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Selective leaching of indium from spent LCD screens by siderophore desferrioxamine E

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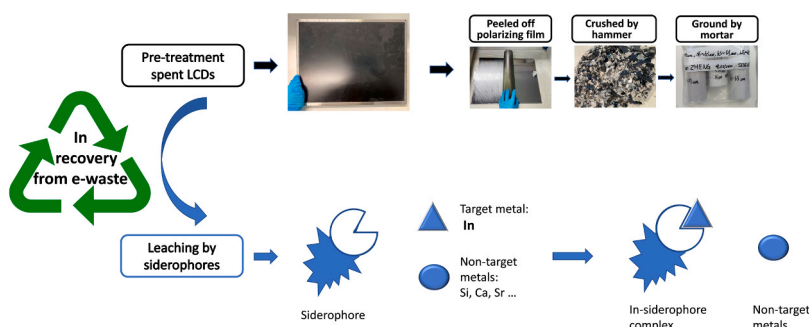
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HIGHLIGHTS

- A novel bio-based indium leaching method is proposed.
- Model elucidates indium leaching mechanism.
- Improved n(DFOE)/n(In) ratio lessens aluminum competition in indium leaching.
- Optimal conditions yield high indium leaching.

GRAPHICAL ABSTRACT



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ABSTRACT

Given the criticality of indium (In) in high-tech applications, spent LCD screens can represent a viable secondary In resource. In this work, an innovative and alternative technology to selectively leach In from spent LCD screens using a microbial chelating agent, desferrioxamine E (DFOE), was developed. Indium was concentrated from spent LCD screens by implementing an adapted pre-treatment procedure, allowing the isolation of an indium-rich glassy fraction. During leaching, the competition between aluminum (Al) and In for complexation with DFOE leads to the precipitation of $\text{In}(\text{OH})_3$ at low DFOE concentrations (12–240 μM). After adjusting the optimal conditions (fraction size: 0–36 μm , pH: 5.5, S/L ratio: 1 g/L, 25 °C), the In leaching yield reached 32%, ten times higher than Al over 90 days with 5 mM DFOE. Thus, achieving high In recovery is possible through i) prolonging leaching durations, ii) selective leaching, and iii) minimizing Al interference. This is the first attempt to selectively leach In using a selected siderophore from end-of-life products with high concentrations of non-targeted elements (i.e. Al, Si, and Ca). This study demonstrates the potential of generating indium-rich leachates, which can be subsequently processed through the GaLlophore technology for In refining.

Abbreviations: LCDs, liquid crystal displays; ITO, indium-tin-oxide; DFOE, desferrioxamine E; WEEE, Waste Electrical and Electronic Equipment; EoL, end-of-life; S/L ratio, solid-to-liquid ratio; F1-F3, fraction size; n, n(DFOE)/n(In) ratio.

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1. Introduction

Critical metals are essential for the transition to a zero-carbon economy, as well as for the telecommunications and electronics sectors [1,2]. Indium (In), known for its unique properties including scalability, electrical conductivity, and optical transparency, is widely utilized in high-tech applications [3]. In is commonly obtained as a by-product from zinc-sulfide ore minerals with relatively low concentrations (1–100 mg/kg). There are no known In specific minerals [4]. The global production of primary In was approximately 900 tons in 2022, with a price of US Dollars (USD) 250/kg [4]. Nevertheless, spent liquid crystal displays (LCDs), a common type of electronic waste, can contain as high as 600 mg/kg of In [5]. The consumption of electronics is high due to their short lifespan and increasing demand [6]. It was reported that 53.6 million tons of electronic waste were generated in 2019, and it was predicted that this amount would exceed 74 million tons in 2030 [1]. Specifically, screens and monitors containing LCDs accounted for 13% of the total electronic waste generated in 2019, highlighting the significant portion of waste that LCDs represent. To counter the anticipated In supply deficit, a sustainable approach would involve the recovery of In from spent LCDs.

In is used in LCDs of flat panel displays and in electrodes, which are made of indium-tin-oxide (ITO: 80–90% In_2O_3 and 10–20% SnO_2) [5,7], accounting for 80% of total In consumption worldwide [8]. However, the In recovery rate has been below 1%, leading to significant cumulative losses due to the lack of suitable recovery technologies and economic incentive barriers [9–11].

The main barrier to In recovery from spent LCDs is the lack of an adapted pre-treatment and selective leaching protocols. Pre-treatment is essential to ensure the optimal extraction of In from spent LCDs. It includes dismantling, cutting, grinding, and even thermal treatment [12]. The methods to remove polarizing films and liquid crystals have been widely studied [5,7,13]. Also, various methodologies have been investigated for comminuting spent LCDs to obtain optimal particle fraction [14,15]. However, there are no established standards for effectively enriching and accessing In_2O_3 due to the complexity of LCDs structure.

The recovery of In from spent LCDs via conventional hydrometallurgical methods generally involves the use of strong acids and organic acids [8,9,12,16,17]. Despite their capability of dissolving low concentrations of targeted elements (i.e. In), the acids are equally proficient at dissolving high concentrations of non-targeted major elements (i.e. Si, Al, Fe, and Ca) [12]. Consequently, the recovery process of high-purity products becomes increasingly complex and entangled [18]. Bio-hydrometallurgy offers a more environmentally friendly approach by avoiding highly acidic, alkaline, or toxic chemicals and consuming less energy [19,20]. However, it requires the adaptation of microorganisms to tolerate toxic substances in complex waste streams, which is time-consuming [13]. It is important to note that none of the methods have reached any high technology readiness level (TRL>6), largely due to the non-selectivity of the process. Ex-situ (away from the original location) bio-based technology is a promising method for element recovery [21,22]. It has been reported that gallium could be recovered from the wastewater of the wafer fabrication industry by microbial natural chelators-siderophores desferrioxamine B (DFOB) and desferrioxamine E (DFOE) [21,23], and used DFOB/E could be recycled by a patent “GaLIophore technology” (No. DE102019108803B4) [21]. Nonetheless, there are currently no documented reports on the utilization of siderophores for the selective leaching of In from spent LCDs.

To bridge this knowledge gap, siderophore DFOE is introduced as a novel agent for In leaching from spent LCDs. A robust sample preparation methodology specific to spent LCDs is established, along with the development of an efficient In recovery protocol using DFOE. Enhanced pre-treatment techniques and leaching parameters, including pH, particle size distribution, solid-to-liquid ratio, DFOE concentration, and temperature, are carefully considered. The application of chemical modeling provided valuable insights into the mechanisms of In leaching

by DFOE, thus complementing the interpretation of the experimental findings.

2. Materials and methods

2.1. Chemicals

DFOE (desferrioxamine E, $\text{C}_{27}\text{H}_{48}\text{N}_6\text{O}_9$, 85% purity) was supplied by ASA Spezialenzyme GmbH company, Wolfenbüttel, Germany. Indium (III) oxide (< 45 μm powder, 99.9% purity) was obtained from Alfa Aesar. Other analytical grade chemicals, including HF 40% w/w, HCl 37% w/w, HNO_3 69.9% w/w, KNO_3 , KOH, pH buffer (HEPES and MES), Extran MA 01 ‘liquid, alkaline, concentrate’ and acetonitrile (HPLC gradient grade) were obtained from Sigma-Aldrich, VWR and Labbox.

2.2. Spent LCD samples and pre-treatment

Spent LCD computer displays were collected from the Waste Electrical and Electronic Equipment (WEEE) storage at the Institut de Physique du Globe de Paris, France. A total of ten discarded LCD panels (not dismantled) prepared from computer displays by major manufacturers were used in this study. Spent LCD panels were manually dismantled using a screwdriver and separated into different fractions (one end-of-life (EoL) LCD panel, as an example, is shown in Fig. S1). These fractions are comparable to spent LCD panels from a previous study [24], which investigated the physico-mechanical pre-treatments necessary to dismantle LCD panels.

After the dismantling process, ten glass pieces of spent LCD screens (thickness approximately 10 mm) (Fig. S1.) were selected for the current study. Their lamination structure is shown in Fig. 1. In exists in two films of ITO layers of approximately tens of nanometers. The polarizing films were manually removed from both the front and back sides of the spent LCD glass. Residuals of cellulose triacetate and polyvinyl alcohol strongly adhered to the surface of the spent LCD glass and were difficult to remove. To expedite the process, the spent LCD screens were immersed in an ‘Extran MA 01 liquid, alkaline, concentrate (Sigma-Aldrich)’ solution for 2 days with a concentrated liquid/water ratio of 1/10. This protocol is more environmentally friendly and less harmful than other traditional solutions using organic solvents, like acetone [13,25]. Subsequently, spent LCDs were rinsed with ultra-pure water and dried. Before grinding, spent LCD glass was roughly shredded into smaller pieces (30 × 30 mm) with a non-metallic hammer and ground for 1 h with a Retsch RM-200 grinder. The resulting powder was screened into three different particle sizes. The pre-treatment steps are shown in Fig. S2.

2.3. Leaching experiment design

Leaching of the spent LCD powder was tested through batch experiments conducted over 7 to 14 days with 10 mM pH buffer (HEPES, pH = 7.33 ± 0.12) and 10 mM KNO_3 as background salt. All batch tubes were agitated at 200 rpm using a digital rotary shaker (Roller 10 Digital, IKA) at room temperature (25 °C except where indicated). Two parallel experiments were set up for each sample and blank controls. All data analyses given in tables and figures are presented as mean \pm standard deviation.

Several leaching tests were conducted to evaluate the influence of different parameters on In recovery. These parameters included a) pH on the solubilization of In (pH ranging from 3 to 9), b) solid-to-liquid (S/L) ratio (ranging from 1 to 20 g/L), c) the ratio between the moles of DFOE added and the moles of In available for leaching in the same solution ($n = n(\text{DFOE})/n(\text{In})$), ranging from 1 to 20, d) LCD mix fraction sizes (F1: 0–36 μm ; F2: 36–63 μm ; F3: 63–125 μm), and e) different leaching temperatures (25 °C, 40 °C, and 55 °C). All conditions are summarized in Table S1. Fraction size F2 with the highest mass percentage and highest In concentration, a neutral pH of 7, and a solid-to-liquid ratio of

5 g/L which was referenced in leaching study [16,26] and 25 °C were utilized for constant conditions. During the leaching tests, each test modified only one parameter while keeping all others constant. In addition, pure mineral In_2O_3 (0.5 mM) was leached by DFOE with n (DFOE)/ $n(\text{In}) = 1, 2, \text{ and } 5$ at pH 7.19 with 10 mM KNO_3 over 14 days.

The In leaching yield (η) was calculated according to Eq. (1).

$$\eta = \frac{C}{1000 \times m \times R} \times 100\% \quad (1)$$

Where C is the concentration of In in the leachate (mg/L), m is the total amount of In in the spent LCD mix powder (mg/kg), and R is the solid-to-liquid ratio (g/L).

2.4. Analytical methods

The compositions of major and detectable trace elements (including In) in spent LCD powder were measured by X-ray fluorescence (XRF) with the Epsilon 3XL. The total concentrations of elements were determined by a quadrupole inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7900) following the full digestion of the samples as detailed in Supporting Information Text S1).

Phase quantification was carried out using a Thermo Fisher Scientific MLA 650 (Mineral Liberation Analyzer) equipped with two Bruker X-Flash detectors (5030). The specific surface area analysis of samples was determined by Brunauer-Emmett-Teller (N_2 -BET) methodology.

Additionally, selected small pieces of spent LCD glass, including both the front and back sides of ITO layers, were examined for cross-section structure and composition by a scanning electron microscope with an energy dispersive X-ray detector (SEM-EDX, Auriga Zeiss). This was to explore the distribution of In within different phases. Samples were carbon-coated by Quorum (Q150T ES) before SEM-EDX analysis.

In the leaching experiments, pH was controlled using either a pH buffer or by adjusting with 1 M / 0.1 M HNO_3 or KOH, pH measurements were performed with a digital pH meter (Orion Star A111, Thermo Scientific) with an uncertainty of 0.01 pH units. Each collected leachate sample was filtered through a 0.22 μm filter (Sartorius, PES) and diluted in 2% HNO_3 for ICP-MS analysis.

The analysis of metal-DFOE complexes after leaching was performed by a reversed-phase high-performance liquid chromatography (RP-HPLC, Agilent 1200 Series) with an Agilent Eclipse XDB-C18 column (5 μm and 4.6 \times 250 mm column) and diode array detector (DAD), as detailed in Supporting Information Text S2.

2.5. Modeling

The Equilibrium Calculation of Speciation and Transport (ECOSAT) program software was utilized to simulate the equilibrium species of In during the leaching process, and was based on similar conditions of experiments, such as pH, ionic strength, possible species, and element composition in aqueous solution. The stability constants (K values) for In and competing element Al, when complexed with DFOE, were added to the current database of ECOSAT to calculate their species under our experimental conditions. For DFOE, we assumed that the K values for the above-mentioned metal ions were similar to those established K values for DFOE complexes, because the data corresponding to DFOE complexes are currently unavailable in the literature, as shown in Table S2. The scientific rationale will be elaborated later in this study. Hydrolysis constants for DFOE and the In(III) ion were also included in the database, as shown in Table S3.

3. Results and discussion

3.1. Characterization of spent LCD glass

The average compositions of major components of ten spent LCD glass powder samples are shown in Table S4. The results indicated that In concentration averaged 257 ± 133 mg/kg, significantly higher than primary ore sources, making spent LCD glass as a promising source of In [4,12]. The major components (i.e. Si, Al, and Ca oxides) constituted over 90 wt% of the sample composition, which is consistent with existing literature [15,26,27]. Additionally, the presence of critical rare elements like strontium (Sr: 3.5 wt%) and antimony (Sb: 0.1 wt%), along with hazardous substances such as barium (Ba: 2.5 wt%) and arsenic (As: 2.3 wt%), were observed in the samples, highlighting potential risks in the recycling process. The fundamental elemental composition of LCD glass is alkali-free glass, primarily consisting of SiO_2 , Al_2O_3 , B_2O_3 , and alkaline earth oxides like BaO [28]. It has been confirmed through MLA analysis that glass phases, which are largely composed of calcium aluminosilicates (with variable Ba), account for more than 99% of the LCD mix, (Fig. S3). Indium-bearing phases constituted less than 0.01% of the total mapped area, which is consistent with low In concentrations (mean assay grade of 274 mg/kg, LCD mix F1). Utilizing spent LCD glass in industries like concrete or porcelain ware may lead to material and energy savings [28,29]. Thus, the recovery of glass materials is a promising approach to process EoL products. However, hazardous substances, such as Sr, As, and Sb, present in spent LCD glass need careful consideration during the recycling process.

SEM images and EDX analysis indicated that In was mostly located in

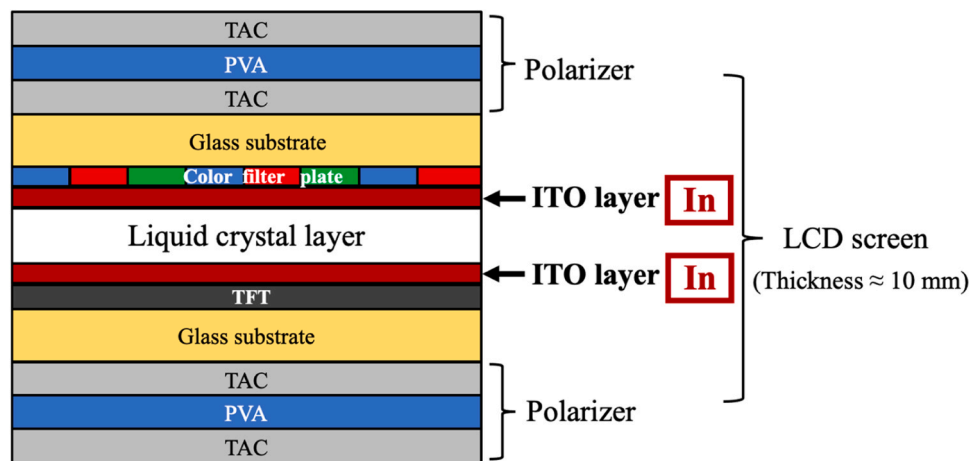


Fig. 1. The lamination structure of the ITO layer from the LCD panel.⁷ TAC: cellulose triacetate; PVA: polyvinyl alcohol; TFT: thin-film transistor; ITO: indium tin oxide.

the ITO (indium tin oxide) layers of spent LCD glass, as depicted in Fig. 1 and Fig. 2, aligning with its presence on the surface rather than within the glass matrix [30,31]. At the specific point of interest, the In composition (approximately 50 wt%) was observed. In is heterogeneously distributed in the investigated spent LCD powder samples due to different manufacturing processes, as well as standardized pre-treatment protocols differences applied before SEM observations (Fig. S4 (c)), which may lead to different results compared to other studies [32,33]. Here, we report that among ten discarded LCD screens sourced from three prominent manufacturers, the In content following pre-treatment within the finest fraction size (F1) ranged from 29 to 465 mg/kg. Over 50% of recorded In concentrations ranged from 170 to 387 mg/kg. These range values were consistent with the broader context outlined in recent literature (last five years), wherein a concentration range of 113 to 415 mg/kg has been reported (Table S5) [27]. Hence, there is no need to consider extreme values exceeding 1000 mg/kg in spent LCDs from mobile phones [34].

The two spent LCD samples (initially named LCD 3 and LCD 7) containing the highest and lowest In concentrations, respectively, were compared. The mass distribution fractions and corresponding In concentrations across three particle size fractions (F1 to F3) are shown in Fig. S5. The In concentration increased as the particle size decreased (F3 to F1: 63–125 μm , 36–63 μm , and 0–36 μm) [17,33]. For instance, the LCD 3 finest fraction F1 (0–36 μm) displayed the highest In concentration (i.e. 465.4 ± 12.1 mg/kg), even though the total mass of the finest fragment only accounted for 10%. In contrast, the lowest In concentration accounted for 29.1 ± 6.4 mg/kg in LCD 7 with the largest fraction F3 (63–125 μm), where the total mass accounted for 36%. This finding is important for the leaching process, as finer particles with higher In concentration may offer a larger surface area for leachate exposure, potentially enhancing leaching kinetics facilitated by DFOE [14,35]. However, regarding the specific surface area of the LCD mix samples analysis, the results were below the detection limit of the equipment used (< 1 m²/g).

In order to prepare a representative sample for the leaching experiments, solid materials from eight spent LCDs were blended together (LCD mix: LCD 1–10 without 3 and 7). This mixture, as well as three size fractions (F1 to F3) were used for the leaching experiments. The In concentrations were 273.7 ± 3.8 mg/kg, 278.6 ± 4.5 mg/kg, and 245.2 ± 7.2 mg/kg in LCD mix fractions F1 (14 mass%), F2 (45 mass%), and F3 (41 mass%), respectively.

3.2. Mineral In₂O₃ leaching

In order to investigate the effect of DFOE on In leaching efficiency independently of other elements (i.e. Si, Al, and Ca), a kinetic study was carried out with pure mineral In₂O₃ in batch experiments. The tests were performed under conditions similar to those utilized with spent LCD mix powders at 25 °C. The evolution of the dissolved In concentration is

shown in Fig. 3. Given the maximum solubility of DFOE, which is approximately 5 mM, we established values of n equals to 1, 2, and 5 for the parameters under investigation. In the absence of DFOE, pure In₂O₃ showed minimal solubility, confirming the poor dissolution/solubility of In₂O₃ at circumneutral pH conditions. This is supported by the aqueous geochemistry of In(OH)₃ and In₂O₃ because their hydrolysis equilibrium stability constants are low, $K = 10^{-36.9}$ and $10^{-35.9}$, respectively [36, 37]. However, in the presence of DFOE, In₂O₃ leaching yields nearly 1 μM of dissolved In, surpassing spent LCD mix (0.5 μM after 14 days, $n = 20$).

The addition of DFOE significantly improved the solubility of In. Furthermore, an increase in the initial total DFOE concentration led to higher solubility. A higher total In dissolved concentration (0.93 μM) was achieved at n equalled 5, compared to that (0.65 μM) at n equalled 1 over 14 days. While the dissolved In concentration increased with leaching time, the amount of solubilized In₂O₃ remained low (< 1 μM over 14 days) even for the highest initial added DFOE concentration (5 mM).

3.3. Effect of leaching conditions on In recovery from spent LCDs

3.3.1. Effect of pH

Various pH conditions, ranging from 3 to 9, during leaching were tested on the spent LCD mix powder over a period of 7 days, both in the presence and absence of DFOE, as shown in Fig. 4. It was observed that both In and Al could be dissolved at pH 3 in the absence of DFOE, suggesting that an acidic environment enhances the leaching yields of In (4.17%) and Al (0.49%). These yields are significantly higher compared to near zero yields at pH 5, 7, and 9 in the absence of DFOE. This outcome is consistent with prior research indicating that acidolysis of In and the subsequent release of In³⁺ species are predominant at pH 3 [36]. Nevertheless, when DFOE was introduced at a pH of 3, the specific extraction of In was impeded due to significant Al dissolution (approximately 100 μM). This occurred despite an elevated In leaching efficiency of up to 5.52%. Conversely, a notable increase (relative to non DFOE conditions) in the dissolved In concentration was noted upon the introduction of DFOE at pH levels of 5, 7, and 9.

The optimum selectivity for In extraction was observed at a pH of 7, which corresponded to the highest In/Al leaching yield ratio (approximately 18/1) (Fig. 4). Consequently, a pH of 7 was selected for subsequent experiments, with HEPES used as a pH buffer to maintain this condition.

3.3.2. Effect of $n(\text{DFOE})/n(\text{In})$ ratio (n)

The effect of different DFOE/In molar ratios (n) on In leaching is presented in Fig. 5. Among the various n values tested (1, 2, 5, and 20), the molar ratio of DFOE/In at 20 exhibited a higher In leaching yield. Fig. 5(a) and (b) show that the In dissolved concentration decreased after 2 days ($n = 1$) and 9 days ($n = 2$), while the Al dissolved

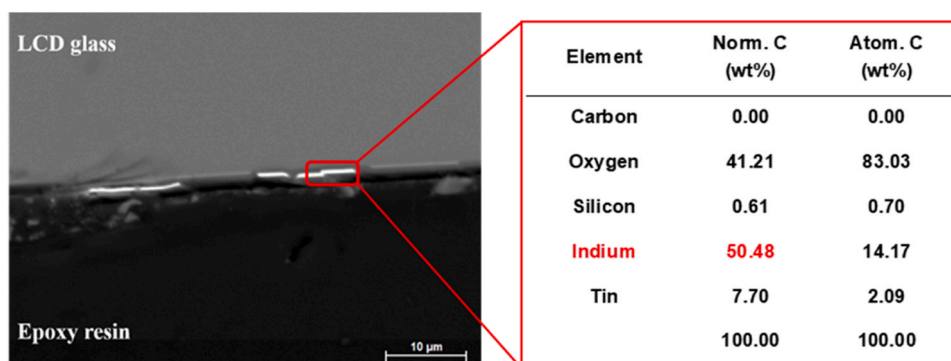


Fig. 2. The spent LCD glass cross-section structure by SEM (black color: epoxy resin, grey color: LCD glass) (left graph) and the compositions of elements on the red square point (right table) of EDX analysis.

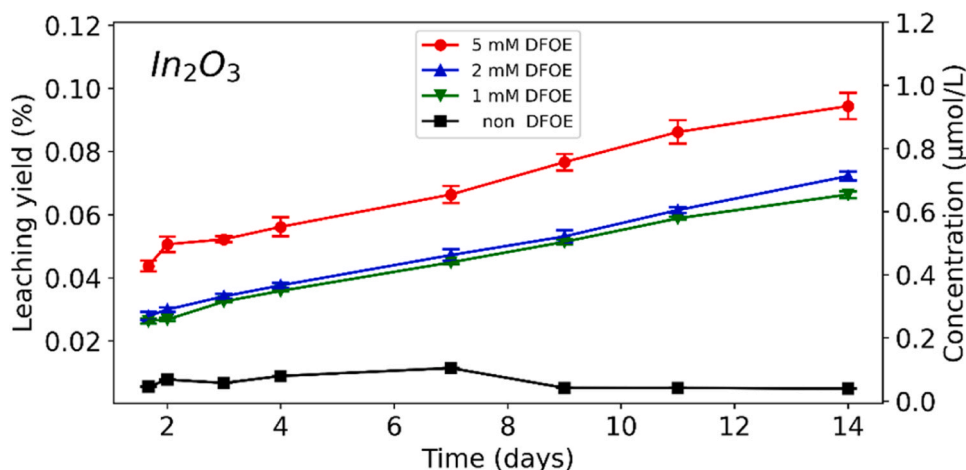


Fig. 3. In leaching efficiency by DFOE from chemical In_2O_3 ($500 \mu\text{M In}_2\text{O}_3$, particle size $< 45 \mu\text{m}$) with $n(\text{DFOE})/n(\text{In}) = 1, 2,$ and 5 at pH 7.19 with 10 mM KNO_3 over 14 days.

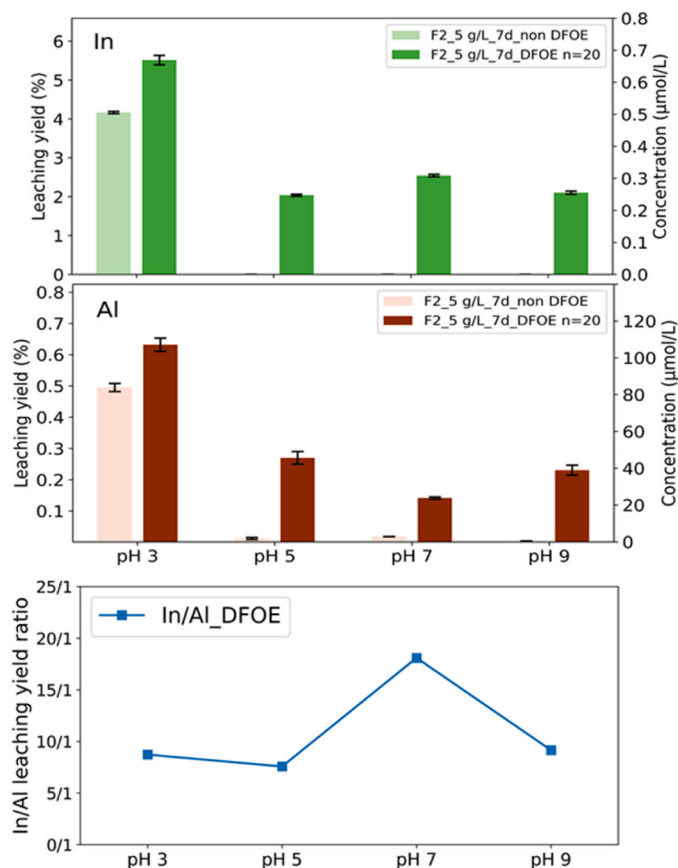


Fig. 4. Leaching yields and dissolved concentrations of In and Al both in the presence and absence of DFOE at different leaching pH levels, with F2 ($36\text{--}63 \mu\text{m}$) and 5 g/L of S/L ratio with $n = 20$ ($240 \mu\text{M DFOE}$) over 7 days, as well as In/Al leaching yield ratio in the presence of DFOE.

concentrations showed a slow increase. The initial total dissolved concentrations of DFOE were set to $12 \mu\text{M}$ ($n = 1$) and $24 \mu\text{M}$ ($n = 2$). It was observed that the total dissolved concentrations of Al after 2 days ($n = 1$) and after 9 days ($n = 2$) almost equalled the initial total dissolved concentrations of DFOE in the leaching process. However, when the DFOE concentration was more than $60 \mu\text{M}$ ($n > 5$), the dissolved Al concentration exceeded $32 \mu\text{M}$. Additionally, the dissolved In concentration also increased, but both of them were less than the initial

dissolved concentration of DFOE ($60 \mu\text{M}$).

In order to better understand the dynamics of DFOE speciation within the leachate, HPLC analyses were performed. These analyses monitored the evolution of Al-DFOE, In-DFOE, and free DFOE, with retention times of $10.10 \pm 0.05 \text{ min}$, $10.50 \pm 0.05 \text{ min}$, and $14.00 \pm 0.05 \text{ min}$, respectively. The results show that the concentration of In-DFOE and Al-DFOE complexes increased with a higher initial total concentration of DFOE (Fig. 5(c)). When n was set to 5 or 20, free DFOE remained detectable even after 14 days. In contrast, at n value of 1 or 2, free DFOE was undetectable, and the signal for In-DFOE complexes was low, despite the peak area of Al-DFOE complexes being relatively high. Higher DFOE concentrations were found to enhance In leaching yields, but the formation of metal-DFOE complexes required time to reach the chemical equilibrium, especially at $240 \mu\text{M DFOE}$ ($n = 20$).

The results show that increasing the total initial dissolved free DFOE improved the leaching yields, not only for Al but also for In. In HPLC analysis, the In-DFOE complex intensity decreased from 2 to 14 days when the n value equals to 2, while the Al-DFOE complex intensity increased (Fig. 5(d)). This increase in Al-DFOE complex intensity was accompanied by a decrease in the free DFOE and In-DFOE complex intensities. One plausible explanation could be the competitive binding of Al with DFOE within the In-DFOE complexes. This competition might have contributed to the solubility of In, followed by its subsequent precipitation. The detailed mechanisms supporting this hypothesis are discussed in Section 3.6.

3.3.3. Effect of particle size

The leaching processes were conducted to determine the optimal particle size (F1 to F3) in spent LCD mix powder, using 5 g/L of $n = 2$ ($24 \mu\text{M DFOE}$) over a period of 14 days (Fig. 6). Optimal yields were obtained with the finest size fraction (less than $36 \mu\text{m}$, F1) within the first 2 days, after which the total dissolved In concentrations began to decrease. Among these fractions, F2 provided the highest In leaching yield after 4 days. Beyond 11 days, F3 outperformed the others, yielding the highest amount of leached In. Decreasing yield was observed in the F2 experiments after 9 days. Meanwhile, the total dissolved Al concentrations remained constant and almost reached the total initial dissolved DFOE concentrations ($24 \mu\text{M}$) after 2 days for F1 and 9 days for F2. In the case of fraction F3, the total concentration of dissolved Al continued to increase over the 14-day period and stayed below the initial total DFOE concentration of $24 \mu\text{M}$. However, the leaching yield for fraction F3 was found to be lower than that observed for fractions F1 and F2 over the same period.

These observations suggest that the decrease of In concentration and the increase of Al concentration are associated with decreasing free

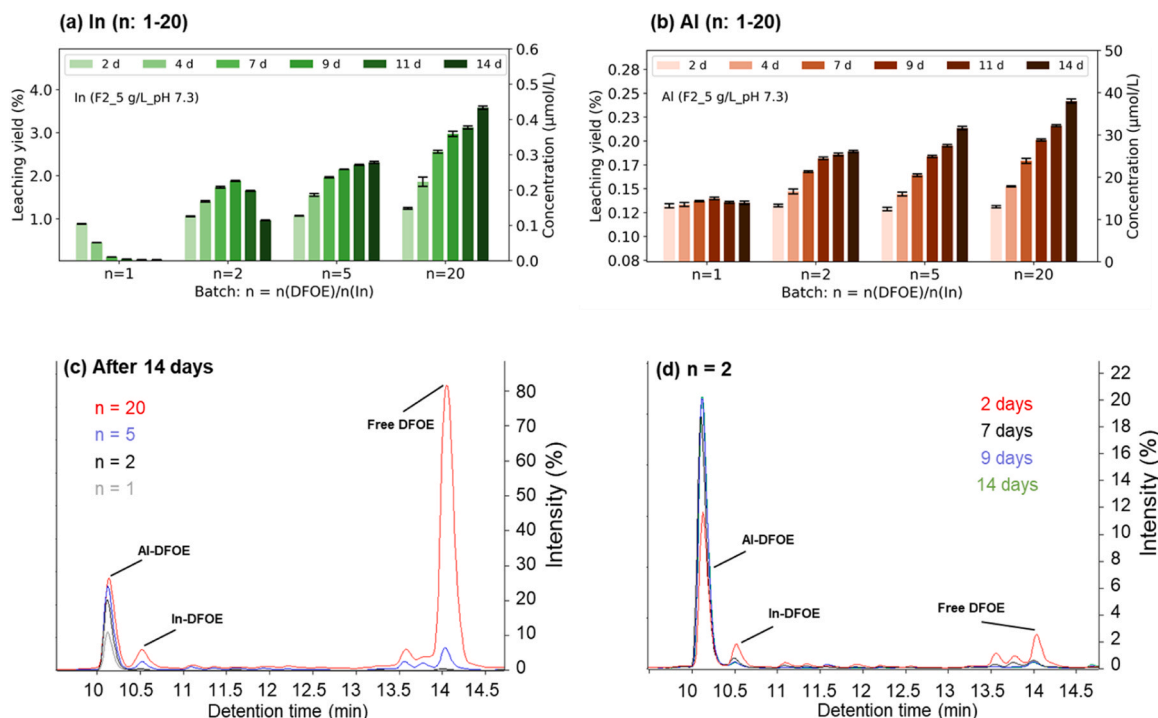


Fig. 5. The dissolved concentration of In (a) and Al (b) in different $n(\text{DFOE})/n(\text{In})$ ratios $n = 1, 2, 5,$ and 20 ($12\text{--}240 \mu\text{M}$ DFOE) in leaching with F2 ($36\text{--}63 \mu\text{m}$) and 5 g/L of S/L ratio at pH 7.33 over 14 days. Leachates analyses after 14 days with different n ($1\text{--}20$) at pH 7.3 (c), and when $n = 2$ ($24 \mu\text{M}$ DFOE), leachates analyzed after $2, 7, 9,$ and 14 days (d) by HPLC.

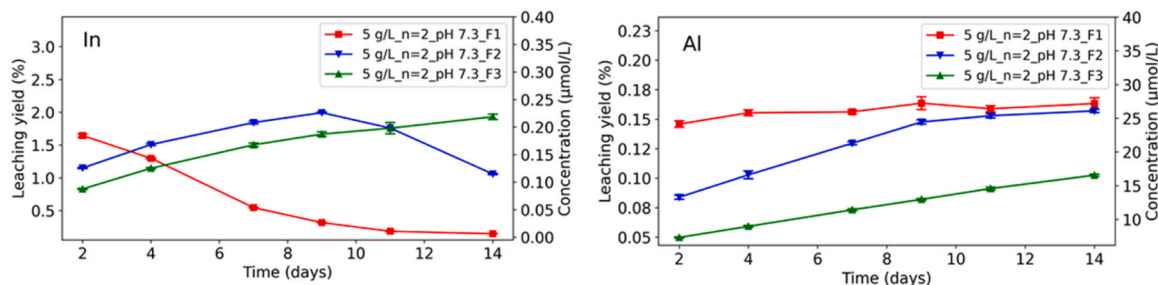


Fig. 6. The dissolved In and Al concentrations in different fractions (F1: $0\text{--}36 \mu\text{m}$; F2: $36\text{--}63 \mu\text{m}$; F3: $63\text{--}125 \mu\text{m}$) in leaching with S/L = 5 g/L of $n = 2$ ($24 \mu\text{M}$ DFOE) at pH 7.33 over 14 days.

DFOE concentrations. Sustaining an adequate concentration of DFOE may mitigate a decline in the In leaching yield and could potentially result in further increases, even beyond 2 days for F1 and 9 days for F2. Therefore, based on these observations, the fraction F1 potentially represents the optimal particle size for leaching with an adequate DFOE concentration.

3.3.4. Effect of solid-to-liquid ratio (S/L ratio)

The total dissolved concentrations of DFOE were adjusted to $4.8 \mu\text{M}$, $24 \mu\text{M}$, and $96 \mu\text{M}$ for distinct S/L ratios of 1 g/L , 5 g/L , and 20 g/L , respectively, to maintain a constant $n(\text{DFOE}/n(\text{In}))$ ratio at 2 . The optimal S/L ratios for achieving a high In leaching yield were found to be 5 g/L within 11 days and 1 g/L beyond 11 days of leaching (Fig. 7). Nevertheless, a decline in the In leaching yield was observed after a 9-day period when the S/L ratios were established at 5 and 20 g/L .

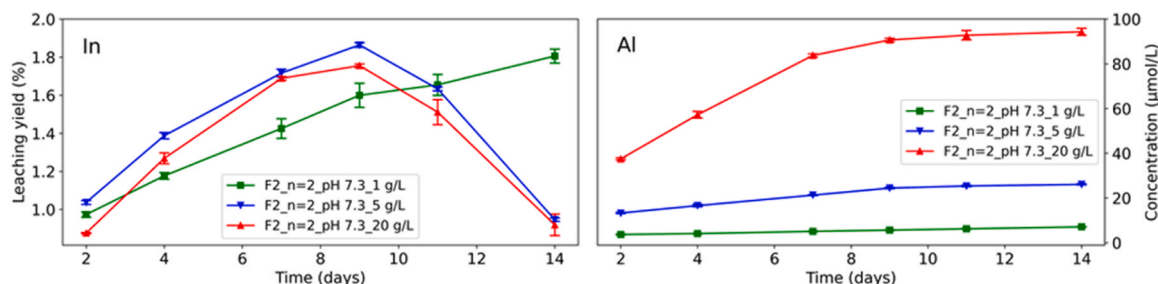


Fig. 7. The leaching yield of In and the dissolved Al concentration in different S/L ratios with F2 ($36\text{--}63 \mu\text{m}$) of $n = 2$ ($4.8\text{--}96 \mu\text{M}$ DFOE) at pH 7.33 over 14 days.

Concurrently, the total dissolved Al concentrations approached the initial quantities of DFOE added, namely 24 μM for the 5 g/L ratio and 96 μM for the 20 g/L ratio, while increasing slowly.

These observations collectively suggest that the main factors influencing the dissolution of In and Al include the availability of DFOE in the leaching medium, as well as particle size and the S/L ratio. Thus, a S/L ratio of 5 g/L potentially represents the optimal condition for leaching with an adequate DFOE condition.

3.3.5. Effect of temperature

The effect of leaching temperature (25 °C, 40 °C, and 55 °C) on the In leaching yields was evaluated at optimal conditions of pH 7.33 with S/L = 5 g/L of $n = 20$ (240 μM DFOE) over 14 days (Fig. 8). The leaching yields of In and Al were improved when the temperature was increased from 25 °C to 55 °C. The dissolved In concentration at 55 °C was twice as high as that at 25 °C after 14 days. Considering the goal to minimize Al dissolution and achieve selective leaching of In, 25 °C was determined to be the most suitable for optimal leaching temperature.

3.4. Characterization of LCD mix powder before and after leaching

The SEM images of the spent LCD mix powder before and after leaching show that a finer particle size might be good for leaching with DFOE, as evidenced by a decrease in the proportion of fine particles after leaching compared to before leaching (Fig. S4 (a) and (b)). Meanwhile, In hot spots were observed at the surface of the leached spent LCD mix particles (Fig. S4 (c) and (d)). This observation suggests that In could be precipitating and becoming visible on the surface of residues after 14 days of leaching. The specific mechanisms underlying this hypothesis are discussed in Section 3.6.

3.5. Modeling by ECOSAT

Before proceeding with the modeling, the stability constants of metal-DFOB and metal-DFOE complexes were compared with the available data, as shown in Fig. S6. Regarding the evaluation of equilibrium partitioning of DFOB/E compounds, the linear free-energy relationships (LFER) were used to understand the binding ability between different chemical species with DFOB/E. The results show that the metal-DFOB/E complexes have a good linear correlation ($R^2 = 0.9963$), with the slope (0.9698) almost equals to 1, which means that metals, such as Fe(III), have almost the same binding properties between DFOB and DFOE. Therefore, the stability constants of In-DFOB and Al-DFOB complexes can serve as proxies for the K values used in modeling In-DFOE and Al-DFOE complexes.

The speciation modeling conducted for the leaching of In_2O_3 by DFOE process, specifically focusing on species variation of different pH levels, was performed independently of other elements. This study utilized the initial total concentration of 10 μM In and 200 μM DFOB, corresponding to n equals to 20. The modeling considered the presence of mineral phases (In_2O_3 and $\text{In}(\text{OH})_3$), as shown in Fig. S7. The calculations showed that the major speciation of In was free In^{3+} when pH

was below 3. The major species was the complex $\text{In}(\text{HDFOB})^+$ (> 80% In) for the pH interval of 4 to 8, while mineral $\text{In}(\text{OH})_3$ was the major form of In for the pH interval of 8 to 10.

The speciation modeling was also performed using spent LCD mix leachates (representing the major dissolved metal concentration after 14 days at pH 7) in the same conditions and initial total solid In concentration with different DFOB concentrations for n ranging from 1 to 20. The modeling initially allowed for the presence of the mineral phase In_2O_3 , and both In_2O_3 and $\text{In}(\text{OH})_3$ minerals were considered to be present during the process (Fig. 9). When n equals to 1 or 2, the leaching process was 100% controlled by mineral $\text{In}(\text{OH})_3$. Even when n equals to 20, mineral $\text{In}(\text{OH})_3$ still controlled about 20% of the In dissolution. Thus, the chemical modeling suggested that In precipitates as $\text{In}(\text{OH})_3$ when $n \leq 20$. The major speciation for the total dissolved In was the complex $\text{In}(\text{HDFOB})^+$, as shown in Fig. 9. Given the analogous characteristics of DFOE and DFOB, the InHDFOE speciation aligns with the experimental findings of In dissolution achieved through the use of DFOB. The presence of DFOE affects the chemical equilibrium by forming highly stable complexes with In, which suppresses the formation of indium hydroxide. Comparable observations in Ga-DFOB complexes illustrate $\text{Ga}(\text{HDFOB})^+$ also as a major speciation at pH 2–9 [38].

This observation indicates that the 'hot spots' observed on the surfaces of the residues after leaching are confirmed to be indium hydroxide ($\text{In}(\text{OH})_3$) (Fig. S4 (d)). This finding could explain the observed decrease of In concentration after an initial increase during the leaching process with different n ratios, particle sizes, and S/L ratios experiments.

3.6. Indium leaching selectivity from spent LCDs in the presence of DFOE

DFOE selectively leaches In without significantly enhancing major elements leaching (i.e. Si, Ca, Sr, and Ba), primarily due to the neutral pH of the leachate. Additionally, the stability constants of major

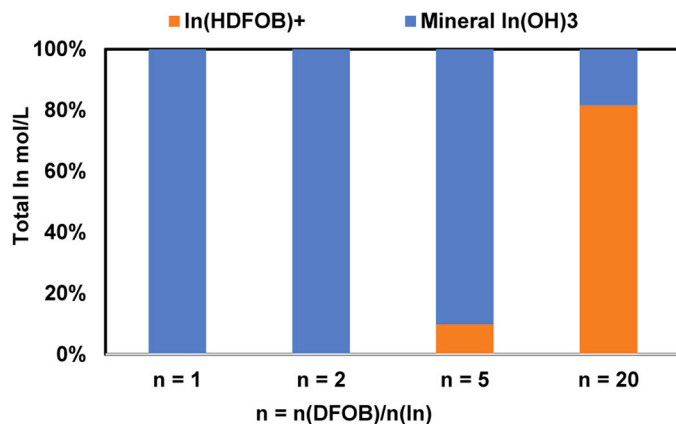


Fig. 9. The speciation modeling running for spent LCD mix leachates analyses with DFOB as proxy of DFOE.

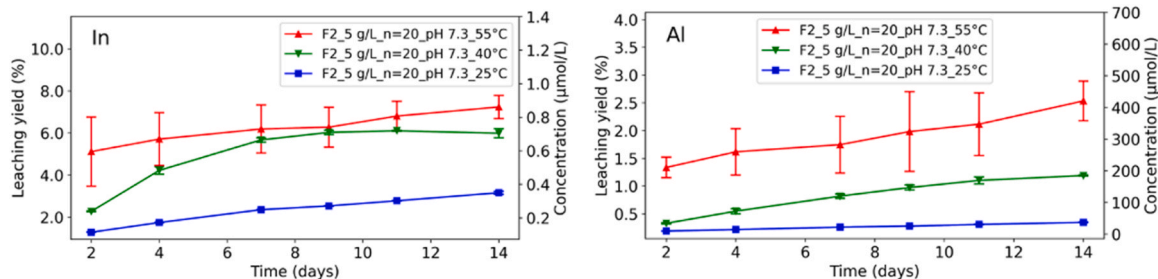


Fig. 8. The dissolved concentration of In and Al at different temperatures in leaching with F2 (36–63 μm) and S/L = 5 g/L of $n = 20$ (240 μM DFOE) at pH 7.33 over 14 days.

elements like Ca^{2+} with DFOE are much smaller than those of In or Al [23]. However, Al, as a critical competitor, negatively influences selective In leaching when DFOE concentration is low. This phenomenon is better understood by contrasting the behaviors observed in pure mineral In_2O_3 -DFOE leaching with those in spent LCD mix leaching under comparable conditions. In the former, there is a continuous increase in the total dissolved In concentration, unlike the latter. This contrast serves to emphasize the impact of Al and other competing elements on the interplay between In and DFOE, as illustrated in Figs. 5–7. The decreasing kinetic trend of dissolved In concentration is observed when n equals to 1 and 2. This is attributed to the competition between Al and In for complexation with DFOE, resulting in the decomplexation of In-DFOE. Decomplexation releases In ions, which can then precipitate as a result of hydrolysis at pH 7, as illustrated in Fig. 10. This phenomenon is further confirmed by HPLC analyses, which validate the competition between Al and In for DFOE complexation. The observed decrease in total dissolved In concentration, as evidenced in the particle size and S/L ratio leaching tests (shown in Fig. 6 and Fig. 7), can be explained by this precipitation. Speciation modeling supports that In $(\text{OH})_3$ precipitation increases with a deficit of DFOE which preferentially binds with Al, as confirmed by SEM-EDX mapping analyses (Fig. S4 (d)). Moreover, similar competitive dynamics have been documented from previous research, where Al also competed with In for DFOE binding, leading to the formation of an Al-DFOE complex and the precipitation of $\text{In}(\text{OH})_3$ [44]. The fast kinetics of siderophore DFOB promoted the dissolution of hausmannite (Mn_3O_4) compared to common iron oxide. The DFOB-promoted dissolution of Mn(III)-bearing minerals may compete with Fe(III)-DFOB complexation from Fe(III)-bearing minerals, mirroring the Al and In competition observed in our study [39].

3.7. Long-term In leaching from LCD mix powder

The previous results indicated that a higher DFOE concentration ($n > 20$, more than 240 μM) and longer leaching time were required to improve the In leaching yield. Therefore, high DFOE concentrations (0.5–5 mM, n ratio: 200–2000) and long leaching times (over 120 days) were tested with the S/L ratio of 1 g/L on the finest LCD mix powder fraction (F1) with pH 5.5 at 25 °C. To achieve a high $n(\text{DFOE})/n(\text{In})$ ratio without exceeding DFOE solubility limits, the S/L ratio was set to 1 g/L. The pH was set to 5.5 to minimize major Si dissolution (Fig. S8). To prioritize energy conservation, we chose 25 °C instead of the optimal leaching temperature of 55 °C. The best In leaching efficiency was around 32%, more than 10 times higher than that of Al (2.6%) after 90 days with 5 mM DFOE (Fig. 11 a and b). A higher DFOE concentration

improved the In leaching yield but reduced the Al leaching yield on the same collection time. For example, the In leaching yield was 32% with 5 mM DFOE, higher than that (22%) with 0.5 mM DFOE over 90 days. In contrast, the Al leaching yield was 2.6% at higher DFOE conditions (5 mM), which was lower than that (3.4%) at 0.5 mM DFOE. HPLC analyses were performed on leachate samples collected after 15 and 90 days. The In-DFOE complex peak area intensity increased with the increasing DFOE concentration (from 0.5 mM to 5 mM). In contrast, the Al-DFOE complex peak area intensity was minimally affected by the increasing DFOE concentration after 15 days (Fig. 11 c) and 90 days (Fig. 11 d) of leaching.

The enhanced efficiency in In leaching and the simultaneous reduction in Al dissolution underscore the selectivity of In when higher concentrations of DFOE are employed. However, there is potential for further improvement in the yield of In leaching. Exploring selective pre-treatment methods before leaching, such as the separation of indium tin oxide (ITO) layers from spent LCD glass, can augment In content while minimizing the presence of competing elements, like Al [40]. The repeated use of fresh or recycled DFOE for subsequent leaching cycles is expected to further elevate the recovery yield of In. Additionally, employing ultrasonic-assisted leaching may expedite the leaching process and improve the liberation of In and hence increasing the binding efficiency of DFOE with In. Alternatively, the use of siderophore with higher solubility can increase the kinetics of In dissolution. It may affect the selectivity and hence a compromise on the increased kinetics and lower selectivity needs to be achieved. These strategies are intended to boost the efficiency of In leaching in future investigations.

Post-leaching, the leachates could undergo further processing using the "GalIophore technology" for the sustainable recycling of In and DFOE [21]. The High-Performance Liquid Chromatography (HPLC) column facilitates the separation of free DFOE and the targeted In-DFOE complex from other chemical species. The addition of an excess amount of ethylenediaminetetraacetic acid (EDTA) enables the displacement of DFOE bound to metal ions, thereby effectively recovering the used DFOE and forming an In-EDTA complex. This recovery is also achieved in the "GalIophore technology" using a chromatography approach. This approach is economically advantageous due to the cost-effectiveness of EDTA and ensures environmental sustainability through a nearly neutral pH process.

For the subsequent recovery and purification of In from the In-EDTA complex, several established methods could be considered. These methods include electrochemistry [41], bipolar membrane electroanalysis [42], substitution by metal ions followed by precipitation, cementation, and electrowinning, all of which could be employed for the recovery and purification of In [12].

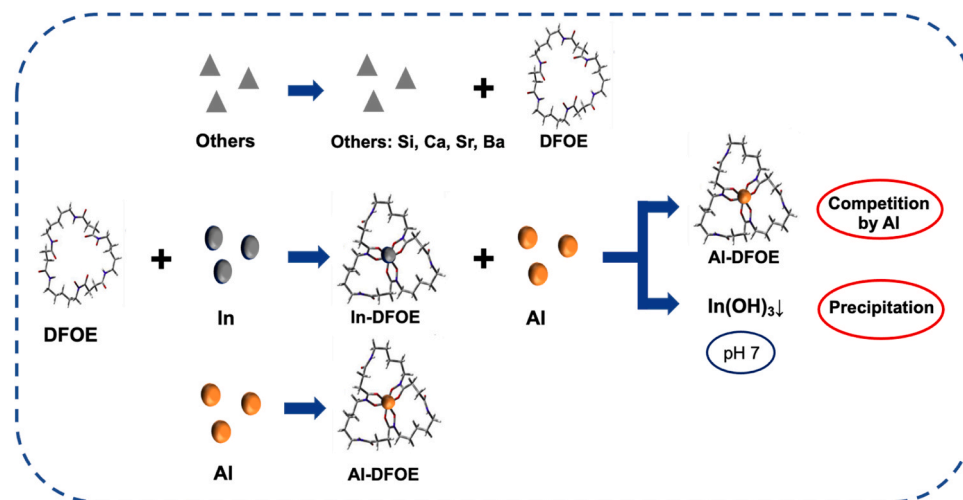


Fig. 10. The competitive interaction in the complexation of DFOE between In and Al.

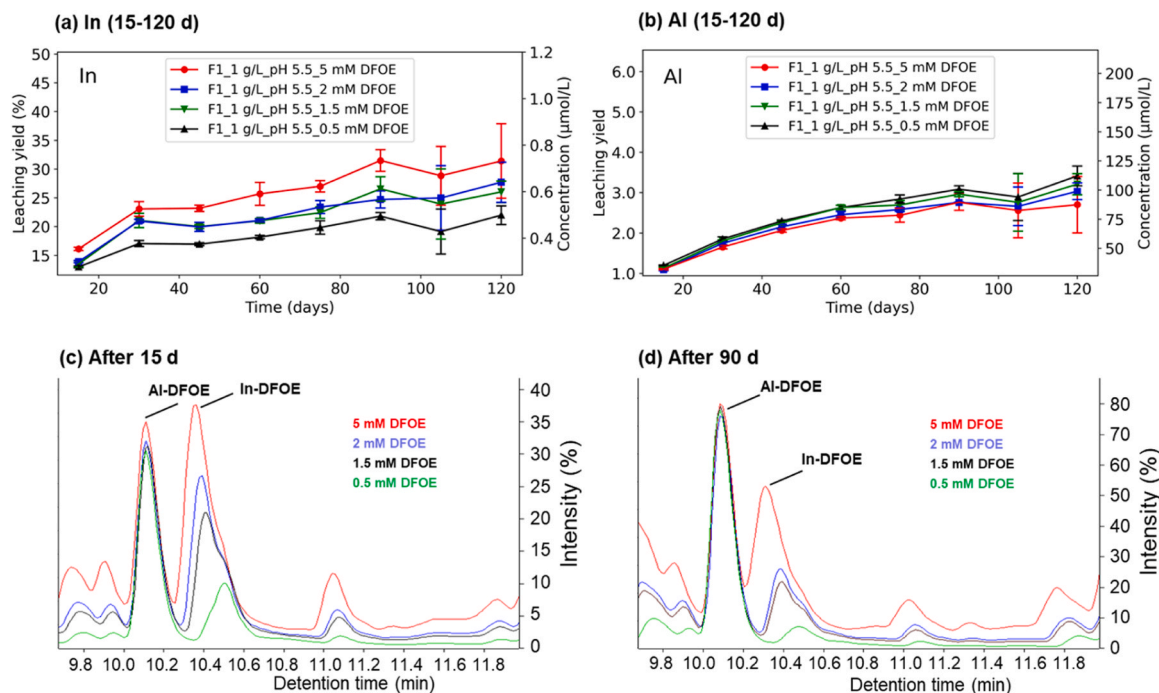


Fig. 11. Leaching kinetics of In (a) and Al (b) from spent LCD mix powder in the presence of increasing DFOE concentration (S/L ratio of 1 g/L on the finest LCD mix powder fraction (F1: 0–36 μm) with pH 5.5 at 25 $^{\circ}\text{C}$). Leachate analyses after 15 days (c) and 90 days (d) by HPLC with higher concentrations of DFOE (0.5 mM to 5 mM) at pH 5.5.

Compared to traditional hydrometallurgy and biohydrometallurgy, our novel bio-based technique, DFOE selective leaching, demonstrates substantial promise for In recovery. Although the use of mineral acids (i. e. HCl, HNO₃, and H₂SO₄) are well-established and generally offer high leaching yields (> 99%), they are accompanied with environmental and safety concerns. Furthermore, it leads to the non-selectively extraction of elements from matrices rich in dominant metals and the requirement for further purification [5,7,24,27,32]. While, organic acids (i.e. oxalic, citric, and malic acids) are more environmentally friendly, they exhibit limitations in efficiency, application, and further purification [13,16, 17]. Bioleaching with *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* is environmentally friendly but slower and requires microbial control and bacterial adaptation [14,19,43]. In our study, we introduce an ex-situ bio-based technology, siderophore-DFOE leaching, which combines the advantages of bioleaching with the environmental benefits of ligand assisted leaching. This innovative approach is environmentally friendly, exhibits high selectivity, allows for the recycling of used DFOE, and eliminates the need for complex purification steps. Siderophore-DFOE selective leaching thus highlights the principles of a sustainable economy.

4. Conclusions

Indium primarily resides within the ITO layer on spent LCD surfaces, with an average concentration of 257 ± 133 mg/kg in spent LCD powders, establishing it as a valuable secondary source of In.

Our methodology, employing the DFOE siderophore, was tailored toward selectively leaching In from spent LCD powder. This approach demonstrated that the leaching process crucially depends on the concentration of DFOE, playing a pivotal role in alleviating Al competitive influence and facilitating efficient In extraction. Our findings, substantiated by ECOSAT speciation modeling, elucidate how DFOE forms stable complexes with In, effectively preventing the formation of indium hydroxide precipitates. However, at lower DFOE concentrations (12–240 μM), Al competes with In for complexation, resulting in the precipitation of In(OH)₃ and formation of the Al-DFOE complex.

The highest achieved In leaching yield reached approximately 32% by elevating the DFOE concentration up to 5 mM after 90 days. This efficiency was attained using a solid-to-liquid ratio of 1 g/L, specifically with the finest LCD mix powder (F1), maintaining a pH of 5.5 at 25 $^{\circ}\text{C}$, thereby delineating the sub-optimal conditions for this process. These outcomes underscore the potential for refining and optimizing the leaching process for enhanced In recovery from waste LCDs.

This bio-based technology represents an environmentally sustainable method and highlights the principles of a sustainable economy. It will allow for the recycling of used DFOE through the “GaLlophore technology”, thereby facilitating the establishment of a closed-loop system within the circular economy framework. Compared to traditional methods, DFOE leaching presents significant potential for selective and sustainable In recovery from electronic waste.

Environmental implication

Improper disposal of e-waste can result in the release of hazardous materials, causing environmental pollution. Waste LCDs, containing significant indium concentration, provide a secondary resource for indium recovery, thereby enhancing e-waste utilization and reducing its environmental footprint. Indium recovery is essential for resource sustainability, yet existing recycling technologies lack comprehensive solutions. Our innovative approach, employing the siderophore DFOE, facilitates the selective leaching of indium even in the presence of highly concentrated non-target elements. This method integrates hydrometallurgy and biohydrometallurgy, presenting an eco-friendly and efficient strategy. Moreover, the used DFOE can be recycled to maintain the integrity of the recycling chain.

CRedit authorship contribution statement

Katrin Pollmann: Funding acquisition. **Bradley Guy:** Formal analysis, Writing – review & editing. **Rohan Jain:** Supervision, Writing – review & editing. **Marc F. Benedetti:** Conceptualization, Funding acquisition, Software, Supervision, Writing – review & editing. **Eric van**

Hullebusch: Conceptualization, Funding acquisition, Supervision, Writing – review & editing. **Kun Zheng:** Conceptualization, Data curation, Writing – original draft, 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.

Data Availability

Data will be made available on request.

Acknowledgments

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Supporting information

Additional methods (Text S1-S2), data collection, calculations, and other results (Figs. S1-S8, Tables S1-S5).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2024.134013](https://doi.org/10.1016/j.jhazmat.2024.134013).

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