

# Effect of various chelating agents on supercritical carbon dioxide extraction of indium(III) ions from acidic aqueous solution

Wei-Lung Chou<sup>\*</sup>, Kai-Chiang Yang

*Department of Industrial Safety and Health, Institute of Occupational Safety and Hazard Prevention, Hungkuang University, Sha-Lu, Taichung 433, Taiwan, ROC*

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## Abstract

Indium and its compounds have numerous industrial applications in the manufacture of liquid crystal displays and semiconductors. Indium compounds are considered hazardous materials that can be carcinogenic. Supercritical fluid extraction using carbon dioxide was utilized in this research as a sample pretreatment step for extraction of indium(III) ions from the synthetic etching wastewater of the semiconductor and optoelectronic industries. Several parameters, including various chelating agents, pH of solution, molar ratio of chelating agent to indium(III) ions, temperature and pressure were systematically investigated. Indium(III) ions were extracted by supercritical CO<sub>2</sub> combined with several various types of chelating agents including β-diketone (AcAcH), fluorinated β-diketone (TTAH), thiopyridine (PySH), and piperidinyldithiocarbamic acid (NCS<sub>2</sub>H) to extract the ions from acidic aqueous solution. The performance of the various chelating agents from different studies indicated that the extraction efficiency by the supercritical CO<sub>2</sub> was in the order: NCS<sub>2</sub>H ≥ PySH > TTAH ≫ AcAcH. The optimum pH for supercritical CO<sub>2</sub> extraction should fall in the range from 2.0 to 3.0. The optimum molar ratio of chelating agents to indium(III) ions was found to be a ratio of 10:1. It was also revealed that the optimal extraction pressure and temperature for the supercritical CO<sub>2</sub> extraction of indium(III) with various chelating agents AcAcH, PySH and NCS<sub>2</sub>H were 70 °C 2000 psi, 60 °C 2000 psi, and 60 °C 2000 psi, respectively.

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**Keywords:** Supercritical fluid extraction; Carbon dioxide; Chelating agents; Indium

## 1. Introduction

Indium is a metallic element in the IIIA column of the periodic table and is incorporated into III–V compound semiconductor materials, such as indium arsenide (InAs) and indium phosphide (InP). Indium and its compounds have numerous industrial applications, and it is extensively used in the manufacture of liquid crystal displays, semiconductors, low-temperature solders and infrared photodetectors [1,2]. The three major uses are derived from indium metal, its alloys and indium–tin oxide (ITO). More than one-half of the world's indium consumption is for indium–tin oxide (ITO) coatings [3]. ITO, which is a sintered alloy containing a large portion of indium oxide and a small portion of tin oxide, is an optically transparent conductor and is used in the making of thin-film transistor liquid crystal

displays (TFT-LCDs) for television screens, portable computer screens, cell phone displays and video monitors. Responding to the expanding demand for such displays, LCD production is rapidly increasing, especially in Asian countries, including Taiwan. Because of the demand for TFT-LCD or semiconductor materials, the consumption of ITO or indium can also be assumed to be increasing. While indium and its compounds exhibit excellent semiconductor properties, they can exist in the discharged etching wastewater from semiconductor or optoelectronic plants, and are suspected to be carcinogenic to human beings, damaging the heart, kidney, and liver [4]. Hence, the extraction of this rare metal (indium) is a promising area to investigate.

One of the most general methodologies for the extraction of metal ions from aqueous is the reaction of a metal ion with a specific chelating agent to form a metal chelation followed by solvent extraction. Most of the papers related to extraction of metal ions from solid and liquid samples used chelation combined with solvent extraction [5–7]. However, these solvent

<sup>\*</sup> Corresponding author. Tel.: +886 4 26318652x4005; fax: +886 4 26319175.  
E-mail address: [wlchou@sunrise.hk.edu.tw](mailto:wlchou@sunrise.hk.edu.tw) (W.-L. Chou).

extraction procedures are usually time-consuming and labor-intensive. In addition, solvent extraction requires many organic solvents and often creates environment problems. Owing to the extensive environmental problems resulted from the pollution of organic solvents and the increased environmental legislation limiting the use of conventional solvents. In contrast, supercritical fluid extraction would be a viable “green” alternative is relatively fast, and its selectivity can be controlled. Supercritical fluids possess densities that are greater than those of gases but corresponding to those of liquids, which mean they are regarded as solvents. The combined liquid-like solvating capabilities and gas-like transport properties of supercritical fluids result in improved mass transfer and reduced extraction time. Furthermore, the dissolving power of supercritical fluids can be modified by altering the extraction pressure or temperature. Supercritical fluid extraction (SFE) has gained increased interest as a promising alternative medium of more environmental soundness for replacement of conventional organic solvent extraction due to the properties of supercritical fluids, such as higher diffusivity and low viscosity [5–8].

Among the supercritical fluid mediums, carbon dioxide ( $\text{CO}_2$ ) is the most favored due to its non-toxicity, non-flammability, good transport properties (density, viscosity, and diffusivity), low critical conditions (304.2 K and 7.38 MPa) and minimization of waste solvent generation and direct removal of analytes from substrates. Most of the studies in the past literature regarding SFE have related to organic compounds, while studies on supercritical  $\text{CO}_2$  extraction of metals from aqueous solutions are relatively few. Carbon dioxide is highly non-polar, so that direct extraction of metal ions by supercritical  $\text{CO}_2$  is known to be highly inefficient because of the charge neutralization requirement and weak solute–solvent interactions. One approach to SFE of metals is by converting charged metal ions into neutral metal chelates using chelating agents dissolved in supercritical  $\text{CO}_2$ . The success of such an *in situ* chelation–supercritical  $\text{CO}_2$  extraction technique for metal extraction from aqueous solution depends mainly on the effectiveness of chelating agents. Therefore, with regard to the selection of proper chelating agents, supercritical  $\text{CO}_2$  extraction may provide a means of metal speciation in various samples. When metal ions are chelated with suitable organic ligands and form neutral species, their solubility in supercritical  $\text{CO}_2$  can be significantly increased [8–13]. As a result of these favorable properties of supercritical  $\text{CO}_2$  as a solvent, this *in situ* chelation–supercritical  $\text{CO}_2$  extraction technique with proper chelating agents seems to have a wide range of applications, including the treatment of metal contaminated waste materials and mineral processing. Most of the papers related to the separation and enrichment of metal ions (including indium) used methods such as co-precipitation [14], solvent extraction [15,16], electroanalytical techniques [17], and solid-phase extraction [18–20]. However, there is scant research in the application of the supercritical  $\text{CO}_2$  extraction of indium(III) ions. It is therefore essential to develop corresponding pollution control and diminution processes to catch up with the growing semiconductor and optoelectronic industries, although these technologies have not so far been extensively employed in these industries. From the view point of this practical motivation, the

main objective of this work was to study the extraction efficiency of indium(III) ions from synthetic etching wastewater of semiconductor and optoelectronic industries in the presence of supercritical  $\text{CO}_2$  under various operating parameters. Several factors, including various chelating agents, pH of solution, molar ratio of chelating agent to indium(III) ions, extraction temperature and pressure, governing the efficiency and throughput of the procedure were investigated. In the following experiments, several different kinds of chelating agents, including  $\beta$ -diketone (AcAcH), fluorinated  $\beta$ -diketone (TTAH), thiopyridine (PySH) and piperidinyldithiocarbamic acid ( $\text{NCS}_2\text{H}$ ) have been also tested for their ability to extract indium(III) ions from acidic aqueous solution in the presence of supercritical  $\text{CO}_2$ .

## 2. Experimental

### 2.1. Chemicals and reagents

The standard reference material used in the experimental studies was the indium standard solution (from NIST,  $\text{In}(\text{NO}_3)_3$  in  $\text{HNO}_3$  0.5 mol/l) from Merck (Darmstadt, Germany) with purity of at least 99%. In addition, methanol was also purchased from Merck with a purity of at least 99%. Supercritical fluid grade carbon dioxide supplied in a cylinder was used as received from a commercial supplier in Taichung, Taiwan. Acetylacetone (AcAcH) and thenoyltrifluoroacetone (TTAH) were used as chelating agents and supplied, respectively, by Merck and Aldrich (St. Louis, MO, USA), with purities of at least 99%. Moreover, thiopyridine (PySH) and piperidinyldithiocarbamic acid ( $\text{NCS}_2\text{H}$ ) were also used as chelating agents, and purchased from Acros (Geel, Belgium) with purities of at least 98%. All water used was distilled and deionized. The chemical structures of the various chelating agents used in this study are given in Fig. 1.

### 2.2. Extraction apparatus

SFE was carried out by using the SFX-220 extraction system (ISCO, Lincoln, NE, USA) that consists of an SFX-220 extractor equipped with a linear coaxially restrictor heater and a 50- $\mu\text{m}$  i.d. fused-silicon capillary restrictor, an SFX-220 controller, and model 260 D syringe pump. The schematic diagram of the experimental apparatus for supercritical  $\text{CO}_2$  extraction is shown in Fig. 2.

### 2.3. Method

The ISCO 260D syringe pump was used to deliver  $\text{CO}_2$  to the extraction unit at constant pressure. The liquid carbon dioxide was delivered to the extractor until the desired pressure and temperature were reached, which varied from run to run between 1500–3500 psi, and 40–80 °C, respectively. All samples of SFE were directly added to a 10-ml extraction vessel with a total  $\text{CO}_2$  volume of 15 ml. In each experiment 50  $\mu\text{l}$  of indium standard, 2 ml acid matrix, and certain amount of chelating agents (AcAcH, TTAH, PySH, and  $\text{NCS}_2\text{H}$ ) were added to the quartz sample vial inside the extraction vessel. Optimized extraction

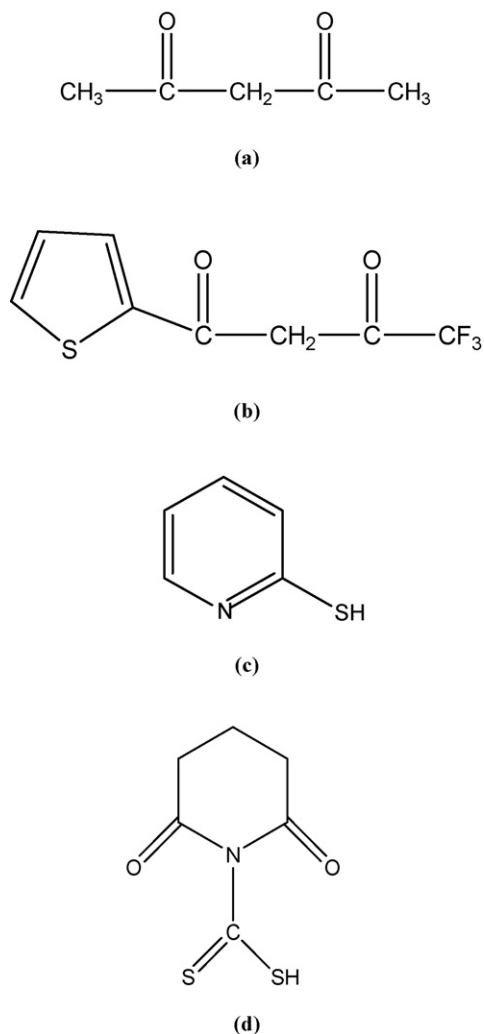


Fig. 1. Structure of chelating agents: (a) acetylacetone (AcAcH); (b) thenoyltrifluoroacetone (TTAH); (c) thiopyridine (PySH); (d) piperidinyldithiocarbamic acid (NCS<sub>2</sub>H).

conditions were obtained by sequentially varying one experimental parameter while all other parameters remained fixed. The vessel contents were extracted with supercritical fluid CO<sub>2</sub> at a temperature of 70 °C and a pressure of 2000 psi. The sample was first extracted statically for 15 min. In this study, “static” indicates that the vessel was charged with CO<sub>2</sub> while the outlet valve was closed. After the static extraction, the outlet valve was opened and the sample was extracted dynamically for 15 min with a CO<sub>2</sub> flow rate of approximately 1.0 ml min<sup>-1</sup>. The outlet of the extraction cell was connected to a thermally controlled variable restrictor which maintained supercritical temperature at 70 °C conditions in the system. The substances extracted were collected into a glass tube filled with methanol at the outlet of the extractor. After extraction, the sample solvent was quantified to 10 ml with methanol.

#### 2.4. Analysis

Each sample was measured three times with a flame atomic absorption spectrophotometer (AA-200, Perkin-Elmer). An indium hollow cathode lamp, operated at 20 mA, was used as the light source. The wavelength was set at the 303.9 nm resonance line for indium. A time-constant of 1 s was used for peak height mode. The flame composition was acetylene (flow rate 2.5 l min<sup>-1</sup>) and air (flow rate 10 l min<sup>-1</sup>). The range of the calibration standards for indium on flame atomic absorption spectrometric determinations was 2–10 mg/l. The correlation coefficient of the calibration curves were generally 0.999. The extraction efficiency was calculated based on the amount of indium remaining in the aqueous phase:

$$\text{extracted (\%)} = \frac{\text{indium loaded } (\mu\text{g}) - \text{indium remaining } (\mu\text{g})}{\text{indium loaded } (\mu\text{g})} \times 100$$

### 3. Results and discussion

To obtain the quantitative extraction efficiency of indium(III) ions from acidic aqueous solution in the presence of supercritical CO<sub>2</sub> extraction, the optimization of various analytical parameters such as pH of solution, molar ratio of chelating agent to indium(III) ions, extraction temperature and pressure in the extraction procedure was conducted. In our study, supercritical CO<sub>2</sub> extraction conditions were optimized using a step-by-step design reported by McNally [21]. This approach has been used as an alternative to the factorial design method, since it has similar results but requires less data processing [22]. All experiments were done in a static–dynamic mode with CO<sub>2</sub> extraction throughout this study. The results of extraction efficiency of indium(III) ions by supercritical CO<sub>2</sub> extraction with various chelating agents are presented and discussed in this section.

When the indium(III) ions were extracted by pure supercritical CO<sub>2</sub> at pH 6 solution without a chelating agent, the extraction efficiency was only 6.5%. It was thus shown that indium ion is not soluble in pure carbon dioxide due to the weak interactions between the positively charged metal ions and non-polar

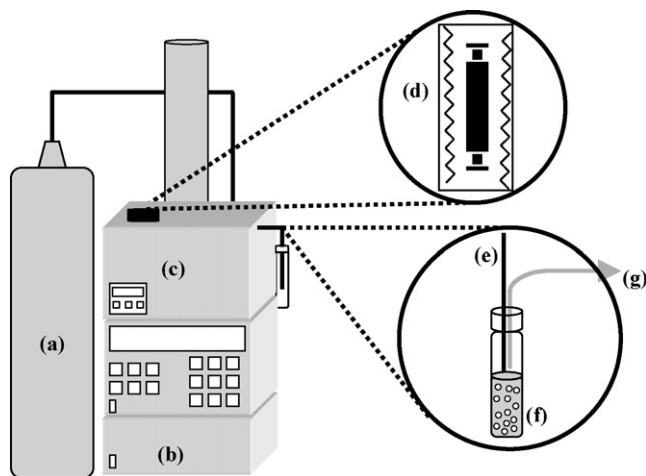


Fig. 2. Experimental apparatus of SF-CO<sub>2</sub> system: (a) CO<sub>2</sub> vessel; (b) syringe pump; (c) extractor; (d) extraction vessel; (e) restrictor; (f) collection solvent; (g) vent gaseous CO<sub>2</sub>.

Table 1  
Influences of extraction pressure and temperature on extraction efficiency of indium(III) ion without chelating agents (pH 2)

Pressure	Temperature		
	60 °C	70 °C	80 °C
2000 psi	11.8%	20.6%	21.5%
2500 psi	18.3%	21.8%	23.0%
3000 psi	22.3%	22.0%	21.3%

CO<sub>2</sub>. Owing to its practical applications, the etching wastewater from semiconductor or optoelectronic plants is favored around acidic solution, thus the synthetic etching wastewater of pH 2 was used without a chelating agent in the process of supercritical CO<sub>2</sub> extraction of indium(III) ions under various pressures and temperatures. The results are shown in Table 1. It was found that the extraction efficiency was improved from 6.5% to around 20% with increasing extraction pressure and temperature at lower pH. As a result, the acidic mediums are more effective than other types for metal extraction from aqueous solution in a supercritical CO<sub>2</sub> extraction system [23]. The properties of CO<sub>2</sub>, such as density and polarity, increased with the increase of the CO<sub>2</sub> pressure and temperature, which leads to the enhancement of the extraction efficiency of indium chelate in supercritical CO<sub>2</sub> extraction. However, the extraction efficiency of indium(III) ions from acidic aqueous solution in supercritical CO<sub>2</sub> without a chelating agent was still unsatisfactory. Accordingly, we can conclude that the extraction of indium ions merely via supercritical CO<sub>2</sub> is not feasible. With proper selection of chelating agents, the supercritical CO<sub>2</sub> extraction may provide a promising means for extracting metal ions directly from aqueous solution. In the subsequent extraction experiments, indium(III) was extracted from acidic aqueous solution by the supercritical CO<sub>2</sub> extraction technique in the presence of various chelating agents.

### 3.1. Effects of various chelating agents

From the previous experiments, the extraction efficiency of indium(III) ions from acidic aqueous solutions was low (11–22%) in pure supercritical CO<sub>2</sub> without a chelating agent. In order to test the effects of chelating agents on the extraction efficiency, the pH of the solution was fixed at 2.0 and the pressure and temperature were set at 2000 psi and 70 °C, respectively. Several types of chelating agents, such as  $\beta$ -diketone (AcAcH), fluorinated  $\beta$ -diketone (TTAH), thiopyridine (PySH) and piperidinyldithiocarbamic acid (NCS<sub>2</sub>H), were been utilized for supercritical CO<sub>2</sub> extraction of indium(III) ions. The influences of the various chelating agents on extraction efficiency of indium(III) ions by supercritical CO<sub>2</sub> are depicted in Fig. 3. In general, the addition of chelating agents led to an increase in extraction efficiency by a factor of 2–4.5, yielding 45–90% indium(III) ions extracted, obviously suggesting the presence of a chelating agent was necessary for more efficient of metal extraction in supercritical CO<sub>2</sub>.

Firstly, the extraction efficiency with a  $\beta$ -diketone chelating agent of AcAcH in supercritical CO<sub>2</sub> state was about 45.6%.

$\beta$ -Diketonate metal complexes in supercritical CO<sub>2</sub> are often poorly extracted from aqueous solutions due to finite mass transfer between the hydrophilic metal ions and the hydrophobic chelating agents [10]. In the same experimental conditions, the extraction efficiency with a fluorinated  $\beta$ -diketone chelating agent TTAH was observed about 75.4%. Significant increases in the extraction efficiency of indium(III) ions in supercritical CO<sub>2</sub> were accomplished between AcAcH and TTAH. It was probably because the solubility of free chelating agents in supercritical CO<sub>2</sub> depends on the chemical structure of the chelating agents and varies substantially from one type to another. Recent NMR studies show that the fluorinated  $\beta$ -diketones are almost exclusively in the enol form under the high temperature and pressure conditions relevant to the SFE system [7]. The non-fluorinated  $\beta$ -diketone chelating agent AcAcH is found to be partly in each form in supercritical CO<sub>2</sub>. The acidity of the chelating agent originates from the enol form and the deprotonated  $\beta$ -diketones involved in the metal complexation process. It has been shown that the presence of electron-withdrawing fluorine substituents can significantly increase chelating agent acidity. As a result, more anions are available to chelate the indium(III) ions in the acidic medium, which can facilitate enhanced extraction efficiency [24,25].

To extend our early investigation of the thio-, dithio-metal complexes and find useful chelating agents, these chelating agents were employed in the supercritical CO<sub>2</sub> system [26,27]. The chelating agents, including PySH and NCS<sub>2</sub>H, of metal ion extraction from acidic aqueous solutions are also shown in Fig. 3. It can be evidently shown that the appreciable extraction efficiencies of 85.4 and 90.9% achieved by using chelating agents PySH and NCS<sub>2</sub>H were superior to the extraction efficiencies obtained by using chelating agents of AcAcH and TTAH. This is because a popular model for predicting whether a metal and a chelating agent are likely to react is the hard–soft acid–base (HSAB) principle, which proposes that hard acids react strongly with hard bases and soft acids with soft bases [28]. Hard acids are likely to be small in size, have a large positive charge, and

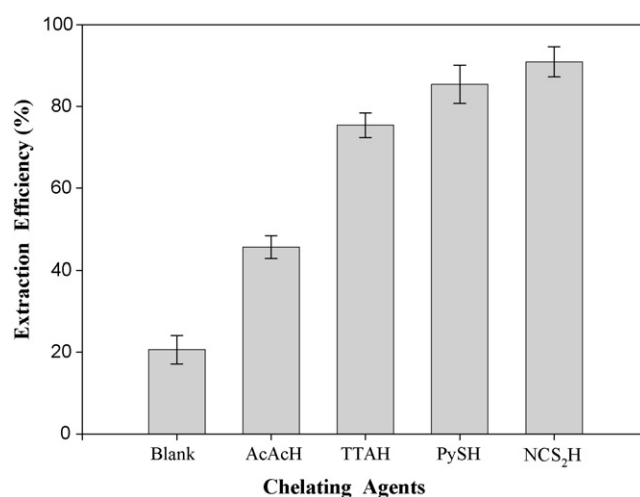


Fig. 3. Influences of the various chelating agents on extraction efficiency of indium(III) ion by supercritical CO<sub>2</sub> ( $T=70^{\circ}\text{C}$ ,  $P=2000$  psi, pH 2.0, molar ratio of chelating agent to indium(III) ion = 10:1).



possess an electron cloud that is non-polarizable. Soft acids are exactly the opposite, in that they are apt to be of large size with respect to their charge and possess polarizable electron clouds. Furthermore, hard and soft bases are analogous to their acid counterparts, except that they are electron-rich species. Reactions between hard acids and hard bases immediately occur because the two reactants have a strong coulombic attraction for each other. Moreover, soft acids and soft bases react by sharing of electrons, due to the closeness in energy of the highest occupied molecular orbital of the base and the lowest unoccupied molecular orbital of the acid. The fifth periodical metal indium reacts more easily with the soft sulfur including chelating agents, such as PySH and NCS<sub>2</sub>H, than the hard oxygen including chelating agents, such as AcAcH and TTAH. That was also confirmed by the reaction of In(AcAc)<sub>3</sub> with PySH or NCS<sub>2</sub>H chelating agents in CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature to obtain In(PyS)<sub>3</sub> or In(NCS<sub>2</sub>)<sub>3</sub> with releasing the AcAcH chelating agent [26].

From the above description, the  $\sigma$ -donor ability of the oxygen, nitrogen and sulfur chelating agents is reflected in the order: NCS<sub>2</sub>H  $\geq$  PySH > TTAH  $\gg$  AcAcH, and metal complexes including these chelating agents show high solubility even in non-polar solvents. Thus, the nitrogen and sulfur chelating agents are good selections in the syntheses of indium complexes for supercritical CO<sub>2</sub> extraction. The future developments in supercritical CO<sub>2</sub> extraction of metals will depend on the design, synthesis and development of chelating agents specifically for a particular application. It would be extremely useful to utilize the HSAB theory in chelating agent selection and design.

### 3.2. Effects of pH

Another critical parameter that should be considered in supercritical CO<sub>2</sub> extraction of metals is the pH of the solution. In order to investigate the effects of pH on the extraction efficiency of indium(III) ions, the molar ratio of the chelating agent to indium(III) ions was set at a ratio of 10:1 and the pressure and temperature in use were carried out at 2000 psi and 70 °C, respectively. As seen in Fig. 4, there is a decrease in pH with an increase in extraction efficiency for all chelating agents. When the pH was varied from 2.0 to 6.0, the extraction efficiency of indium(III) ions with AcAcH was found to change from 45.6 to 36.9%. Besides, for the chelating agents of TTAH, PySH and NCS<sub>2</sub>H, as the pH was increased from 2.0 to 6.0, the extraction efficiencies of indium(III) ions were in the range of 87.2–82.6, 75.4–68.5, and 90.9–87.5%, respectively. A previous report showed that when water is in contact with CO<sub>2</sub> under supercritical fluid conditions, the pH at equilibrium is less than 3.0 due to the formation and dissociation of carbonic acid in water [23]. Furthermore, the chelating agents, which form a stable neutral complex with metal ions at pH 3, are considered effective in supercritical CO<sub>2</sub>. Accordingly, acidic mediums are more effective than other types for metal extraction from aqueous solution in a supercritical CO<sub>2</sub> extraction system. Nevertheless, when all experiments for supercritical CO<sub>2</sub> extraction were carried out in more acidic mediums as well as under the high pressure state (mostly greater than 2000 psi), the additional effects were apt to cause abrasion to the parts within the supercritical CO<sub>2</sub> extraction instrument, as

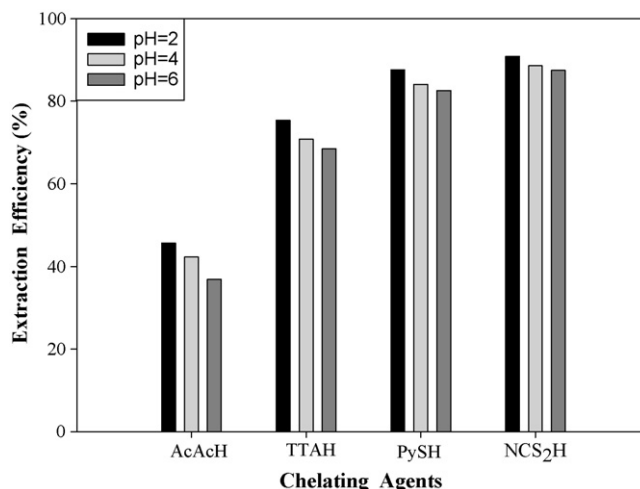


Fig. 4. Effect of pH on extraction efficiency of indium(III) ion with various chelating agents by supercritical CO<sub>2</sub> ( $T=70\text{ }^{\circ}\text{C}$ ,  $P=2000\text{ psi}$ , molar ratio of chelating agent to indium(III) ion = 10:1).

well as cause safety concerns. Therefore, the optimum pH for supercritical CO<sub>2</sub> extraction should fall in the range from 2.0 to 3.0.

### 3.3. Effect of molar ratio of chelating agent to indium(III) ions

Under the condition of pH 2.0, 2000 psi, and 70 °C, the effects of the amount of AcAcH, PySH and NCS<sub>2</sub>H on the extraction efficiency of indium(III) ions were investigated. The extraction efficiency of indium(III) ions as a function of chelating agent-to-indium(III) molar ratio is presented in Fig. 5. The extraction efficiency was found to increase conspicuously from 1:1 ratio to 10:1 ratio and then reached a steady value no matter what kind of chelating agent was used. For example, AcAcH, PySH, and NCS<sub>2</sub>H improved markedly from 30.1 to 45.6, 43.7 to 85.4, and 50.4 to 90.9%, respectively. Owing to the presence

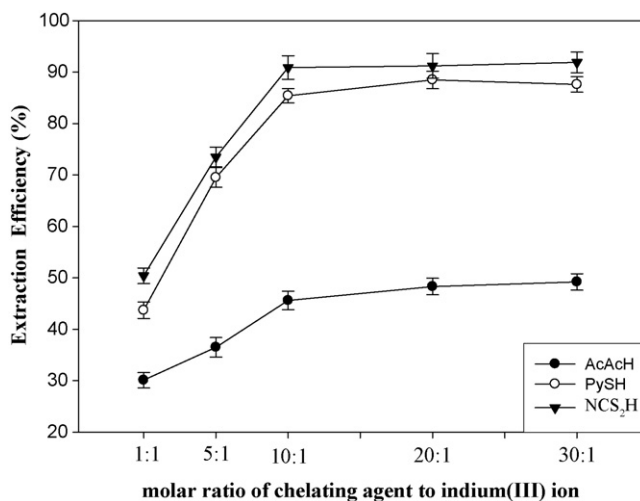


Fig. 5. Comparison of the extraction efficiency versus molar ratio of chelating agent to indium(III) ion with various chelating agents by supercritical CO<sub>2</sub> ( $T=70\text{ }^{\circ}\text{C}$ ,  $P=2000\text{ psi}$ , pH 2).

of acidic aqueous solution, chelating agents tend to decompose in a supercritical CO<sub>2</sub> extraction system, which indicated that an excess amount of chelating agents is usually required in order to achieve enhanced metal extraction efficiencies in supercritical CO<sub>2</sub> [23]. This increase in chelating agents was naturally accompanied by generation of more anions available to chelate with the indium(III) ions in the acidic aqueous solution. However, no significant improvement in extraction efficiency was observed at the ratio above 10:1, and these excess chelating agents were apt to block the outlet of the restrictor within the supercritical fluid extraction system. Consequently, a 10:1 ratio of chelating agents to indium(III) ions was chosen as the optimum molar ratio for the following supercritical CO<sub>2</sub> extraction experiments.

### 3.4. Optimization of extraction temperature and pressure

The molar ratio of 10:1 and pH 2.0 were used as the conditions for investigating the effects of extraction temperature and pressure. The fluid pressure has an essential effect on the extraction efficiency in supercritical CO<sub>2</sub> extraction because it is directly associated with the fluid density. Temperature also plays an important role in the extraction efficiency of supercritical CO<sub>2</sub> extraction. All extraction experiments were performed at pressures from 1500 to 3500 psi in 500 psi increments, and temperatures from 40 to 80 °C in 10 °C increments. The effects of pressure and temperature on the extraction efficiency of indium(III) ions with AcAcH from acidic aqueous solution are shown in Fig. 6(a). Increasing the pressure of the supercritical CO<sub>2</sub> from 1500 to 3500 psi did not substantially improve the extraction efficiency range from 34.5 to 39.4% as the extraction temperature varied from 40 to 50 °C. However, an enhancement in the extraction efficiency of indium(III) ions was observed at higher temperature (70 °C) when the pressure was raised from 1500 to 2000 psi, which facilitated the extraction efficiencies from 37.8 to 45.6%. No significant improvement in the extraction efficiency was obtained at higher pressure (2000–3500 psi). In addition, it can be seen that the optimal extraction pressure and temperature for the supercritical CO<sub>2</sub> extraction of indium(III) with AcAcH as the chelating agent was accomplished at 2000 psi and 70 °C, respectively.

The effects of pressure and temperature on the extraction efficiency of indium(III) ions with PySH from acidic aqueous solution are demonstrated in Fig. 6(b). In general, with increasing pressure, the density of supercritical fluid CO<sub>2</sub> increased, thus enhancing the solubilities of chelating agents and the metal accordingly, which could cause enhanced extraction efficiency [9]. Surprisingly, as shown in Fig. 6(b), no substantial enhancement in the extraction efficiency was achieved at different temperatures (50, 60, 70 and 80 °C) as the extraction pressure increased from 1500 to 3500 psi. This was probably because the solubility of these analytes with PySH had considered less pressure dependence or poor collection efficiency. Owing to the expensive operating cost and safety considerations of using high pressures, the pressure of 2000 psi was selected as the optimum pressure used in supercritical CO<sub>2</sub> extraction of indium(III) with PySH. Increasing the temperature from 40 to 60 °C would improve the extraction efficiency from about 60 to

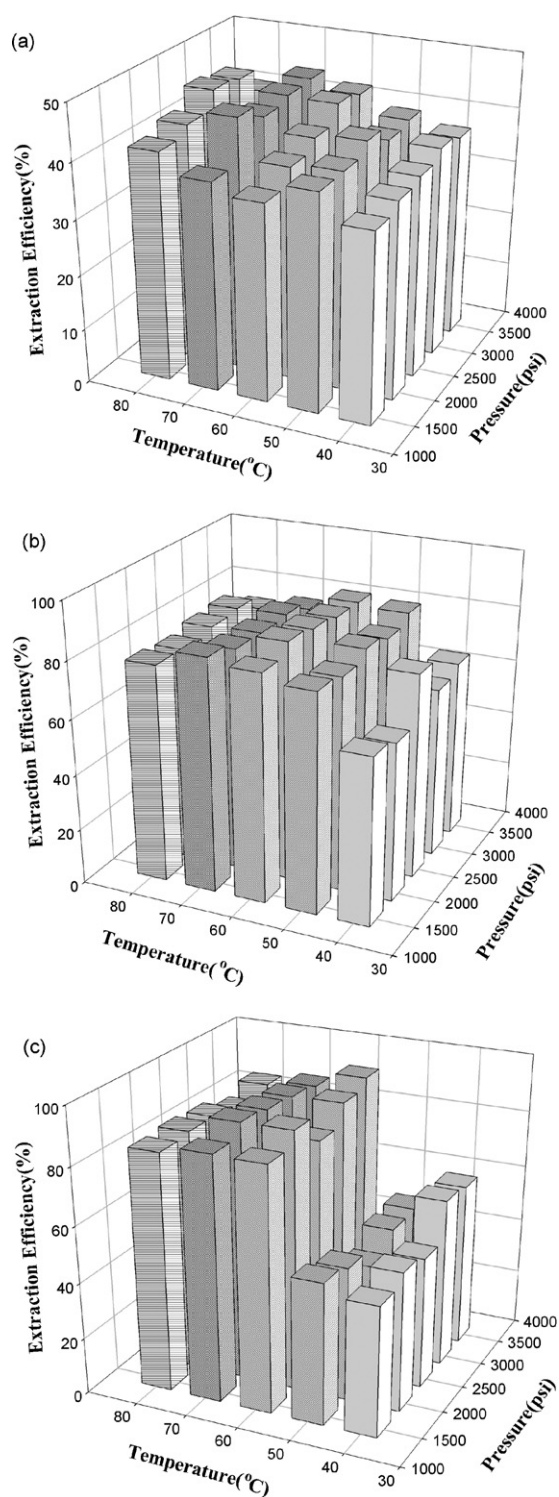


Fig. 6. (a) The effect of pressure and temperature on the extraction efficiency of indium(III) ion with chelating agent (AcAcH) by supercritical CO<sub>2</sub> (pH 2, molar ratio of chelating agent to indium(III) ion = 10:1). (b) The effect of pressure and temperature on the extraction efficiency of indium(III) ion with chelating agent (PySH) by supercritical CO<sub>2</sub> (pH 2, molar ratio of chelating agent to indium(III) ion = 10:1). (c) The effect of pressure and temperature on the extraction efficiency of indium(III) ion with chelating agent (NCS<sub>2</sub>H) by supercritical CO<sub>2</sub> (pH 2, molar ratio of chelating agent to indium(III) ion = 10:1).

85% with pressures ranging from 1500 to 3500 psi. Moreover, a decrease in the extraction efficiency of indium(III) ions was observed above 60 °C. This phenomenon could be explained by the following reasons. In terms of the rule of kinetics, the higher the temperature, the more intense the heat motion of solutes in the aqueous solution. This enables the solutes to overcome the adsorbing energy of the solution and to desorb more rapidly from active sites of the matrix by supercritical CO<sub>2</sub> at higher temperatures. According to the law of thermodynamics, the saturated vapor pressure increases accordingly with temperature, which enables solutes to dissolve in supercritical CO<sub>2</sub> more easily. However, increasing the temperature usually reduces the density of supercritical CO<sub>2</sub>, which also decreases its solubilizing ability, and therefore decreases the solubility of metal chelate in supercritical CO<sub>2</sub>. As a result, these three types of influences competed with each other and resulted in a reverse effect on the extraction efficiency, which implied an optimum temperature for practical purposes [29]. The most efficient extraction was achieved at 60 °C and is shown in Fig. 6(b). We can conclude that the optimal extraction pressure and temperature for the supercritical CO<sub>2</sub> extraction of indium(III) ions with PySH was accomplished at 2000 psi and 60 °C. Similar results were observed in the case of NCS<sub>2</sub>H and are summarized in Fig. 6(c). No matter what temperature was used, no change in the extraction efficiency was found when the pressure was set from 1500 to 3500 psi, as shown in Fig. 6(c), while increasing pressure increases the distribution coefficients of both the chelating agent and the metal chelate complex. Since these two distribution coefficients had opposite influences on extraction efficiencies, no improvement was observed [30]. Owing to expensive operating cost and security concerns when working with high pressures, 2000 psi was selected as the optimum pressure in supercritical CO<sub>2</sub> extraction of indium(III) with NCS<sub>2</sub>H. As the temperature increased from 40 to 60 °C, the extraction efficiency rose dramatically at 2000 psi, from 49.7 to 90.9%, respectively. However, there was a downtrend when the temperature was above 60 °C. Consequently, 60 °C was chosen as the optimum temperature. We can conclude that the optimal extraction pressure and temperature for the supercritical CO<sub>2</sub> extraction of indium(III) ions with NCS<sub>2</sub>H was accomplished at 2000 psi and 60 °C, respectively.

#### 4. Conclusion

The *in situ* chelation–supercritical CO<sub>2</sub> extraction technique in this study provides a new means for extracting indium(III) ions directly from acidic aqueous solutions. With proper selection of chelating agents, our experimental data indicated that chelating agents, usually forming highly soluble metal complexes in supercritical CO<sub>2</sub>, are very effective for the supercritical CO<sub>2</sub> extraction process. We have demonstrated that PySH and NCS<sub>2</sub>H chelating agents showed higher extraction efficiency in supercritical CO<sub>2</sub> extraction of indium(III) ions than the AcAcH and TTAH chelating agents. Furthermore, the key parameters in the extraction procedure, for example, pH of solution, molar ratio of chelating agent to indium(III) ions, extraction temperature, and extraction pressure, were also optimized in this study. The optimum pH for supercritical CO<sub>2</sub> extraction should

fall in the range from 2.0 to 3.0. The optimum molar ratio of chelating agents to indium(III) ions was found to be a ratio of 10:1. It was also revealed that the optimal extraction pressure and temperature for the supercritical CO<sub>2</sub> extraction of indium(III) with various chelating agents AcAcH, PySH and NCS<sub>2</sub>H were accomplished at 70 °C 2000 psi, 60 °C 2000 psi, and 60 °C 2000 psi, respectively.

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