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Chelant-Induced Reclamation of Indium from the Spent Liquid Crystal Display Panels with the Aid of Microwave Irradiation

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Abstract

Indium is a rare metal that is mostly consumed as indium tin oxide (ITO) in the fabrication process of liquid-crystal display (LCD) panels. The spent LCD panels, termed as LCD-waste hereafter, is an increasing contributor of electronic waste burden worldwide and can be an impending secondary source of indium. The present work reports a new technique for the reclamation of indium from the unground LCD-waste using aminopolycarboxylate chelants (APCs) as the solvent in a hyperbaric environment and at a high-temperature. Microwave irradiation was used to create the desired system conditions, and a substantial abstraction of indium ($\geq$ 80%) from the LCD-waste with the APCs (EDTA or NTA) was attained in the acidic pH region (up to pH 5) at the temperature of $\geq$ 120 °C and the pressure of ~ 50 bar. The unique point of the reported process is the almost quantitative recovery of indium from the LCD-waste that ensured via the combination of the reaction facilitatory effect of microwave exposure and the metal extraction capability of APCs. A method for the selective isolation of indium from the extractant solution and recycle of the chelant in solution is also described.

1.0 Introduction

Indium is an element having no ore of its own and rather available in association with zinc, lead, copper, and tin ores [1]. The most important end use of indium in recent years is to manufacture indium-tin oxide (ITO), which consume about two-third of the global indium production [2]. ITO, the Sn-doped In_2O_3, is widely used to fabricate various optoelectronic devices, such as, liquid-crystal displays (LCD), plasma displays and solar-energy cell [3]. The technology revolution and the economic policies of the nations with indium reserves (*e.g.,* China and South Korea) has created increasing demand for indium and so also a boom in its price resulting in a tag of 'rare metal' for indium. Consequently, other than the refinery production, the reclaim processing of indium from secondary materials also become important [1, 2, 4]. The ITO-scrap is the most potential secondary resource of indium that extensively studied for the recovery of indium [3-6], while the etching waste [7, 8] and the LCD powder [4, 9, 10] are the other prospective waste resources of indium.

The spent LCD panels, termed as LCD-waste hereafter, from computer and TV sets are an emergent contributor to the global e-waste burden owing to their popularity as consumer goods and the decreasing life-span of the electronic products due to the fast-paced innovations or built-in obsolescence [11, 12]. Besides the environmental impact, an assuming possibility of indium-induced cytotoxicity and the risk for interstitial lung damage due to the emission of sparingly soluble indium compounds from the ITO manufacturing and recycling plant have been reported [8, 13, 14]. Although the reclamation of indium from LCD-waste using a safer and cleaner process is becoming an increasing concern in terms of the economics, environment or owing to the possibility of toxic exposure, a few research reports are available in the literature [4, 9, 10].

Several solvent types, which include carboxylic acids, phosphoric acid derivatives (*e.g.,* di-2-ethylhexylphosphoric acid), chelating compounds (*e.g.,* hydroxyoximes and azoles), and solvating extractants (*e.g.,* tributyl phosphate, trioctylphosphine oxide and methyl isobutyl ketone) have been used to recover indium from the potential resources [4, 15]. EDTA, the most acclaimed aminopolycarboxylate chelants (APCs), has been used for the selective back-extraction of indium from an anion-exchange resin during the process of indium separation

from the spent catalysts [16]. However, APCs have rarely been used to treat any vitrified waste [10] in spite of being praised for excellent metal-binding capacities and extensive use in the treatment of contaminated soil solids [17-20]. Hence, the current report is an effort to comprehend the potential of APCs for indium extraction from the ITO-film composed to a dense vitrified structure. The use of controlled microwave irradiation is indispensable in modern organic synthesis due to its affectivity in the enhancement of reaction velocity [21, 22]. The reaction facilitatory effect attained from the microwave exposure induced high temperature and hyperbaric condition, and the superior affinities of the APCs toward metals are successfully combined in the proposed process for the quantitative reclamation of indium from the LCD-waste, which was not reported before. In addition, a schematic outline for the selective isolation of indium from the indium-enriched chelant solution is discussed.

2.0 Experimental

2.1 Materials

2.1.1 LCD-Waste

LCD panels supplied from Furuchi Chemical Corporation (Tokyo, Japan) were cut into 1 cm × 1 cm size, and were used as the LCD-waste sample.

2.1.2 Aminopolycarboxylate chelants

Imminodisuccinic acid (IDSA) from LANXESS AG (Leverkusen, Germany), nitrilotriacetic acid (NTA) and disodium dihydrogen ethylenediamine tetraacetate dihydrate (EDTA) from Kanto Chemical (Tokyo, Japan), N-(2-hydroxyethyl)iminodiacetic acid (HIDA) and diethylenetriamine-N,N,N´,N´´,N´´´-pentaacetic acid (DTPA) from Dojindo Laboratories (Kumamoto, Japan) was used. The chemical structures of APCs are available as the supplementary material (see Fig. S1), and the data-sets used to explain the complexation behavior of indium with the APCs are listed in Table 1. The acid dissociation constants (pK_a) of the chelants and the stability constants ($\log K_{ML}$) of indium-chelant complexes are extracted from the 'NIST standard reference database of critically selected stability constants of metal complexes' [23]. The conditional stability constants ($\log K´_{ML}$) at different solution pH for 1:1 chelant-to-indium ratio is calculated using the computer program HySS2009 [24].

2.1.3   Solid-phase extraction materials

Five solid-phase extraction (SPE) options of the AnaLig TE-series (TE 01, TE 06, TE 07, TE 09 and TE 13) from GL Sciences (Tokyo, Japan) were evaluated for the treatment of the indium-containing chelant solution. The SPE-type contains macrocyclic materials, covalently attached to the inert silica or polymeric support materials, and commonly known as molecular recognition technology (MRT) gel. The particles of the MRT-SPE materials have the mesh size of 60–100 and binding capacity of 0.1–0.3 mmol g^{-1}.

2.1.4   Reagents

Analytical reagent grade chemicals were used throughout without further purification. The Plasma-CAL multi-element solution A and B from SCP Science (Québec, Canada) and Sn-1000 from Kanto Chemical (Tokyo, Japan) were used to prepare the standards for metal concentration measurements. The solution pH was adjusted as desired using either HCl or NaOH (1 mol L^{-1}) from Kanto Chemical (Tokyo, Japan). Acetic acid/sodium acetate from Kanto Chemical (Tokyo, Japan) or 2-(*N*-morpholino)ethanesulfonic acid monohydrate (MES) from Sigma-Aldrich (St. Louis, MO), and 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) from Nacalai Tesque (Kyoto, Japan) were used as the buffer reagents to maintain the solution pH in the acidic and neutral domains, respectively. The pH in the alkaline domain was maintained using *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (TAPS) or 3-(cyclohexylamino)-1-propanesulfonic acid (CAPS) buffer from MP Biomedicals (Solon, OH).

2.1.5   Laboratory wares

Low-density polyethylene bottles from Nalge Nunc (Rochester, NY), perfluoroalkoxy tubes and micropipette tips from Nichiryo (Tokyo, Japan) were used throughout the experiments. A careful cleaning of the laboratory wares was ensured following the process described by Hasegawa *et al.* [25] before and after each use.

2.2 Instrumentation

The Multiwave 3000 microwave reaction system from Anton Paar GmbH (Graz, Austria) equipped with 8-position rotor and hydraulic pressurized sensing system for all

vessels was used. The heating program of the microwave reaction system is available as the supplementary material (See Fig. S2). The Digiprep Jr block heater from SCP Science (Quebec, Canada) and the MLS-3750 automatic autoclave from Sanyo Electric (Osaka, Japan) were also used as the instruments for heating.

The BP-1 ceramic pot mill with alumina balls (HD-8, HD-10 or HD-15) from AS ONE (Osaka, Japan) combined with the AV-1 mill pot rotator from Asahi Rika (Chiba, Japan) was used for the milling treatment of the LCD-waste to prepare the ground powder sample used for the comparative study and process parameter optimization. The milling was conducted for a period of 0.5−10 h and at a rotating speed of 150 rpm.

The inductively coupled plasma optical emission spectrometer (ICP-OES) used for the metal analysis was the iCAP 6300 from Thermo Fisher Scientific (Waltham, MA) equipped with an EMT duo quartz torch, glass spray chamber and concentric glass nebulizer. The operating conditions of the ICP-OES system are available as the supplementary material (see Table S1).

The high-performance liquid chromatography (HPLC) system used to verify the chelant concentrations was TOSOH 8020 from Tosoh (Tokyo, Japan). The HPLC system was composed of a DP-8020 pump, an AS-8021 auto sample injector, a CO-8020 column oven, a PD-8020 UV-VIS detector, the PD-8020 data processing software, and TSK-gel ODS-80TM octadecylsilica columns (4.6 mm i.d. × 250 mm and 4.6 mm i.d. × 150 mm). The mobile phase solution (5 mM ammonium dihydrogenphosphate, pH 2.4) was pumped at a flow rate of 0.5 mL min^{-1} at 25°C. The injection volume was 20 µL, and detection was performed at 254 nm.

The Arium Pro water purification system from Sartorius Stedim Biotech GmbH (Göttingen, Germany) was used to prepare the ultrapure water (resistivity > 18.2 MΩ cm). The ultrapure water was used throughout either as the diluent for preparing the working solutions from the stock or for cleaning the laboratory wares. The Epsilon 3 energy dispersive X-ray fluorescence (XRF) analyzer from PANalytical (Almelo, Netherlands) was used to record the XRF data. The GL-SPE vacuum manifold kit from GL Sciences (Tokyo, Japan) in combination with the CAS-1 air pump from AS ONE (Osaka, Japan) was used during SPE

treatment. The Navi F-52 pH meter from Horiba Instruments (Kyoto, Japan) and a combination electrode was used for pH measurements.

2.3 Methods

2.3.1 Chemical analysis of the LCD-waste for the metal content

The LCD-waste sample was milled and 1.0 g of the sample was transferred into the pre-cleaned PTFE vessels of the microwave reaction system, and 10 mL of 6 mol L^{-1} HNO$_3$ was added to it. The microwave-assisted digestion process was conducted at 230 °C for 2 h. The microwave sample preparation and treatment process was based on the EPA method 3052, which allows variations in reagents and methodology depending on the variety of matrices and elements and frequently recommended for the multi-element chemical analysis [26-28].

After finishing the instrumental procedure, the extracts from the digestion process were filtered through the cellulose membrane filters of 0.45 µm pore size from Advantec (Tokyo, Japan) combined with a MAS-1 suction assembly from AS ONE (Osaka, Japan). The filtrate was then evaporated on a hot plate at 60 °C to reduce the volume to a few mL. Afterwards, the residue was diluted to 100 mL with ultrapure water and stored at 4 °C until being analyzed for metal concentrations using ICP-OES. A blank was treated with the same as the samples.

2.3.2 Chelant-assisted extraction of indium from LCD-waste

The 0.05 mol L^{-1} solutions of chelants (IDSA, HIDA, NTA, EDTA and DTPA) were prepared using ultrapure water and used for the extraction experiments. A series of pre-experiments using the milled LCD-waste as sample and EDTA as the reference chelant (0.01, 0.05, 0.10 and 0.15 mol L^{-1}) at room temperature and atmospheric pressure (solid/solution ratio – 1:100, pH – 7) were conducted to ascertain the chelant dose. In each case, the chelant concentrations were verified by the HPLC analysis. The pH of chelant solutions were adjusted using 0.1 mol L^{-1} buffer reagents (pH 3 and 5: acetic acid/sodium acetate, pH 7: HEPES, pH 9: TAPS, pH 11: CAPS), and a similar procedure was followed with ultrapure water to use as control.

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The effect of temperature changes on the indium extraction capability of chelants from LCD-waste was checked using a mixture of chelant and LCD-waste prepared at a ratio 100. The Digiprep Jr block heater assembly was used to study the temperature effect at 30–98 °C. The effect of both temperature and pressure on the extraction yield in the range of 120–135 °C was checked using the autoclave, while the microwave reaction system was used for 80–240 °C. The extracts were separated from the solid fractions after each of the processes using the cellulose membrane filter, and sent for ICP-OES analysis. Three replicates for each of the experiments were performed, and the average values are reported.

2.3.3 *Separation of indium from the washing solution*

MRT-SPE material packed in 5 mL polypropylene cartridges were used for the isolation of indium from the chelant solution at different pH-environment (5, 6.5, 8 and 10). The total process consisted of five individual steps namely rinsing, conditioning, sample loading, washing and elution. The HNO_3 and ultrapure water was used at the rinsing step while the SPE-cartridges were conditioned at the desired pH-conditions using MES, HEPES or TAPS buffer solution. Sample solution, pH-adjusted with appropriate buffer solution, was loaded at the flow rate of 0.2 mL min^{-1}. The next step was the washing with the ultrapure water followed by elution (1 and 6 mol L^{-1} HNO_3 + ultrapure water). More detail about the adopted separation arrangement, including the optimization of the aforementioned steps is described elsewhere [25].

3.0 Results and discussion

3.1 Chemical analysis of the LCD-waste

The microwave-assisted digestion extract of the LCD-waste sample was analyzed using ICP-OES against the multi-element standard containing Be, Mg, Al, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Cd, In, Ba, Pb, Bi, Y, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, U and Sn. The contents of other elements in the extract except In and Sn was below 14 mg kg^{-1}. The ITO-target mainly composed of In_2O_3 and SnO_2 at a mass ratio of 9:1 [29], which is applied on glass panels using DC magnetron sputtering process for the fabrication of LCD panels [3]. Therefore, such data pattern from the chemical analysis is expected. The

indium content in the LCD-waste samples was in the range of 380–410 mg kg^{-1} (averaged content $\pm$ SD – 393 $\pm$ 10 mg kg^{-1}, $n = 5$).

3.2 Effect of heat treatment approaches

Conventional heating methods transfer heat to the target by convection or conduction, and the reactor wall often receives more heat to achieve the required inner system temperature resulting in heat loss. On the contrary, microwave heating has the benefit to heat the target compounds without heating the entire reactor saving the time and energy [30]. Furthermore, microwave reaction system is equipped with the facility of pressure/temperature sensor to achieve accurate control of reaction environment at high temperatures and raised up pressure conditions [28]. The dissimilarity in the conventional heat transfer route with that of the microwave is illustrated in Fig. 1.

A comparison of the heat treatment approaches, *e.g.,* hotplate, autoclave and microwave exposure, indicate remarkable improvement in the chelant-induced extraction rates with the microwave irradiation (Fig. 2). The increase in the indium extraction with the intensification of the system temperature was notable only above 70 °C, and it became the maximum at 100 °C and 135 °C, respectively, with the hotplate and autoclave approaches. However, the dissolution rate was below 10%. The improvement in the indium dissolution rate with the microwave exposure was occurred rapidly starting from 100 °C and moved toward the equilibrium at ~140 °C. A high pressure condition of ~50 bar was also maintained within the reaction system during the process. Although the chelant-assisted extraction yield of indium increased from 10% to about 70% with the microwave exposure, the extraction of total indium content was not accomplished and an equilibrium condition was appeared instead. The reason might be the limited extractability of the chelants at the employed experimental condition. The dissolution of indium with the microwave exposure might have resulted from the distortion of the crystal structure, electronic polarization, etc. The occurrence can be accredited either to the temperature gradient between the bulk liquid and the solid phase known as the hot-spot effect [21] or the change in character of the water-based chelant solution system at high temperature and hyperbaric condition [31], as shown schematically in Fig. 3. Such changes cannot be expected through the application of conventional heat

treatment approaches, such as, hotplate, autoclave, even if the system temperature is raised to the possible maximum range.

3.3 Effect of the system conditions created by the microwave reaction system

3.3.1 Temperature

A varying number of temperature conditions is possible to create using microwave reaction system setup [30], and the effect of system temperature created in the range of 85–195 °C have been checked at a system pressure of ~50 bar (Fig. 4). The rate of indium dissolution from the LCD-waste has been increased with the increase in the system temperature at the constant hyperbaric condition and became almost quantitative at 195 °C (chelant: 0.05 mol L^{-1} EDTA, pH: 7, extraction time: > 60 min). However, the decomposition possibility of chelant is prominent at the high-temperature range in spite of the substantial rate of indium extraction (Fig. 5). The indium extraction yield above 150 °C remained unchanged (Fig. 2) in spite of the decomposition trend at temperatures ≥ 120 °C (Fig. 5). The manifestation is attributable to the presence of excess of chelant in solution (solid/solution ratio – 1:100). Although a partial decomposition of the chelant in solution was started to occur at ≥ 120 °C, the chelant-assisted extraction was accomplished with those remain in excess in the solution.

It should be noted that the commercial-scale application of the chelant-assisted solid waste treatment process is by far limited mostly due to the higher cost of reagents [17, 32]. Hence, the metal-extraction process that includes the use of chelant should have the option for recycling of the chelant for concurrent application after the recovery of metal to reduce the cumulative cost-factor [25, 33, 34]. It was observed that the temperature within the reaction system is better to be maintained ~120 °C for considerable removal of indium from the waste source without the eradication of the chelant and is, therefore, practiced.

3.3.2 Processing time

Microwave exposure assists to achieve a higher reaction velocity within the closed system in a hyperbaric environment and reduces the overall processing period [21, 30]. The effect of extraction time on the rate of indium dissolution at different temperature condition

can be assumed from Fig. 4. The rates of extraction yield have an increasing pattern until ~60 min and remain mostly constant thereafter (chelant: 0.05 mol L^{-1} EDTA, pH: 7). The XRF spectrum recorded at 135 °C in the presence of chelant in solution showed a decreasing peak for indium with the progress of time (see supplementary material, Fig. S3). Such XRF pattern can be correlated not only with the increase of the amorphous character of the LCD-waste but also with the time-dependent dissolution extent of indium from the vitrified panel. Hence, the removal of indium from the LCD-waste is possible to achieve at a very short treatment time (≥ 1 h) with the aid of microwave irradiation.

3.4 Extraction behavior of the chelants under the influence of microwave exposure

The chelants interact with the metal ions in solution usually leading to the formation of 1:1 molar ratio complexes, and the corresponding stability of the metal-chelant (ML) complexes depends on the total number of donor atoms and coordinating sites, and types of the donor atoms in the chelant [35]. The chelants (IDSA, HIDA, NTA, EDTA and DTPA) interact in a different way with the indium attached to the LCD-waste at the high temperature (135 °C) and high pressure (~ 50 bar) conditions created via microwave exposure than that observed at relatively mild temperature (85 °C) and atmospheric pressure (Fig. 6). The order of indium-chelant complex formation preferences at 85 °C was NTA > EDTA > DTPA > HIDA > IDSA while it was EDTA > NTA > HIDA > IDSA > DTPA at 135 °C (at neutral pH). The order of EDTA and NTA were in correspondence with their indium-chelant stability constant values at high-temperature hyperbaric condition (Table 1). The trend is, however, opposite when the temperature is comparatively mild and without any external pressure effect. The behavior can be attributable to the tendency of NTA of forming ML$_2$ species other than the ML species in solution when present in excess, while such propensity was absent for the EDTA [10]. However, such an effect may be suppressed at the high temperature and/or at a pressure-persuaded condition due to the higher dissolution proclivity of indium, or lesser rate of re-sorption of the ML complexes in the active surface sites of the solid matrix, etc. [20, 36].

The behavior of DTPA is an exception showing the much-lower extraction rate in spite of having the highest indium-chelant stability constants compared to the NTA or EDTA. In a

pure solution system, DTPA with five carboxylic groups and three amine groups can have higher complex formation constants with most heavy metals than NTA or EDTA as attributable to the eight coordinated complex formation capability of DTPA. However, the steric hindrance between DTPA and dissolved metals might play an important role in the mixed matrix solution. A slower rate of interaction between DTPA and the target metal species irrespective of the temperature conditions or at neutral pH can thereby be assumed [18, 20]. The lower pH of EDTA in solution is also mentioned as a reason for the lesser metal extraction capability of DTPA than the EDTA [37]. Such sub-standard metal-DTPA complex formation rate compared to the NTA or EDTA was also mentioned in the literatures [38, 39].

The stability information of the complexes of IDSA or HIDA with indium is yet to be available from any trustworthy sources and, hence, excluded from the comparative discussion. However, the corresponding patterns establish the fact that DTPA, IDSA or HIDA is not as suitable as EDTA or NTA for chelant-induced extraction of indium.

3.5 Effect of solution pH at varying range of microwave exposures

Extractant solution pH can influence the mechanisms of metal extraction from the solid waste by controlling the metal species concentration in the aqueous state and the solubility of chelants in solution [40-43]. However, the pH-dependent study with the chelants was required to be restricted within the pH range of 3–11 because of the insufficient solubility of the chelants (*e.g.*, EDTA) at very low pH in aqueous media [44]. The solution pH showed a diverse effect on the indium extraction yield at varying range of microwave exposures (Fig. 7). A considerable chelant-induced extraction of indium continued to occur at acidic pH until pH 5 with an inclination at neutral pH and became subtle in the alkaline domain. The extraction yields with NTA and EDTA at 135 °C were comparable with the change in the solution pH, while NTA showed superior performance than that of EDTA at 85 °C. The behavior of NTA at the mild temperature was presumably due to its better reaction velocity ($[In^{3+}]/dt$]) at acidic pH.

3.6 Ground powder vs. unground LCD-waste: Effect of chelant-assisted extraction aided by microwave irradiation

Ground powder sample of LCD-waste was usually recommended for the recovery of indium by solvent-induced extraction [9, 45]. However, we assumed the possibility of indium dissolution from the unground LCD-waste using the chelants with the aid of the microwave exposure because it facilitates the dispersion of heat energy within the reaction system via the excitation of molecules [30]. The comparison in the indium extraction yield with the change in system temperatures using the LCD-waste powder and unground sample is showed in Fig. 8. The rate of indium dissolution from the unground sample is superior. The reason may be the difference in the vibration frequencies between the vitrified surfaces of LCD-waste than that of the ITO thin-film, which cause the detachment of the indium-rich ITO layer. It should be considered that such an effect should also be present on smaller grains, as reported elsewhere [10]. However, the resonance effect exists on the larger pieces of LCD-waste, while such an action was absent for the powdered sample.

3.7 Isolation of indium from the chelant-rich aqueous solution

Strong basic mesoporous and macroporous anion exchange resins (Cl$^-$ form) can be used for the sequestration of indium [16], while the chelant used for the indium extraction in the proposed process might obstruct the separation behavior of the ion-exchange resins due to the competition effect [39]. A MRT-SPE, AnaLig TE-01, showed better separation efficiency than the chelating resins and the ion-exchange resins for the separation of toxic metal ions from the washing effluent containing APCs [25]. In the current work, four other MRT-SPE options (TE 06, TE 07, TE 09 and TE 13) from the AnaLig TE-series, including the AnaLig TE-01, have been evaluated for the separation of indium from chelant solution. The comparative indium retention and recovery behavior with the MRT-SPE cartridges were studied in terms of the solution pH (Fig. 9). A simulated sample solution composed of 1.0 mmol L^{-1} of indium and 10 mmol L^{-1} EDTA in H$_2$O matrix were used. A $\geq$ 90% retention and recovery rate was obtained with AnaLig TE 01 at pH 5.0 and with AnaLig TE 13 at pH 5.0 and 6.5. The selectivity in the indium isolation with the MRT-SPE is attributable to the formation of the 'host-guest' complex between the macrocycle and the target element in the

matrix based on the combination of size, configuration, electronic interaction, charge, wetting, and other factors [46]. The proposed separation scheme with the use of MRT-SPE has the subsequent advantage of recycle the chelant [25]. However, the ITO-thin film in the LCD-waste also contains tin as an ingredient, and the chelant-induced co-extraction of tin was likely with indium according to its corresponding ratio in the ITO. Hence, a sequential or preceding separation step using either the multiple-SPE combination [47], electrolytic [34] or cation exchange membrane separation [48] is required to collect indium in its purest form.

4.0 Conclusion

APCs are capable of extracting indium from the LCD-waste, and the efficiency can be substantial ($\geq 80\%$) with the application of microwave irradiation. The optimum conditions for the chelant-assisted recovery of indium from the LCD-waste with the aid of microwave exposure are as follows: temperature – 120–135 °C, pH – acidic (~5), processing time – ≥ 1 h, chelant – NTA or EDTA. The proposed technique has the following distinctive points to consider as compared to the other techniques: (a) application of chelant as the extractant that can be reused, (b) elimination of any pre-crushing step of the LCD-waste before the dissolution treatment, and (c) a significant reduction in the cumulative processing time. A close-loop system design is evaluated to make certain about the simultaneous isolation of indium from the chelant solution and reuse of chelant, and reduce the operating cost thereby.

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Table 1: Acid dissociation constants (pK_a) of the chelants, stability constants (logK_{ML}) of indium-chelant complexes, and conditional stability constants (logK'_{ML}) at different solution pH for 1:1 chelant-to-indium ratio

Chelants [a]	pK_a [b]					logK_{ML} [b]	logK'_{ML} [c]				
	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	pK_{a5}		pH 3	pH 5	pH 7	pH 9	pH 11
IDSA	10.0	4.24	3.24	1.97	−	−	−	−	−	−	−
HIDA	8.68	2.2	(1.6)	−	−	−	−	−	−	−	−
NTA	9.84	2.14	(1.81)	−	−	13.81	6.89	6.34	4.74	3.56	−1.19
EDTA	10.37	6.13	2.69	2.0	−	25.0	13.78	14.73	13.24	10.68	10.67
DTPA	9.9	8.4	4.28	2.7	2.00	29.5	15.67	18.38	17.57	16.58	7.58

[a] IDSA: imminodisuccinic acid, HIDA: N-(2-hydroxyethyl)iminodiacetic acid, NTA: nitrilotriacetic acid, EDTA: ethylenediaminetetraacetic acid, DTPA: diethylene triamine pentaacetic acid (see Fig. S1 in the supplementary material for the chemical structures of the chelants).
[b] The pK_a and logK_{ML} values of the chelants are at 25 °C ($\mu = 0.1$ mol L^{-1}), and extracted from the NIST Critically Selected Stability Constants of Metal Complexes Database' [23].
[c] The change in the conditional stability constants in terms of pH is calculated using the computer program HySS2009 [24].
'−' stands for 'no data available in the NIST Critically Selected Stability Constants of Metal Complexes Database' [23].
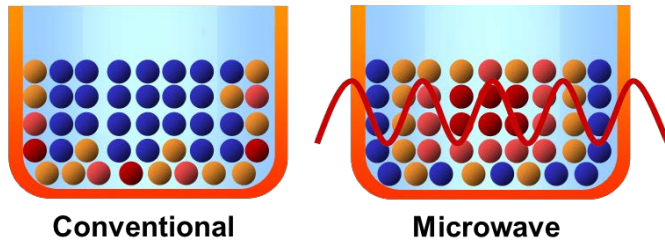
Figure 1: Schematic representation of the dissimilarity in the heat-transfer mechanism between the conventional and microwave approaches.
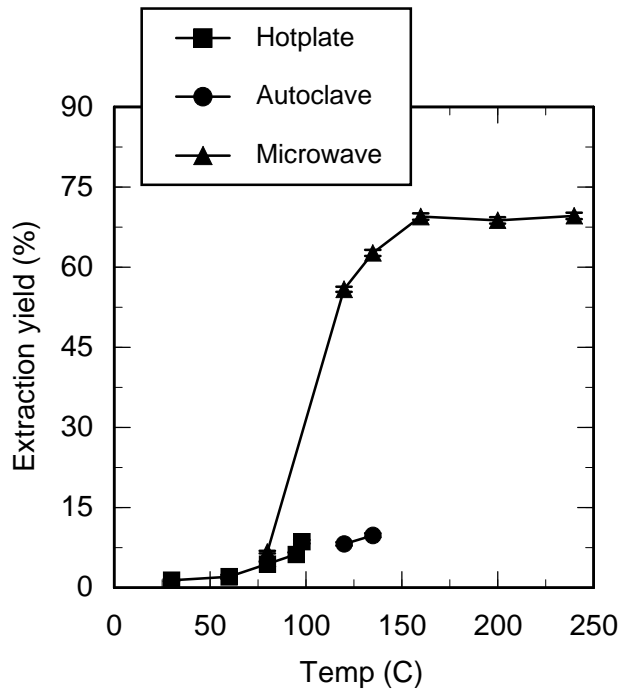
Figure 2: Effect of the heating approaches on the chelant-assisted dissolution of indium from the LCD-waste (chelant: 0.05 mol L^{-1} EDTA, pH: 7, processing time: 1–2 h, $n = 3$).
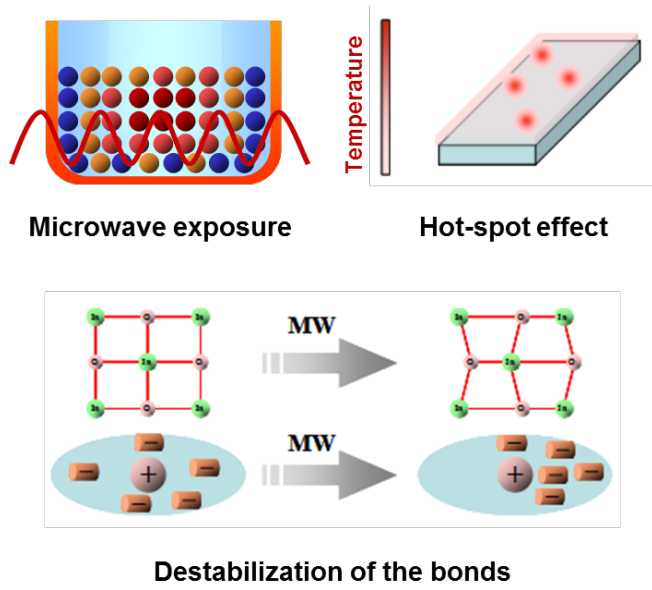
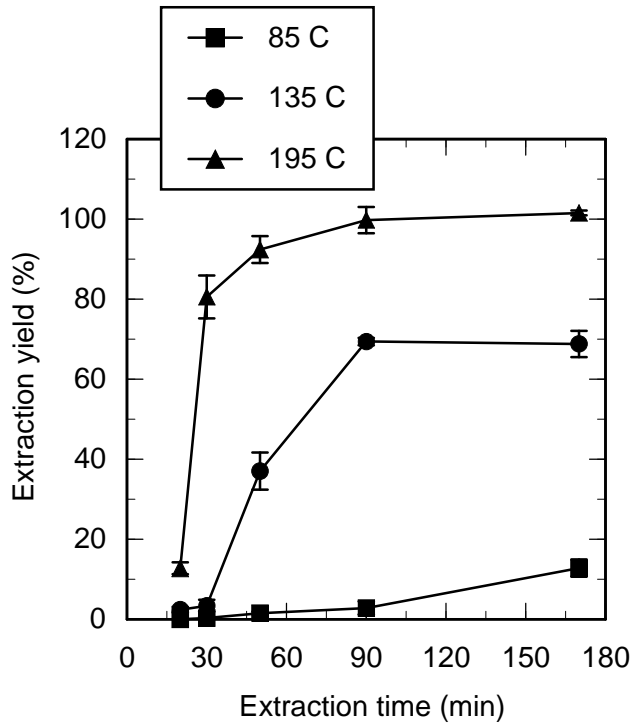**Figure 3:** Schematic representation of the ITO-dissolution mechanism from the LCD-waste.

Figure 4: Effect of the varying temperature conditions created by the microwave reaction system on the chelant-assisted dissolution of indium from the LCD-waste (chelant: 0.05 mol L^{-1} EDTA, pH: 7, $n = 3$).
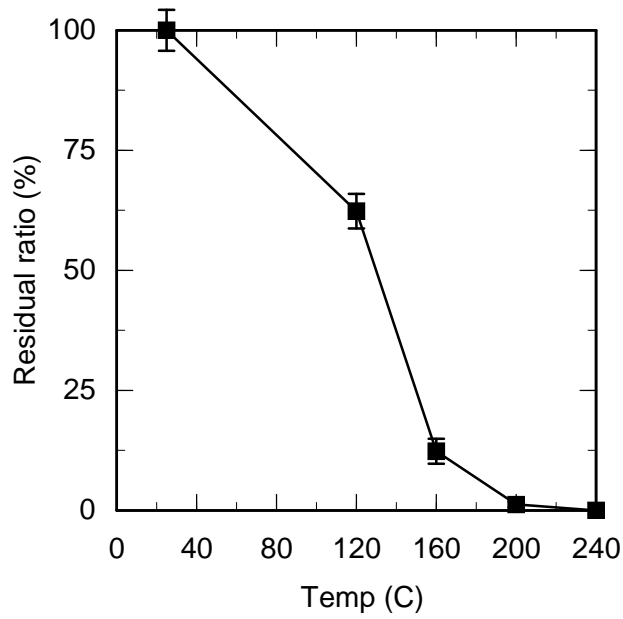
Figure 5: Effect of system temperature on the comparative ratio of chelant in the solution (chelant: 50 µmol L^{-1} EDTA, pH: 7, processing time: 2 h, $n = 3$).
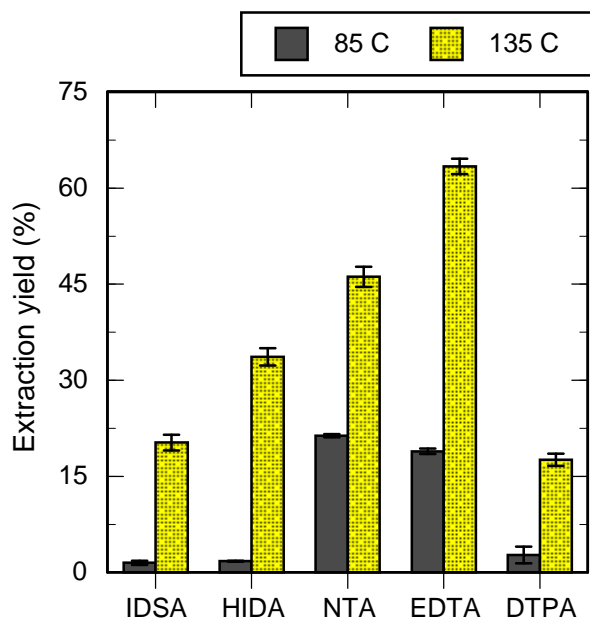
Figure 6: Performance of the chelants at varying temperature conditions created within the microwave reaction system for the dissolution of indium from the LCD-waste (chelant concentration: 0.05 mol L^{-1}, pH: 7, processing time: 2 h, $n = 3$).
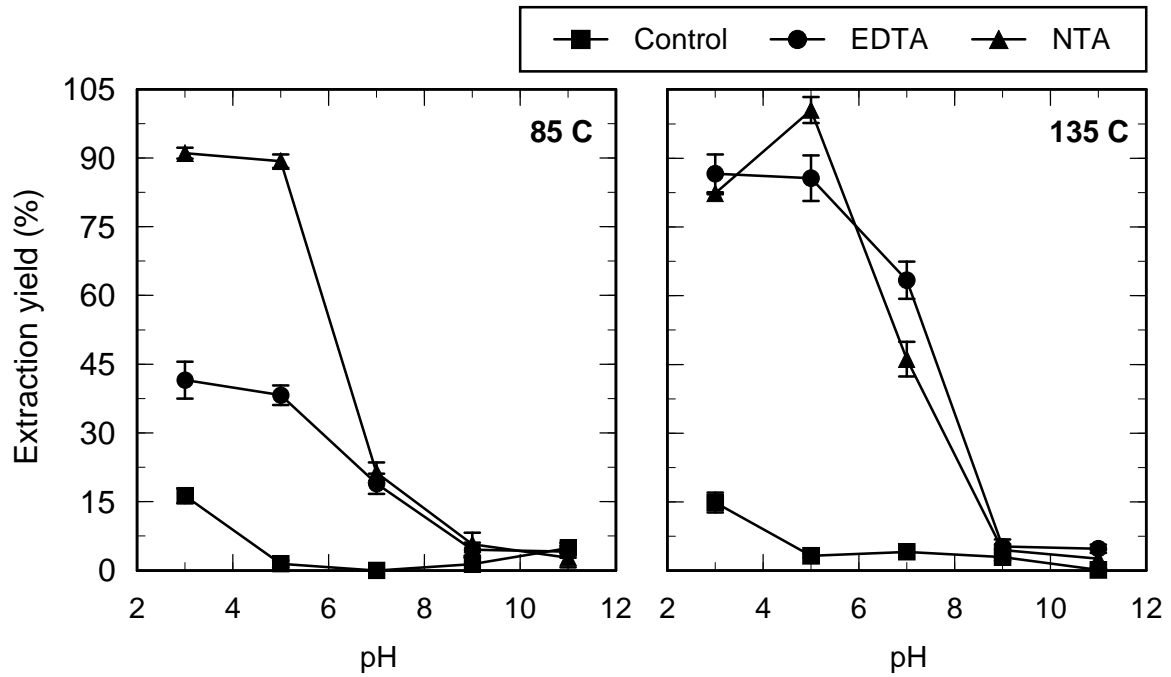
Figure 7: Effect of solution pH on the chelant-assisted dissolution of indium from the LCD-waste at varying temperature conditions (chelant: 0.05 mol L^{-1} EDTA or NTA, processing time: 2 h, $n = 3$).
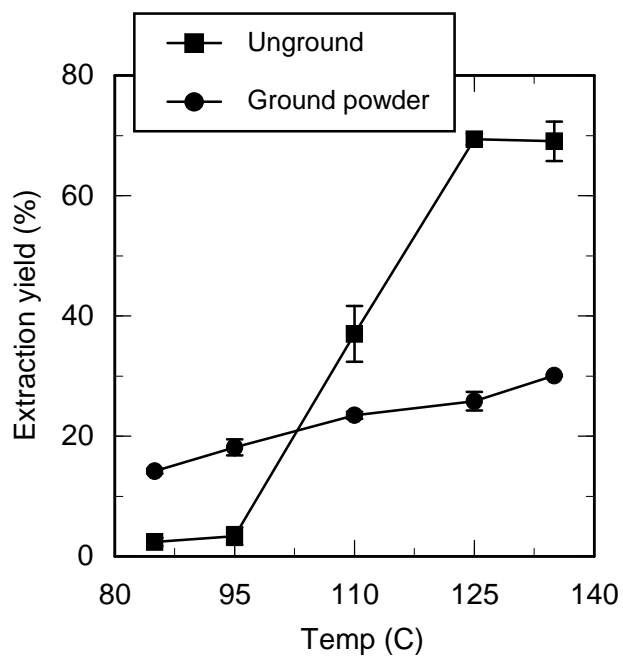
Figure 8: Comparative chelant-assisted dissolution of indium from ground powder and unground samples of the LCD-waste at varying temperature conditions (chelant: 0.05 mol L^{-1} EDTA, pH: 7, processing time: 2 h, $n = 3$).
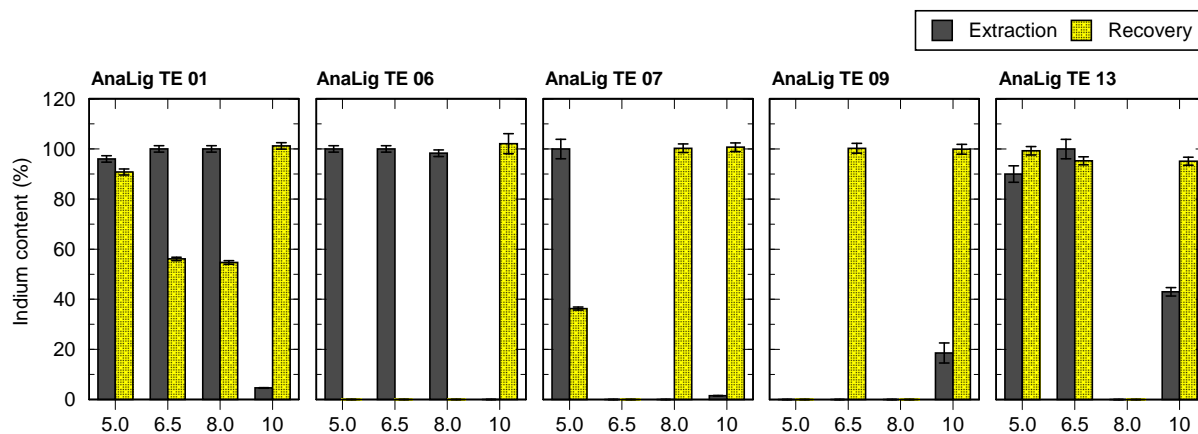
Figure 9: Comparative extraction and recovery of indium with the MRT-SPE cartridges as a function of pH (indium: 1 mmol L^{-1}, chelant: 10 mmol L^{-1} EDTA, matrix: H$_2$O; $n = 3$).