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Recovery of Indium from End-of-Life Liquid-Crystal Display Panels Using Aminopolycarboxylate Chelants with the Aid of Mechanochemical Treatment

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Abstract

The metal indium termed as 'rare' in recent days due to its increasing demand in the formulations of electronic and energy-related gadgets and scarce supply resources. Hence, the attempts to recover indium from the secondary resources, such as recycling of the indium abundant waste materials, received increasing research focus. The major indium consumption happens in the form of indium tin oxide (ITO) that used for the fabrication of liquid-crystal displays (LCD). The end-of-life LCD screens, termed as ITO-glass hereafter, are an emerging contributor to the global e-waste load and can be an impending secondary source of indium. The present work introduces a new technique for the treatment of waste ITO-glass using aminopolycarboxylate chelants (APCs) in combination with a mechanochemical treatment process. APCs are capable of forming stable complexes with the indium deposited on the ITO-glass, whereas the rate of recovery was not substantial. The mechanochemical treatment induces the destruction of crystalline structure with which the ITO fragments are attached and facilitate the increased indium dissolution with the chelants. The increase was more prominent followed by a decrease in the cumulative processing time from 24 to 6 h when the vitrified ITO-glass was simultaneously crushed and washed with the chelants. The extraction of indium was better at the acidic pH condition, and it was further intensified when the operating temperature was raised to ≥ 120 °C.

Keywords:

Indium; Indium tin oxide; Liquid crystal display; Waste; Recovery; Mechanochemical treatment

1.0 Introduction

Indium has emerged as an important strategic element in electronic and energy-related industries due to its specific applications [1, 2]. The most important end use of indium in recent years is to manufacture indium-tin oxide (ITO) thin film, an optoelectronic material with the characteristics of transparency to visible light, electric conduction and thermal reflection [2, 3]. ITO thin film is widely used in designing liquid-crystal displays (LCD), plasma displays and solar-energy cell [3], and consume about two-third of the global indium production [4].

Indium has no ore of its own and is generally found in low concentrations in some sulphide ores of zinc, copper and lead, from which it is procured as a by-product [5]. The technology revolution created an increasing demand for indium while the boom in its price is due to the policies of the nations with indium reserves (*e.g.* China, South Korea). Hence, the recovery of indium from the waste resources received sincere focus from the researches [4-6]. The ITO-scrap resulted from the ITO ceramic target during the conversion and application of ITO thin films on glass panels using the DC magnetron sputtering process is the most potential secondary resource of indium [2, 3, 6, 7]. The other prospective waste resources of indium are the etching waste [1, 8] and the LCD powder [6, 9].

The end-of-life (EoL) LCDs are a growing supplier to the global e-waste load owing to their popularity as consumer goods and the decreasing life-span of the corresponding electronic gadgets [10, 11]. Although the study on the indium recovery from the EoL LCDs, termed as ITO-glass hereafter, is becoming economically and environmentally justified, the number of reports in literature is by far very limited [6, 9].

Extraction with solvents is a commonly used method for the recovery of indium from the potential resources, and several extractant types have been checked including 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) [6, 12]. However, the

aminopolycarboxylate chelants (APCs) have not been evaluated for the recovery of indium in spite of their widespread acclaim for excellent metal-binding capacities [13-15].

A novel way for processing of solid materials is the co-grinding with suitable additives, commonly known as mechanochemical treatment [16-18]. The process includes the treatment of the materials in a closed mill containing balls that aid repeated fracturing via high-energy collisions either between balls or ball and inner wall of the mill container [19]. Even though the technique covers a wide range of practical and industrial applications, a very little attention has been paid to its applications related to the processing of the waste materials for metal recovery [20, 21].

In this paper, a mechanochemical method has been applied for the treatment of waste ITO-glass and to develop a new process for the recovery of indium using APCs as the extractant.

2.0 Experimental

2.1 Materials

2.1.1 ITO-glass samples

The LCD panels were collected from the Furuchi Chemical Corporation (Tokyo, Japan) and were used as the ITO-glass samples.

2.1.2 Aminopolycarboxylate chelants

The APCs used in the current study are as follows: (a) imminodisuccinic acid (IDSA), (b) N-(2-hydroxyethyl)iminodiacetic acid (HIDA), (c) nitrilotriacetic acid (NTA), (d) disodium dihydrogen ethylenediamine tetraacetate dihydrate (EDTA), and (e) diethylenetriamine-N,N,N',N'',N'''-pentaacetic acid (DTPA). IDSA was procured from LANXESS AG (Leverkusen, Germany), Kanto Chemical (Tokyo, Japan) was the supplier of NTA and EDTA, and Dojindo Laboratories (Kumamoto, Japan) supplied the HIDA and DTPA. The chemical structures of APCs, and the protonation constants and the stability information of the corresponding complexes with the indium are shown in [Table 1](#).

2.1.3 Other materials

All the chemicals were of analytical reagent grade, and used without any additional purification. The standards for metal concentration measurements were prepared by dilution using a PlasmaCAL multi-element solution in 5% HNO₃ (SCP Science; Québec, Canada). The pH was adjusted using the 1 M solution of either HCl or NaOH (Kanto Chemical; Tokyo, Japan). The buffer reagents used were as follows: (a) acetic acid/sodium acetate (Kanto Chemical; Tokyo, Japan) (for acidic pH), (b) 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) (Nacalai Tesque; Kyoto, Japan) (for neutral pH), (c) N-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (TAPS) or 3-(cyclohexylamino)-1-propanesulfonic acid (CAPS) (MP Biomedicals; Solon, OH) (for alkaline pH).

Low-density polyethylene bottles (Nalge Nunc; Rochester, NY), perfluoroalkoxy tubes and micropipette tips (Nichiryo; Tokyo, Japan) were used throughout. The laboratory wares were cleaned before and after each use following the process as described elsewhere [22].

2.2 Instrumentation

An iCAP 6300 inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo Fisher Scientific; Waltham, MA) was used for the metal analysis. The ICP-OES was composed of an EMT duo quartz torch, glass spray chamber and concentric glass nebulizer. The RF power at the torch was 1.15 kW, the plasma gas flow was 12 L min⁻¹, the auxiliary gas flow was 1 L min⁻¹, the nebulizer gas flow was 0.5 L min⁻¹, and the integration time was 30 s.

A TOSOH 8020 high-performance liquid chromatography (HPLC) system (Tosoh; Tokyo, Japan) was used for chelant concentration confirmation. The HPLC system contain a DP-8020 pump, an AS-8021 auto sample injector, a CO-8020 column oven, a PD-8020 UV-VIS detector, 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 contains 5 mM ammonium dihydrogenphosphate (pH 2.4) and the pumping flow rate was 0.5

mL min⁻¹ at 25 °C. The injection volume was 20 µL, and the detection was performed at 254 nm.

The Multiwave 3000 microwave reaction system (Anton Paar GmbH; Graz, Austria) equipped with 8-position rotor and hydraulic pressurized sensing system for all vessels was used. The vessels can sustain a controlled pressure of 6 MPa, maximum operating pressure of 12 MPa and highest temperature of 2600 °C.

A D2 Phaser x-ray diffraction (XRD) system (Bruker AXS; Madison, WI) was used to record the XRD patterns of the ITO-glass before and after the milling treatment. The high dynamic range (HDR) images of the dry- and wet-milled samples were captured using a VHX-1000E digital microscope (Keyence; Osaka, Japan) with a magnification range from 0.1× to 5000× and equipped with a high speed camera.

A Digiprep Jr block heater (SCP Science; Quebec, Canada) or a MLS-3750 automatic autoclave (Sanyo Electric; Osaka, Japan) were employed for the temperature-based experiments. A Navi F-52 pH meter (Horiba Instruments; Kyoto, Japan) and a combination electrode were used for pH measurements. An Arium Pro water purification system (Sartorius Stedim Biotech GmbH; Göttingen, Germany) was used to prepare the ultrapure water (resistivity > 18.2 MΩ cm).

2.3 Methods

2.3.1 Preparation of ITO-glass sample

ITO-glass was cut into pieces of approximately 3 cm × 5 cm size and then crushed in a BP-1 ceramic pot mill (AS ONE; Osaka, Japan) combined with a AV-1 mill pot rotator (Asahi Rika; Chiba, Japan) using alumina balls. The HD-8, HD-10 and HD-15 alumina balls (AS ONE; Osaka, Japan) were used, and the milling process was performed for 0.5 to 10 h at a rotating speed of 150 rpm.

2.3.2 Indium content in the ITO-glass

Microwave-assisted digestion of the milled ITO-glass sample was performed with 6 M HNO₃ at 230 °C for 2 h. The digested extracts were separated using 0.45 µm pore sized

cellulose membrane filters (Advantec; Tokyo, Japan) combined with a MAS-1 suction assembly (AS ONE; Osaka, Japan). Indium content in the range of 380 to 410 mg kg⁻¹ in the ITO-glass samples was confirmed via ICP-OES analysis.

2.3.3 *Chelant-assisted extraction of indium from ITO-glass*

The solutions of IDSA, HIDA, NTA, EDTA and DTPA were prepared in the concentration range of 0.01 to 0.15 M. The chelant solutions pH were adjusted using 0.1 M buffer reagents (pH 1, 3 and 5: HCl and acetic acid/sodium acetate, pH 7: HEPES, pH 9: TAPS, pH 11: CAPS) while the same prepared using ultrapure water only were used as controls. Two different approaches were adopted to check the indium extractions from the ITO-glass using chelants. In the first approach, the pH-adjusted chelant solutions (10 mL) were used to treat the 6 h milled ITO-glass (0.1 g) at a rotating speed of 150 rpm for 24 h. The second approach included co-grinding of the unground waste (5 g) with the chelants (liquid to solid ratio = 10) for 6 h. The extracts were separated from the solid fractions in the mixtures using 0.45 µm pore sized cellulose membrane filter for ICP-OES analysis. The averaged values of three replicate measurements for each of the experiments were considered.

3.0 Results and discussion

3.1 *Effect of dry milling used for sample pre-treatment*

The ITO-glass contains the indium in a deposited form on the vitrified structure, and the samples were pre-treated via mechanical milling. The solid structures were repeatedly fractured through collisions between the balls or ball and the mill container in a high-energy ball milling process, which facilitate mechanochemical solid phase reactions [16, 19]. The XRD data (Fig. 1a) confirmed the distortion in the crystalline arrangement of the ITO-glass after the dry milling treatment. The effect of the milling treatment is also shown schematically in the Fig. 1b.

3.2 *Effect of milling period on the chelant-assisted extraction*

It has been postulated that the surface area of the solid increased due to the creation of finer particles when crushed and ease the chemical induced interactions with the surface

components [17, 23, 24]. The impact of milling treatment on the solvent-induced extraction yield was expected to proceed as the milling progresses [21], and an increment in the milling period at least up to 6 h promoted the efficiency of after-milling chelant-induced extraction rates of indium from the ITO-glass (Fig. 2).

3.3 Effect of chelant concentration and solution pH

Chelants in solution may perturb the natural speciation of metals in a system leading to subsequent remobilization [25]. EDTA is commonly utilized among the APCs for solid waste remediation [26, 27] and, hence, employed as the reference chelant to regulate the operating variables (chelant concentration, solution pH) that may influence the dissolution of indium from the ITO-glass. The extraction yield of indium increased with the increase in the EDTA concentration until 0.05 M and remain constant thereafter (Fig. 3a), which confirmed the requirement of an excess of chelant to achieve a steady removal rate. A higher rate of extraction achieved at the acidic pH region was presumably attributable to the $[\text{In}^{3+}]/\text{dt}$ rate, while the decline in the indium extraction rate above pH 7 may be due to the lowering of indium solubility in the alkaline pH region (Fig. 3b).

3.4 Effect of chelant type and corresponding metal-chelant stability constants

The interaction extent of a chelant in solution to the target metal ion and stability of the corresponding metal-chelant complex depend greatly on the total number of donor atoms and coordinating sites, and types of the donor atoms in the chelant [28]. The rates of indium extraction with HIDA, IDSA, NTA, EDTA and DTPA were estimated using In_2O_3 powder (≥ 0.99 mass fraction purity) and mechanically pulverized ITO-glass samples (Figs. 4a-I and 4b-I) showing similar order of extraction aptitude: $\text{NTA} > \text{EDTA} > \text{HIDA} > \text{IDSA} > \text{DTPA}$. The superior extraction capability of NTA was more prominent in the case of In_2O_3 powder than that observed for the ITO-glass, which was likely due to the comparative differences in the indium availability. The extraction yield increased steadily until six hours of treatment time and continued to equilibrium except that with NTA for In_2O_3 powder, while a comparable pattern observed for the ITO-glass (Figs. 4a-II and 4b-II). The behavior of NTA can be

explained by assuming a comparatively slower rate of interaction at the early hours followed by the increases with time, and can be attributed to its diversity in the reaction velocity with indium when available at excess in solution.

The metal-chelant (ML) complex formation preference is, however, not in the order to their corresponding stability constant ($\log K_{ML}$) values at 25 °C (DTPA: 29.5, EDTA: 25.0, NTA: 13.8; the data are cited from the ‘NIST Critically Selected Stability Constants of Metal Complexes Database’ [29] and the relevant information for IDSA and HIDA are not available from any trustworthy sources). The complexation of the APCs with indium usually occurs at the ratio of 1:1, and the ML complexes appear as the dominant species even at excess chelant conditions for EDTA and DTPA. An exception was observed for NTA with the formation of dominant ML_2 species when the chelant ratio increases in the solution (Fig. 5). The comparative formation rate of the soluble dominant species in solution may be one of the possible factors that controls the mechanism of chelant-induced transport of indium from the ITO-glass phase other than the solid phase association of the metals, the precipitation propensity of indium in the reaction system, re-sorption of the ML complexes in the active surface sites of the solid matrix, etc. [30, 31]. Furthermore, the kinetic hindrance occurred at varying extent during the coordination interactions between the metal ion and the multidentate chelants [25] may precede the usual extraction preferences.

3.5 Effect of co-grinding of the ITO-glass with the chelants

The unground ITO-glass was simultaneously crushed and treated with the chelants, and the process was termed as the ‘wet milling’ process. The comparative extraction yield achieved via the chelant washing of 6 h dry milled sample and wet milling process at different time intervals (up to 6 h) are shown in Fig. 6a. The chelant-induced (EDTA or NTA) dissolution of indium from the dry milled sample occurred promptly in first 60 min and then decelerated proceeding to the equilibrium with time. An opposite trend was observed for wet milling, which may be attributable to the insufficient amount of crushing in the first hours of the milling process. As the time progresses, a better extraction rate was accomplished with the wet milling process. Such a tendency was explained by assuming

improved strength reduction action of the wet milling process through finer pulverization of a crystalline material [32]. However, the comparative HDR images (Fig. 6b) showed that the particle sizes were between ≤ 1 to $3 \mu\text{m}$ in the 6 h dry milling of ITO-glass while even $10 \mu\text{m}$ particle was remained along with the $\leq 1 \mu\text{m}$ particles after 6 h of wet milling. Therefore, the promoted extraction efficiency achieved with the wet milling process was may not only be due to the extent of crushing and rather originated from the mechanochemical effect due to the co-grinding treatment.

3.6 Influence of the operating temperature

The rate of indium extraction with the chelants was increased with the intensification of the system temperature, and the change is remarkable at $> 75 \text{ }^\circ\text{C}$ showing ~ 10 times rise in the extraction rate at $125 \text{ }^\circ\text{C}$ (Fig. 7). A further improvement in the extraction rate is thus expected under high temperature and hyperbaric condition.

4.0 Conclusion

APCs are capable of extracting indium from the ITO-glass at room temperature conditions, and the efficiency was enhanced via the milling treatment (~ 6 h). The effectiveness can be increased further using the wet milling than the sole treatment after milling. Although the indium extraction efficiency at room temperature conditions was not substantial, a significant enhancement in the yield of indium dissolution was achieved when the operating temperature was increased. The recommended optimum conditions for the chelant-assisted recovery of indium with the aid of mechanochemical treatment are as follows: pH – acidic (~ 5), temperature – $\geq 120 \text{ }^\circ\text{C}$, Chelant – NTA or EDTA.

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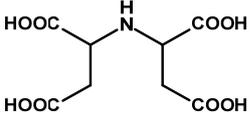
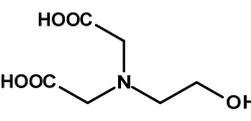
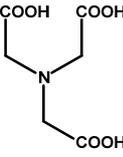
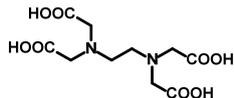
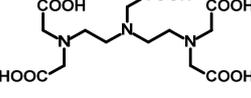
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Table 1: The chemical structures, acid dissociation constants (pK_a) of the aminopolycarboxylate chelants, stability constants ($\log K_{ML}$) of indium-chelant complexes, and conditional stability constants ($\log K'_{ML}$) at different solution pH for 1:1 chelant-to-indium ratio

Chemical structures of the APCs											
IDSA	HIDA				NTA	EDTA	DTPA				
											
pK _a of the aminopolycarboxylate chelants, and the logK _{ML} and logK' _{ML} at 1:1 chelant-to-indium ratio											
Chelants	pK _a					logK _{ML}	logK' _{ML} ^b				
	pK _{a1}	pK _{a2}	pK _{a3}	pK _{a4}	pK _{a5}		pH 3	pH 5	pH 7	pH 9	pH 11
IDSA ^a	10.0	4.24	3.24	1.97	–	–	–	–	–	–	–
HIDA ^a	8.68	2.2	(1.6)	–	–	–	–	–	–	–	–
NTA ^a	9.84	2.14	(1.81)	–	–	13.81	6.89	6.34	4.74	3.56	–1.19
EDTA ^a	10.37	6.13	2.69	2.0	–	25.0	13.78	14.73	13.24	10.68	10.67
DTPA ^a	9.9	8.4	4.28	2.7	2.00	29.5	15.67	18.38	17.57	16.58	7.58

^a At 25 °C ($\mu = 0.1$ M) [29].

^b The change in conditional stability constants in terms of the solution pH is calculated using the computer program HySS2009 [33].

'–' stands for 'no data available in the NIST Critically Selected Stability Constants of Metal Complexes Database [29]'.

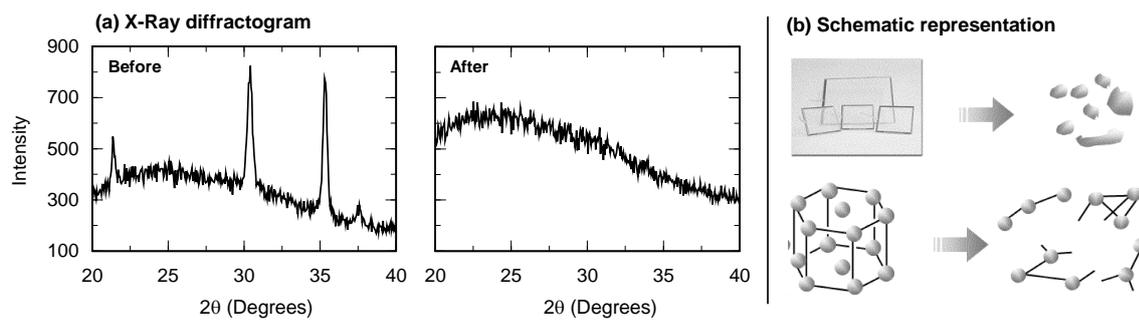


Figure 1. Dry milling pre-treatment of the ITO-glass: (a) x-ray diffractogram before and after the milling and (b) schematic representation of the milling effect.

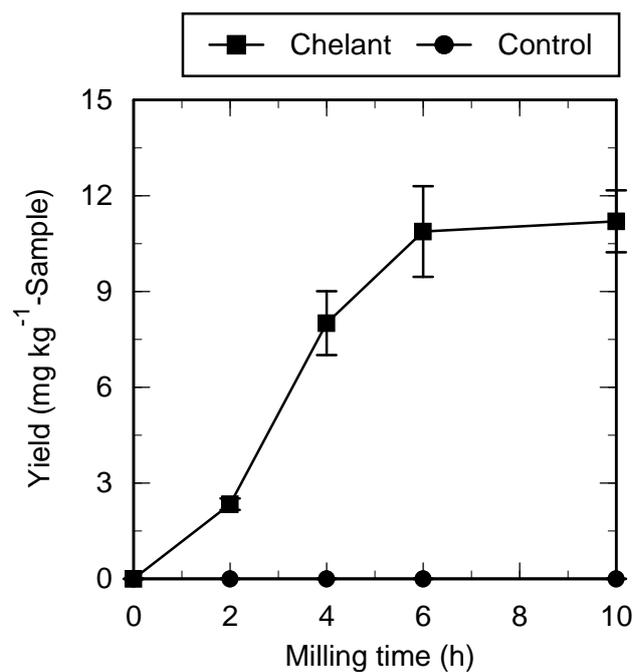


Figure 2. Influence of milling period on the chelant-assisted dissolution of indium from the ITO-glass at $25 \pm 2^\circ\text{C}$. Chelant: EDTA 0.05 M, pH: 7 ($n = 3$).

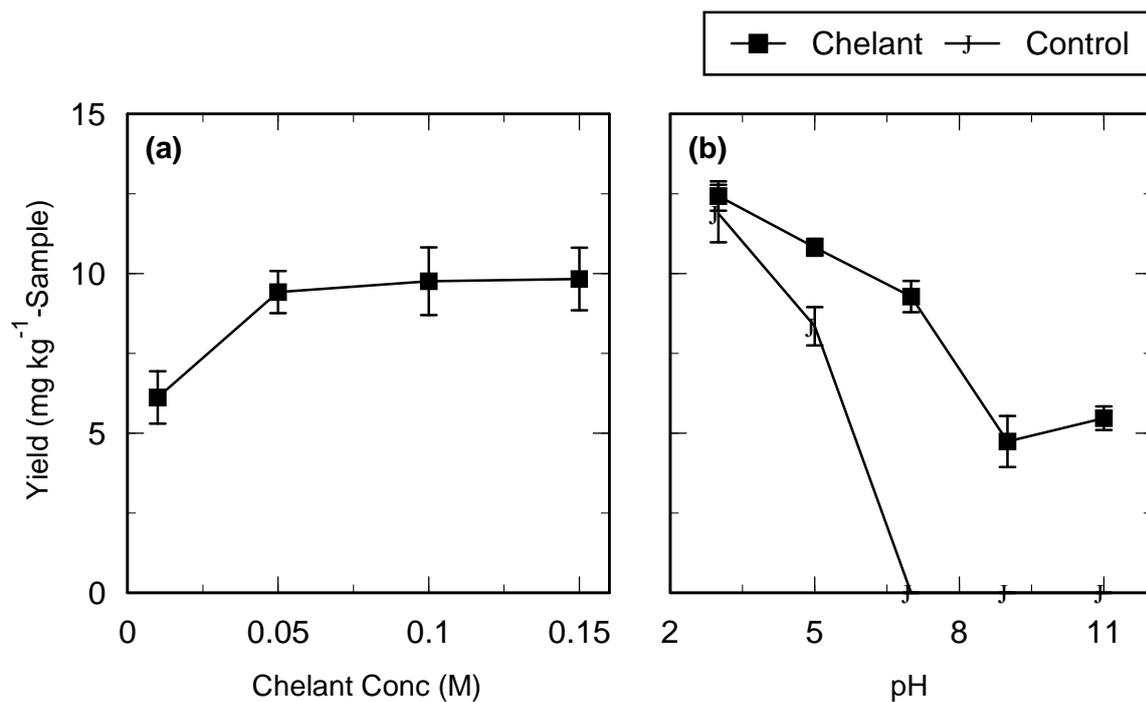


Figure 3. Influence of the (a) chelant concentration, EDTA 0.01–0.15 M at pH 7 and (b) solution pH, 3–11 using EDTA 0.05 M on the chelant-assisted dissolution of indium from the ITO-glass at $25 \pm 2^\circ\text{C}$ ($n = 3$).

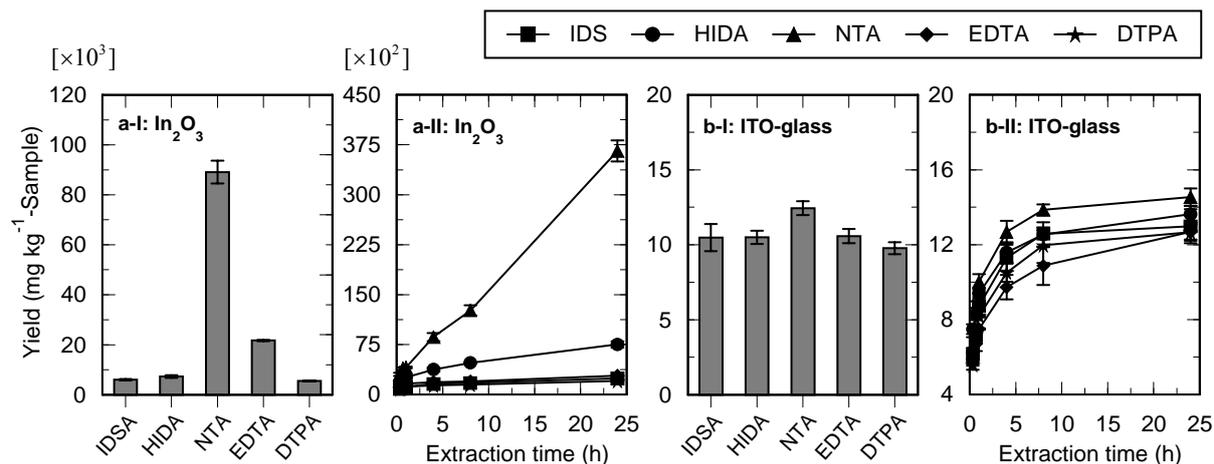


Figure 4. Influence of chelant types (a-I and b-I) and extraction time (a-II and b-II) on the chelant-assisted dissolution of indium from the In_2O_3 powder ($\geq 99\%$ mass fraction purity) and ITO-glass at $25 \pm 2^\circ\text{C}$. Chelant concentration: 0.05 M, pH: 7, Chelant/ In_2O_3 powder ratio– 150, Chelant/ ITO-glass ratio– 10, extraction time– 24 h (a-I and b-I) ($n = 3$).

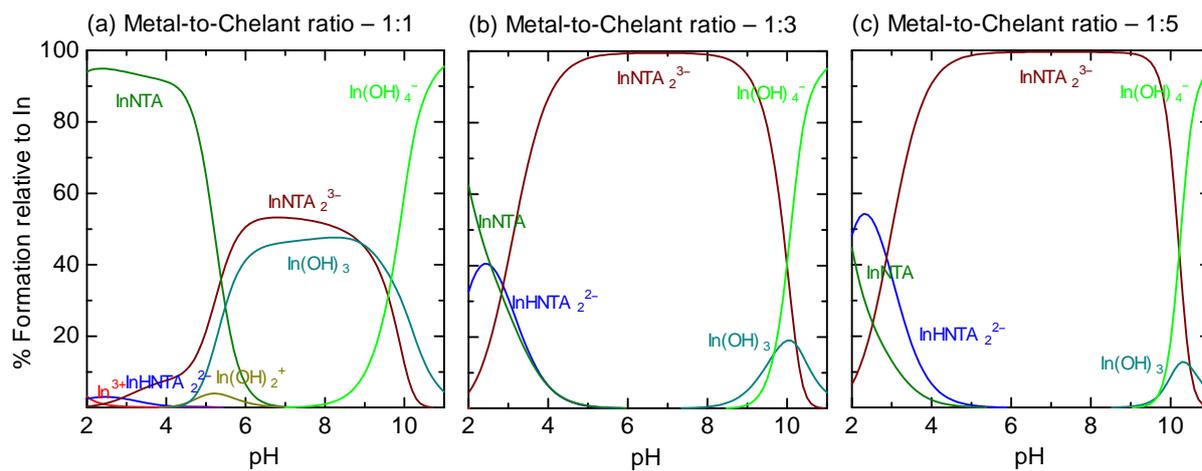


Figure 5. The species distribution curves for the indium-NTA systems (Indium-to-NTA ratio = 1:1, 1:3 and 1:5) in the aqueous medium at the ionic strength, $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ and at $25 \pm 0.1^\circ\text{C}$

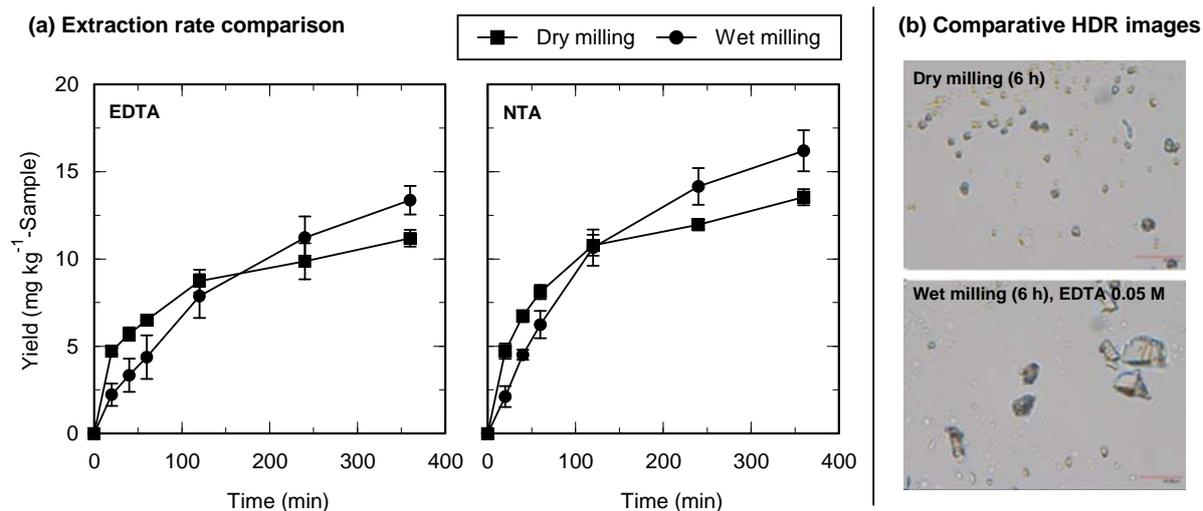


Figure 6. Effect of mechanochemical treatment on the chelant-assisted dissolution of indium from the ITO-glass at $25 \pm 2^\circ\text{C}$: (a) comparative extraction behavior using EDTA or NTA (0.05 M) and (b) High Dynamic Range (HDR) images at dry and wet milling conditions. Extraction time: 6 h, pH: 7 ($n = 3$).

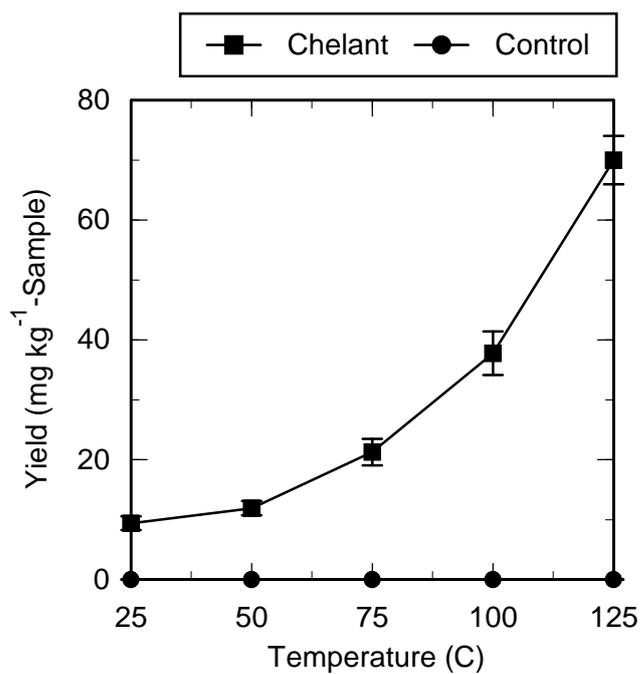


Figure 7. Effect of operating temperatures on the chelant-assisted dissolution of indium from ITO-glass with 0.05 M EDTA at pH 7 ($n = 3$).