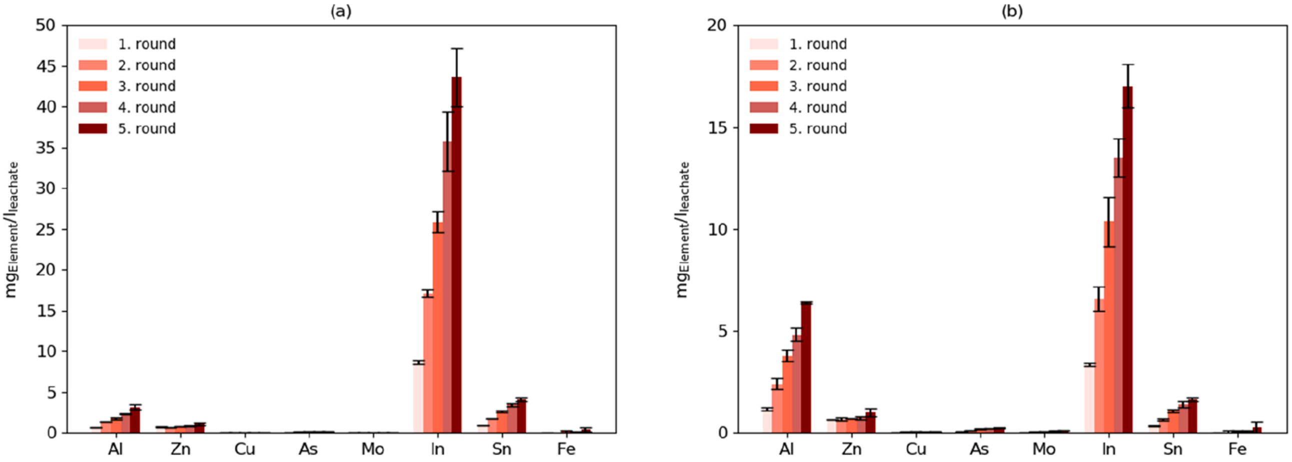

Fig. 11. Reuse of 1 M sulfuric acid, front (a) and back (b) side, organic layer removed (ITO glass), 48 h each round, S/L = 0.1, room temperature (25 ± 1 °C).

The outcome of these experiments can mainly be used for the further indium recovery process. Therefore, solvent extraction can be considered as a possible methodology to continuation of indium and other valuable metal recycling. Promising development has already been achieved with this method from different indium bearing solutions in previous studies [4,15,40]. However, direct use of the leachate from LCD recovery for SX is a challenge because of low metal concentrations and amount of different metals. The increased concentration of the indium and other valuable metals in the leachate by resusing the leachate for the metal extraction points out that the recovered metals can be separated and purified by the solvent extraction process. On the other hand, additional knowledge should be created on the solvent extraction due to the complexity of the recovered metal solution, and thus the possible solvent extraction stage needs detailed research considering several parameters such as extractant, type of solvent, shaking time, aqueous/organic ration, stripping acid etc.

4. Conclusion

This study investigated the leaching of indium and other metals from ungrounded LCD glass to recovery focus on indium. Therefore, relatively high indium concentration combined with low concentration of impurities such as metals or organic components in the leachate is desirable to succeed in efficient indium recycling from end-of-life LCD waste.

Considering the indium and other metals concentrations, inorganic acids are more successful for indium extraction than the investigated organic acids. Sulfuric and nitric acids shows the best leaching results for both sides of LCD glass. Leachates have indium concentrations between 70 mg/ $kg_{ITO\ glass}$ equivalent to 77% recovery efficiency for front side and around 30 mg/ $kg_{ITO\ glass}$ that means 82% recovery efficiency for back side depending on leaching periods from 168 h at room temperature.

Although organic acids have low efficiency in extracting indium, maleic and glycolic acid reached maximum indium concentrations between 40 and 50 mg/$kg_{ITO\ glass}$ for the front side and 20 mg/$kg_{ITO\ glass}$ for the back side for 168 h leaching period run at room temperature. In other words, maleic and glycolic acid reached a maximum indium recovery efficiency between 48 and 55% for front side and 48 and 50% for back side, respectively.

It is significant to state that the observance of the impurities in the leachate presents significant differences between front and back side, as well as between inorganic and organic acids.Furthermore aluminium is identified as the main impurity element with a high appearance at the back side, especially for long leaching durations.

Experiments by leaching the LCD with the organic layer on top and leaching the organic layer by itself showed a relatively high TOC concentration for nitric acid leaching compared to sulfuric acid leaching. The high TOC concentration can cause upcoming issues for further solvent extraction processes using nitric acid as a leaching agent. Therefore, the optimal leaching conditions in the frame of this research are 1 M sulfuric acid leaching for 48 h duration at room temperature considering high indium concentration and minimized other metals concentrations. It is crucial to highlight that variation of the sample weight between 0.6 and 2.5 g in laboratory-scale experiments at the optimum conditions did not influence the selective indium leaching performance.

The reuse of the sulfuric acid leachate for continuing leaching steps shows a constant increase of the indium concentration to a maximum around 43.6 $mg/l_{leachate}$ for the front side and 17 $mg/l_{Leachate}$ for the back side by reusing it up to five times. It is clear that indium concentration in the leachate can be increased higher values by reusing the leachate until it becomes feasible to process, which can open a new way for industrial recycling of indium from end-of-life LCDs.

CRediT authorship contribution statement

Jonas Schuster: Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Visualization. **Burçak Ebin:** Conceptualization, Methodology, Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

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

Acknowledgements

This research was supported by the Åforsk Foundation, Sweden (Grant No: 17-539).

References

[1] R.G. Charles, P. Douglas, I.L. Hallin, I. Matthews, G. Liversage, An investigation of trends in precious metal and copper content of RAM modules in WEEE: Implications for long term recycling potential, Waste Manag. 60 (2017) 505–520, https://doi.org/10.1016/j.wasman.2016.11.018.
[2] F. Ferella, G. Belardi, A. Marsilii, I. De Michelis, F. Vegliò, Separation and recovery of glass, plastic and indium from spent LCD panels, Waste Manag. 60 (2017) 569–581, https://doi.org/10.1016/j.wasman.2016.12.030.
[3] S. Salhofer, M. Spitzbart, K. Maurer, Recycling of LCD Screens in Europe - State of the Art and Challenges (2011), https://doi.org/10.1007/978-3-642-19692-8.
[4] S. Virolainen, D. Ibana, E. Paatero, Recovery of indium from indium tin oxide by solvent extraction, Hydrometallurgy 107 (1-2) (2011) 56–61, https://doi.org/10.1016/j.hydromet.2011.01.005.
[5] European Commission, On the review of the list of critical raw materials for the EU and the implementation of the Raw Materials Initiative, 2014.
[6] A. Tessier, C. Gobeil, L. Laforte, Reaction rates, depositional history and sources of indium in sediments from Appalachian and Canadian Shield lakes, Geochim. Cosmochim. Acta. 137 (2014) 48–63, https://doi.org/10.1016/j.gca.2014.03.042.
[7] M. Lokanc, R. Eggert, R. Redlinger, The Availability of Indium: The Present, Medium Term, and Long Term (2015) www.nrel.gov/publications.
[8] G. Gunn, Critical Metals Handbook, wiley (2013), https://doi.org/10.1002/9781118755341.
[9] G. Phipps, C. Mikolajczak, T.G.-R. energy Focus, U. 2008, Indium and gallium: long-term supply, Elsevier. (2008). https://www.sciencedirect.com/science/article/pii/S1471084608701409 (accessed October 19, 2020).
[10] A. Elshkaki, T.E. Graedel, Solar cell metals and their hosts: A tale of oversupply and undersupply, Appl. Energy. 158 (2015) 167–177, https://doi.org/10.1016/j.apenergy.2015.08.066.
[11] K. Zhang, Y. Wu, W. Wang, B. Li, Y. Zhang, T. Zuo, Recycling indium from waste LCDs: A review, Resour. Conserv. Recycl. 104 (2015) 276–290, https://doi.org/10.1016/j.resconrec.2015.07.015.
[12] C.H. Choi, J. Eun, J. Cao, S. Lee, F. Zhao, Global strategic level supply planning of materials critical to clean energy technologies – A case study on indium, Energy. 147 (2018) 950–964, https://doi.org/10.1016/j.energy.2018.01.063.
[13] H. Wang, Y. Gu, Y. Wu, Y.N. Zhang, W. Wang, An evaluation of the potential yield of indium recycled from end-of-life LCDs: A case study in China, Waste Manag. 46 (2015) 480–487, https://doi.org/10.1016/j.wasman.2015.07.047.
[14] K.N. Han, S. Kondoju, K. Park, H.-M. Kang, Recovery of indium from indium/tin oxides scrap by chemical precipitation, Geosystem Eng. 5 (4) (2002) 93–98, https://doi.org/10.1080/12269328.2002.10541193.
[15] J. Yang, T. Retegan, C. Ekberg, Indium recovery from discarded LCD panel glass by solvent extraction, Hydrometallurgy 137 (2013) 68–77, https://doi.org/10.1016/j.hydromet.2013.05.008.
[16] Y. Li, Z. Liu, Q. Li, Z. Liu, L.i. Zeng, Recovery of indium from used indium-tin oxide (ITO) targets, Hydrometallurgy 105 (3-4) (2011) 207–212, https://doi.org/10.1016/j.hydromet.2010.09.006.
[17] Z. Liu, Z. Xu, H. Huang, B. Li, A study of waste liquid crystal display generation in mainland China, Waste Manag. Res. 34 (1) (2016) 58–66, https://doi.org/10.1177/0734242X15611736.
[18] A.V.M. Silveira, M.S. Fuchs, D.K. Pinheiro, E.H. Tanabe, D.A. Bertuol, Recovery of indium from LCD screens of discarded cell phones, Waste Manag. 45 (2015) 334–342, https://doi.org/10.1016/j.wasman.2015.04.007.
[19] C.-H. Lee, M.-K. Jeong, M. Fatih Kilicaslan, J.-H. Lee, H.-S. Hong, S.-J. Hong, Recovery of indium from used LCD panel by a time efficient and environmentally sound method assisted HEBM, Waste Manag. 33 (3) (2013) 730–734, https://doi.org/10.1016/j.wasman.2012.10.002.
[20] J. Li, S. Gao, H. Duan, L. Liu, Recovery of valuable materials from waste liquid crystal display panel, Waste Manag. 29 (7) (2009) 2033–2039, https://doi.org/10.1016/j.wasman.2008.12.013.
[21] L. Rocchetti, A. Amato, V. Fonti, S. Ubaldini, I. De Michelis, B. Kopacek, F. Vegliò, F. Beolchini, Cross-current leaching of indium from end-of-life LCD panels, Waste Manag. 42 (2015) 180–187, https://doi.org/10.1016/j.wasman.2015.04.035.
[22] L. Rocchetti, F. Beolchini, Recovery of valuable materials from end-of-life thin-film photovoltaic panels: Environmental impact assessment of different management options, J. Clean. Prod. 89 (2015) 59–64, https://doi.org/10.1016/j.jclepro.2014.11.009.
[23] D. Fontana, F. Forte, R. De Carolis, M. Grosso, Materials recovery from waste liquid crystal displays: A focus on indium, Waste Manag. 45 (2015) 325–333, https://doi.org/10.1016/j.wasman.2015.07.043.
[24] K. Zhang, B. Li, Y. Wu, W. Wang, R. Li, Y.N. Zhang, T. Zuo, Recycling of indium from waste LCD: A promising non-crushing leaching with the aid of ultrasonic wave, Waste Manag. 64 (2017) 236–243, https://doi.org/10.1016/j.wasman.2017.03.031.
[25] M. Souada, C. Louage, J.Y. Doisy, L. Meunier, A. Benderrag, B. Ouddane, S. Bellayer, N. Nuns, M. Traisnel, U. Maschke, Extraction of indium-tin oxide from end-of-life LCD panels using ultrasound assisted acid leaching, Ultrason. Sonochem. 40 (2018) 929–936, https://doi.org/10.1016/j.ultsonch.2017.08.043.
[26] V. Lahtela, S. Virolainen, A. Uwaoma, M. Kallioinen, T. Kärki, T. Sainio, Novel mechanical pre-treatment methods for effective indium recovery from end-of-life liquid-crystal display panels, J. Clean. Prod. 230 (2019) 580–591, https://doi.org/10.1016/j.jclepro.2019.05.163.
[27] A.B. Argenta, C.M. Reis, G.P. Mello, G.L. Dotto, E.H. Tanabe, D.A. Bertuol, Supercritical CO2 extraction of indium present in liquid crystal displays from discarded cell phones using organic acids, J. Supercrit. Fluids. 120 (2017) 95–101, https://doi.org/10.1016/j.supflu.2016.10.014.
[28] G.P. Nayaka, Y. Zhang, P. Dong, D. Wang, Z. Zhou, J. Duan, X. Li, Y. Lin, Q.i. Meng, K.V. Pai, J. Manjanna, G. Santhosh, An environmental friendly attempt to recycle the spent Li-ion battery cathode through organic acid leaching, Artic. J. Environ. Chem. Eng. 7 (1) (2019) 102854, https://doi.org/10.1016/j.jece:2018.102854.
[29] J. Cui, N. Zhu, D. Luo, Y. Li, P. Wu, Z. Dang, X. Hu, The Role of Oxalic Acid in the Leaching System for Recovering Indium from Waste Liquid Crystal Display Panels, ACS Sustain. Chem. Eng. 7 (4) (2019) 3849–3857, https://doi.org/10.1021/acssuschemeng.8b0475610.1021/acssuschemeng.8b04756.s001.
[30] M. Gergoric, A. Barrier, T. Retegan, Recovery of Rare-Earth Elements from Neodymium Magnet Waste Using Glycolic, Maleic, and Ascorbic Acids Followed by Solvent Extraction, J. Sustain. Metall. 5 (1) (2019) 85–96, https://doi.org/10.1007/s40831-018-0200-6.
[31] X. Chen, D. Kang, L. Cao, J. Li, T. Zhou, H. Ma, Separation and recovery of valuable metals from spent lithium ion batteries: Simultaneous recovery of Li and Co in a single step, Sep. Purif. Technol. 210 (2019) 690–697, https://doi.org/10.1016/j.seppur.2018.08.072.
[32] L.W. Ma, X.L. Xi, Z.Z. Zhang, Z.Q. Huang, J.P. Chen, Hydrometallurgical Treatment for Mixed Waste Battery Material, IOP Conf. Ser. Mater. Sci. Eng. 170 (2017), https://doi.org/10.1088/1742-6596/755/1/011001.
[33] L.P. He, S.Y. Sun, Y.Y. Mu, X.F. Song, J.G. Yu, Recovery of Lithium, Nickel, Cobalt, and Manganese from Spent Lithium-Ion Batteries Using l -Tartaric Acid as a Leachant, ACS Sustain. Chem. Eng. 5 (2017) 714–721, https://doi.org/10.1021/acssuschemeng.6b02056.
[34] T.W. May, R.H. Wiedmeyer, A Table of Polyatomic Interferences in ICP-MS, At. Spectrosc. 19 (1998) 150–155. https://www.perkinelmer.com/CMSResources/Images/44-74379ATL_TableOfPolyatomicInterferences.pdf.
[35] A.S. Medvedev, P.V. Aleksandrov, Investigations on processing low-grade molybdenum concentrate by the nitric-acid method, Russ. J. Non-Ferrous Met. 50 (4) (2009) 353–356, https://doi.org/10.3103/S1067821209040087.
[36] M. Vemic, Leaching and recovery of molybdenum, nickel and cobalt from metals recycling plants mineral sludges, HAL Arch. (2016). https://tel.archives-ouvertes.fr/tel-01373244/document%0Ahttps://tel.archives-ouvertes.fr/tel-01373244.
[37] J. Yang, T. Retegan, B.M. Steenari, C. Ekberg, Recovery of indium and yttrium from Flat Panel Display waste using solvent extraction, Sep. Purif. Technol. 166 (2016) 117–124, https://doi.org/10.1016/j.seppur.2016.04.021.

[38] A.V. Levanov, O.Y. Isaikina, V.V. Lunin, Dissociation constant of nitric acid, Russ. J. Phys. Chem. A. 91 (7) (2017) 1221–1228, https://doi.org/10.1134/S0036024417070196.

[39] A.V. Levanov, O.Y. Isaikina, U.D. Gurbanova, V.V. Lunin, Dissociation Constants of Perchloric and Sulfuric Acids in Aqueous Solution, J. Phys. Chem. B. 122 (23) (2018) 6277–6286, https://doi.org/10.1021/acs.jpcb.8b0194710.1021/acs.jpcb.8b01947.s001.

[40] J. Yang, C. Ekberg, T. Retegan, Optimization of indium recovery and separation from LCD waste by solvent extraction with bis(2-ethylhexyl) phosphate (D2EHPA), Int. J. Chem. Eng. 2014 (2014) 1–9, https://doi.org/10.1155/2014/186768.