



Removal of gallium (III) ions from acidic aqueous solution by supercritical carbon dioxide extraction in the green separation process

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ABSTRACT

Supercritical carbon dioxide extraction, which is a feasible “green” alternative, was applied in this study as a sample pretreatment step for the removal of gallium (III) ions from acidic aqueous solution. The effect of various process parameters, including various chelating agents, extraction pressure and temperature, dimensionless CO₂ volume, the concentration of the chelating agent, and the pH of the solution, governing the efficiency and throughput of the procedure were systematically investigated. The performance of the various chelating agents from different studies indicated that the extraction efficiency of supercritical CO₂ was in the order: thiopyridine (PySH) > thenoyltrifluoroacetone (TTAH) > acetylacetone (AcAcH). The optimal extraction pressure and temperature for the supercritical CO₂ extraction of gallium (III) with chelating agent PySH were found to be 70 °C and 3000 psi, respectively. The optimum concentration of the chelating agent was found to be 50 ppm. A value of 7.5 was selected as the optimum dimensionless CO₂ volume. The optimum pH of the solution for supercritical CO₂ extraction should fall in the range of 2.0–3.0.

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1. Introduction

Gallium is a metallic element in Group IIIA of the periodic table. This metal attracted a lot of interest in the 1970s when it was discovered that gallium combined with elements of group 15 displayed semiconducting properties [1–3]. In the microelectronics industry, silicon is the predominantly used substrate. In recent years, however, a number of other semiconductor materials (e.g. III–V intermetallic semiconductors) have been employed in many applications, such as microwave transceivers, DVD's, laser diodes in compact discs, and other electronics [4]. Gallium arsenide (GaAs) is a potential substrate due to its superior electronic and optical properties compared to those of silicon-based semiconductors [5]. The supply and demand of gallium-bearing products has gradually increased during the past decade. Many studies indicate that gallium is able to interrupt iron metabolism and can affect cellular immune function as well as reveal antiproliferative activities [6–7]. Hence, the industrial extraction of gallium is an important investigation topic.

One of the most used general methods for the extraction of metal ions from aqueous solutions is the reaction of a metal ion with a specific chelating agent to form a metal chelation followed by solvent extraction [1,8–10]. This method is unfavorable due to the

environmental contamination associated with the use of chemical solvents and its resulting health risks. Furthermore, strict new regulatory requirements on the use organic solvents worldwide, motivated by health and environmental concerns, have prompted the need for research on new green technologies [11]. Supercritical fluid extraction (SFE) has gained increased interest as a promising “green” alternative medium to replace conventional organic solvent extraction due to the properties of supercritical fluids, such as higher diffusivity and low viscosity [12–14].

Among the supercritical fluid mediums, carbon dioxide (CO₂) is often promoted as an environmentally friendly medium having desirable properties for a wide range of chemical and biochemical processes. Supercritical CO₂ can be a viable “green” alternative; however, its use has been restricted by its limited solvent power. Above its critical point (304.15 K and 7.38 MPa), where the distinction between a liquid and a gas disappears, the density of CO₂ varies with changes in temperature or pressure. Accordingly, its solvating power can be regulated and controlled, whereas the requirement of high pressure is unavoidable. Most previous studies on SFE have focuses on organic compounds and there have been few studies on supercritical CO₂ extraction of metals from aqueous solutions. Carbon dioxide is highly non-polar so that direct extraction of metal ions by supercritical CO₂ is highly inefficient because of the charge neutralization requirement and weak solute–solvent interactions. One SFE approach to convert charged metal ions into neutral metal chelates using chelating agents dissolved in supercritical CO₂. The success of such an in situ chelation-supercritical CO₂ extraction

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technique for metal extraction from aqueous solution depends mainly on the effectiveness of the chelating agents. Therefore, the selection of proper chelating agents is of paramount importance. Supercritical CO₂ extraction may provide a means of metal speciation in various samples. If metal ions are chelated with suitable organic ligands and form neutral species, their solubility in supercritical CO₂ can be significantly increased [15–19]. As a result of these favorable properties of supercritical CO₂ as a solvent, an in situ chelation-supercritical CO₂ extraction technique with proper chelating agents has a wide range of applications, including the treatment of metal contaminated waste materials and mineral processing. Most papers related to the separation and enrichment of metal ions used coprecipitation [20], solvent extraction [21–22], electroanalytical techniques [23], concentrated strong acid extraction [24–25], or solid phase extraction [26–30]. However, there is little research on the application of the supercritical CO₂ extraction of metal ions outside of our earlier study [31]. Our earlier investigation [31] used the in situ chelation-supercritical CO₂ extraction technique to extract indium (III) ions directly from acidic aqueous solutions. It is therefore essential to develop a corresponding pollution control and diminution processes to catch up with the growing use of semiconductor technologies although these technologies have not so far been extensively employed in this industry. With this practical motivation, the main objective of this work was to investigate the removal efficiency of gallium (III) ions from synthetic etching wastewater of the semiconductor industry in the presence of supercritical CO₂ under various operating parameters. The effect of various process parameters, including various chelating agents, extraction pressure and temperature, dimensionless CO₂ volume, the concentration of the chelating agent, and the pH of the solution, governing the efficiency and throughput of the procedure were systematically investigated. Several kinds of chelating agents, including β-diketones (AcAcH), fluorinated β-diketones (TTAH), and pyridines (PySH), were tested for their ability to remove gallium (III) ions from acid aqueous solutions in the presence of supercritical CO₂.

2. Experimental

2.1. Chemicals and reagents

The standard reference material used in the experimental studies was the gallium standard solution (from NIST, Ga(NO₃)₃ in HNO₃ 0.5 mol/L) from Merck (Darmstadt, Germany) with a purity of at least 99%. In addition, methanol was 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. 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%. Thiopyridine (PySH) was used as a chelating agent, purchased from Acros (Geel, Belgium) with a purity of at least 98%. All water used was distilled and deionized. The chemical structures of various chelating agents used in this study are given in Fig. 1.

2.2. Extraction apparatus

SFE was carried out 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 μm I.D. fused-silica capillary restrictor, an SFX-220 controller, and a model 260 D syringe pump. The extractor includes an on/off valve connected to a 10 mL extraction cell. The extraction cell was located in an oven, where temperature was controlled by a computer. A fused-silica capillary was used as the pressure restrictor for the exit gas. The

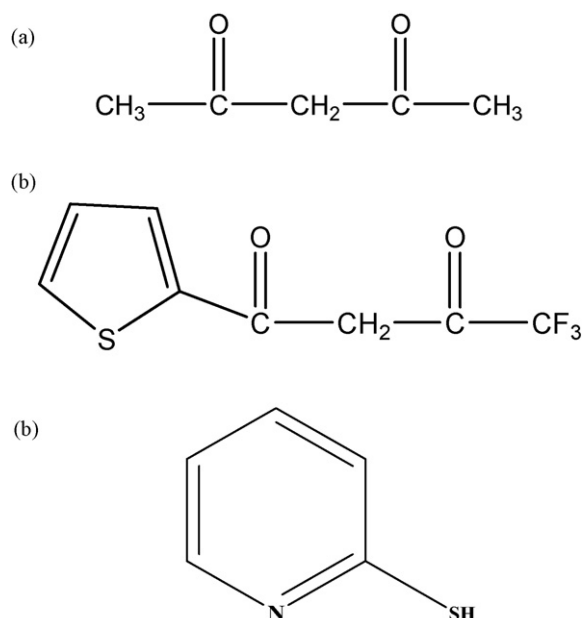


Fig. 1. Structure of chelating agents: (a) acetylacetone (AcAcH); (b) thenoyltrifluoroacetone (TTAH); (c) thiopyridine (PySH).

SFE system allowed static and dynamic extraction to be performed using the on/off valves.

2.3. Method

The ISCO 260D syringe pump was used to deliver CO₂ 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 psi and 3500 psi, and 40 °C to 80 °C, respectively. All SFE samples were directly added to a 10 mL extraction vessel with a total CO₂ volume of 15 mL. In each experiment, 50 μL of the gallium standard, 2 mL of the acid matrix, and various amounts of chelating agents (AcAcH, TTAH, and PySH) were added to the quartz sample vial inside the extraction vessel. Optimized extraction conditions were obtained by sequentially varying one experimental parameter while all other parameters remained fixed. The vessel contents were extracted with supercritical fluid CO₂ at various temperatures and pressures. Each sample was first statically extracted for 15 min. In this study, “static” indicates that the vessel was charged with CO₂ while the outlet valve was closed. After the static extraction, the outlet valve was opened and the sample was dynamically extracted for 15 min with a CO₂ flow rate of approximately 1.0 mL/min. The outlet of the extraction cell was connected to a thermally-controlled variable restrictor which maintained the supercritical temperature at 70 °C in the system. As the CO₂ evaporated at the restrictor outlet due to decompression, the expanding fluid from the extraction vessel was bubbled into a glass tube containing methanol to collect the extracted metal chelate at the outlet of the extractor. After extraction, the sample solvent was quantified to 10 mL with methanol in a volumetric flask.

2.4. Analysis

The extracted metal concentration was determined three times using a Flame Atomic Absorption Spectrophotometer (AA-200, PerkinElmer). A gallium hollow cathode lamp, operated at 20 mA, was used as the light source. The wavelength was set at 303.9 nm resonance line for gallium. A time-constant of 1 s was used for the

peak height mode. The acetylene flow rate was slightly leaner than is recommended by the manufacture. The range of the calibration standards for gallium on flame atomic absorption spectrometric determinations was 2–10 mg/L. The correlation coefficients of the calibration curves were generally 0.999. The extraction efficiency was calculated based on the amount of gallium remaining in the aqueous phase:

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

3. Results and discussion

To obtain the quantitative extraction efficiency of gallium (III) ions from acidic aqueous solution in the presence of supercritical CO₂ extraction, the optimization of various analytical parameters, such as various chelating agents, extraction pressure, extraction temperature, dimensionless CO₂ volume, the concentration of the chelating agent, and the pH of solution in the extraction procedure, was conducted. In our study, supercritical CO₂ extraction conditions were optimized using a step-by-step design represented by McNally [32]. This approach can be used as an alternative to the factorial design method because it produces similar results with less data processing [33]. All samples were extracted in a static–dynamic mode with CO₂ throughout this study. The results of the extraction efficiency of gallium (III) ions using supercritical CO₂ extraction with various chelating agents are presented and discussed in this section.

When the gallium (III) ions were extracted by pure supercritical CO₂, in a pH 6 solution without a chelating agent, the extraction efficiency was only 10.5%. Gallium ions are only slightly soluble in pure carbon dioxide due to the weak interactions between the positively charged metal ions and non-polar CO₂. For practical applications, etching wastewater from semiconductor plants is favored to be acidic. Thus, the synthetic etching wastewater of pH 2 was used without a chelating agent in the supercritical CO₂ extraction process of gallium (III) ions. It was found that the extraction efficiency was improved from 10.5% to around 20.9% when the pH was varied from 6.0 to 2.0. Therefore, acidic mediums are more effective than other types of mediums for metal extraction from aqueous solution in a supercritical CO₂ extraction system [34]. However, the extraction efficiency of gallium (III) ions from an acidic aqueous solution in supercritical CO₂ without a chelating agent is unsatisfactory. The extraction of gallium ions using just supercritical CO₂ shows little feasibility. With the proper selection of chelating agents, supercritical CO₂ extraction is a promising means of extracting metal ions directly from aqueous solution. In the subsequent extraction experiments, gallium (III) ions were extracted from acid aqueous solutions using the supercritical CO₂ extraction technique in the presence of various chelating agents.

3.1. Effects of various chelating agents

As mentioned above, the extraction efficiency of gallium (III) ion from acidic aqueous solutions was low in pure supercritical CO₂ 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 to 2000 psi and 70 °C, respectively. Various types of chelating agents, such as AcAcH, TTAH, and PySH, were utilized for the supercritical CO₂ extraction of gallium (III) ions. The influences of the various chelating agents on the extraction efficiency of gallium (III) ions using supercritical CO₂ are demonstrated in Fig. 2. In general, the addition of chelating agents led to an increase in the extraction efficiency by a factor of 2.2–4.0, yielding about 45%–80% of gallium (III) ions extracted.

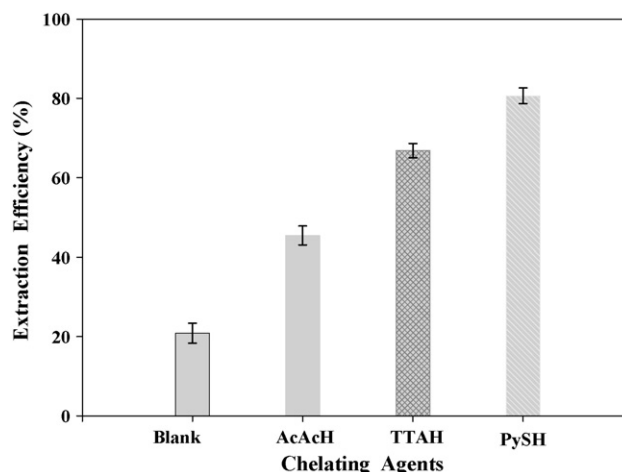


Fig. 2. Influences of the various chelating agents on extraction efficiency of gallium (III) ions by supercritical CO₂ ($T=70\text{ }^{\circ}\text{C}$, $P=2000\text{ psi}$, $\text{pH } 2$, dimensionless CO₂ volume = 7.5, concentration of chelating agent = 50 ppm).

This suggests that the presence of a chelating agent is necessary for increasing the efficiency of metal extraction in supercritical CO₂.

The extraction efficiency with AcAcH in the supercritical CO₂ state was about 45.4%. β -Diketonate metal complexes in supercritical CO₂ are often poorly extracted from aqueous solutions due to finite mass transfer between the hydrophilic metal ions and the hydrophobic chelating agents [16]. Under the same experimental conditions, the extraction efficiency with TTAH was observed to be about 66.8%. A significant increase in the extraction efficiency of gallium (III) ions in supercritical CO₂ was accomplished by using TTAH instead of AcAcH. This was probably due to the solubility of free chelating agents in supercritical CO₂ depending on the chemical structure of the chelating agents and varying substantially from one type to another. The chemical structures of various chelating agents used in this study are given in Fig. 1. Recent NMR studies show that TTAH is almost exclusively in the enol form under the high temperature and pressure conditions relevant to the SFE system [15]. AcAcH was in each of its forms in supercritical CO₂. The acidity of the chelating agent originates from the enol form and the deprotonated β -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 gallium (III) ions in the acidic medium, which can enhance the extraction efficiency [35–36].

To extend our early investigation on the thio-, dithio-metal complexes and to find useful chelating agents, these complexes were employed in the supercritical CO₂ system [37–38]. The chelating agent PySH, used for metal ion extraction from acidic aqueous solutions, is shown in Fig. 2. It can be evidently shown that the appreciable extraction efficiency of 80.6%, achieved using chelating agent PySH, was superior to the extraction efficiencies obtained using AcAcH and TTAH. This result agrees with a popular model for predicting whether a metal and a chelating agent are likely to react, called the hard–soft acid–base (HSAB) principle, which proposes that hard acids react strongly with hard bases and that soft acids react strongly with soft bases [39]. Hard acids are likely to be small in size, have a large positive charge, and 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. Hard and soft bases are analogous to their acid counterparts except that they are electron-rich species. Reactions between hard acids and hard bases occur imme-

diately because the two reactants have a strong columbic attraction for each other. Moreover, soft acids and soft bases react by sharing 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 fourth periodic metal, gallium, react easier with soft sulfur, including a chelating agent such as PySH, than with hard oxygen, including chelating agents such as AcAcH and TTAH.

From the above description, the σ -donor ability of the oxygen, nitrogen, and sulfur chelating agents is reflected in the order: PySH > TTAH \gg AcAcH. 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 gallium complexes for supercritical CO₂ extraction. Future developments in supercritical CO₂ 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. As a result of the superior extraction efficiency of PySH as a chelating agent in the extraction of gallium (III) ions, all subsequent extraction experiments were conducted and investigated using the supercritical CO₂ extraction technique in the presence of the chelating agent PySH.

3.2. Effect of pressure

The properties of CO₂, such as density and polarity, increased with increasing CO₂ pressure, which led to the enhancement of the extraction efficiency of gallium chelate in supercritical CO₂ extraction. In this section, the pH of aqueous solutions and the concentration of the chelating agent were kept constant at 2.0 ppm and 50 ppm, respectively, to investigate the effects of extraction pressure. Fluid pressure has an essential effect on the extraction efficiency in supercritical CO₂ extraction because the fluid density is directly associated with the pressure. All extraction experiments were performed at pressures from 1500 psi to 3500 psi, in 500 psi increments, at fixed a temperature (50 °C). The samples in supercritical CO₂ extraction were extracted statically for 15 min, and then extracted dynamically for 15 min with a CO₂ flow rate of approximately 1.0 mL/min. The effect of pressure on the extraction efficiency of gallium (III) ions with PySH from acidic aqueous solution was demonstrated in Fig. 3. In general, with an increase in pressure, the density of supercritical fluid CO₂

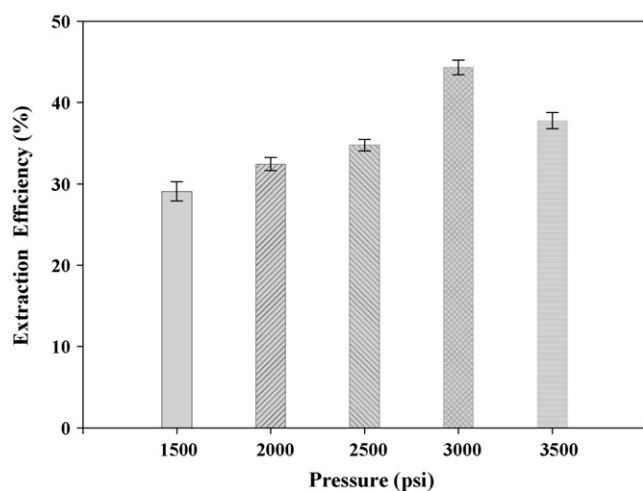


Fig. 3. Effect of pressure on the extraction efficiency of gallium (III) ions at 50 °C with PySH by supercritical CO₂ (pH 2, dimensionless CO₂ volume = 7.5, concentration of chelating agent = 50 ppm).

increases, thus enhancing the solubilizing ability of the chelating agent and metal correspondingly, which can enhance the extraction efficiency [40]. However, as the density approached its ceiling value, additional pressure did not increase density. Accordingly, the solubility of metal chelate in supercritical CO₂ also approached a limit as shown in Fig. 3. As the pressure increased, the flow rate of CO₂ emitted from the restrictor increased, which resulted in losses of metal chelate increasing rapidly due to both the formation of aerosols and volatilization. Therefore, there was a downward trend when the pressure was above 3000 psi. The optimal extraction pressure for the supercritical CO₂ extraction of gallium (III) ions with chelating agent (PySH) was accomplished at 3000 psi.

3.3. Effect of temperature

Changing the temperature of the supercritical CO₂ extraction also had a major effect as it altered the analyte volatility, extraction kinetics, and supercritical CO₂ density. In this section, the effect of temperature at the optimized pressure (3000 psi) on the extraction efficiency of gallium (III) ion was investigated. All extraction experiments were performed at temperatures from 40 °C to 80 °C, in 10 °C increments, at the optimized pressure (3000 psi). The results are shown in Fig. 4. With other conditions fixed, increasing the temperature from 40 °C to 70 °C dramatically improved the extraction efficiency from about 33.9% to 82.8%. Conversely, a negative effect on the extraction efficiency of gallium (III) ions was observed when the temperature was above 70 °C. This phenomenon could be explained as follows. In terms of the rule of kinetics, the higher the temperature, the more intensive the heat motion of solutes in the aqueous solution. The solutes overcome the absorbing energy of the solution and desorb from active sites of the matrix by supercritical CO₂ at higher temperatures. According to the laws of thermodynamics, the saturated vapor pressure enhances with an increase in temperature, which enables solutes to dissolve in supercritical CO₂ more easily. However, increasing the temperature usually reduces the density of supercritical CO₂, which can decrease the solubilizing ability of supercritical CO₂, resulting in a decrease in the solubility of metal chelate in supercritical CO₂. As a result, these three factors compete with each other and have a negative effect on the extraction efficiency, which implies that there is an optimum temperature for practical purposes [41]. Fig. 4 shows that the most efficient extraction was achieved at 70 °C. As the temperature increased from 40 °C to 60 °C, the extraction efficiency increased

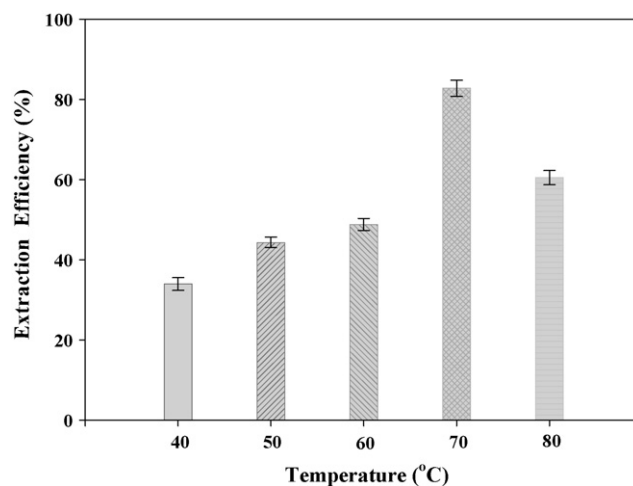


Fig. 4. Effect of temperature on the extraction efficiency of gallium (III) ions at 3000 psi with PySH by supercritical CO₂ (pH 2, dimensionless CO₂ volume = 7.5, concentration of chelating agent = 50 ppm).

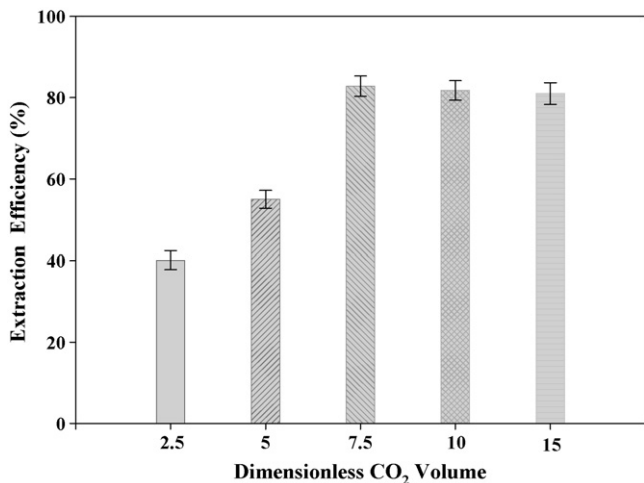


Fig. 5. Effect of dimensionless CO₂ volume on the extraction efficiency of gallium (III) ions with PySH by supercritical CO₂ ($T=70^{\circ}\text{C}$, $P=3000$ psi, pH 2, concentration of chelating agent = 50 ppm).

dramatically at 3000 psi from 33.9% to 82.8%. There was a downward trend when the temperature was above 70°C . Consequently, a value of 70°C was selected as the optimum temperature in this study.

3.4. Effect of dimensionless CO₂ volume

A dynamic mold was used to measure the solubility of a compound in a supercritical fluid. In the dynamic extraction, the solute is continuously, but slowly, swept with supercritical fluid. The solubility of the analyte was a function of the CO₂ flow rate through the extraction vessel. The supercritical dynamic extraction time was varied from 5 min to 30 min with a CO₂ flow rate of approximately 1.0 mL/min. In order to characterize the gallium (III) solution extracted by the total CO₂ volume effectively, the total CO₂ volume was normalized by the gallium (III) solution volume (2 mL), which is defined as the dimensionless CO₂ volume in this study. The effect of the dimensionless CO₂ volume on the extraction efficiency of gallium (III) at pH = 2.0, $T=70^{\circ}\text{C}$, $P=3000$ psi, and 50 ppm concentration of chelating agent, is demonstrated in Fig. 5. Fig. 5 shows the effect of the supercritical solvent flow rate on the extraction efficiency as a function of the dimensionless CO₂ volume that has been passed through the extraction vessel. As the total volume of supercritical CO₂ increased, the balance of extraction shifted to facilitate extracting the metal chelate. The extraction efficiency was enhanced from 40.1% to 82.8% when the dimensionless CO₂ volume was increased from 2.5 to 7.5. However, with the dimensionless CO₂ volume increased, the amount of CO₂ emitted from the restrictor increased, resulting in more collection losses of metal chelate due to both the formation of aerosols and volatilization, which were not favorable to enhance the extraction efficiency. In the range 2.5–7.5, the extraction efficiency significantly increased, while in the range 7.5–15, the extraction efficiency seemed to reach a steady value of around 81%–82%. Consequently, a value of 7.5 was selected as the optimum dimensionless CO₂ volume.

3.5. Effect of the concentration of the chelating agent

Under the conditions of pH 2.0, 3000 psi, and 70°C , the effects of the amount of PySH chelating agent on the extraction efficiency of gallium ions were investigated. The extraction efficiency of gallium (III) ions as a function of concentration of chelating agent is presented in Fig. 6. The extraction efficiency increased signifi-

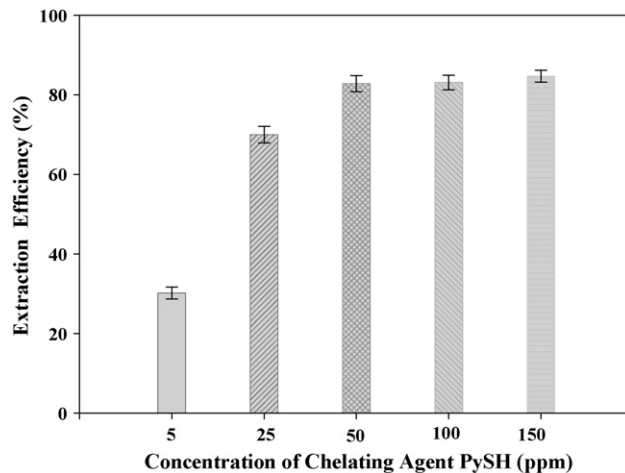


Fig. 6. Comparison of the extraction efficiencies versus concentrations of chelating agent PySH by supercritical CO₂ ($T=70^{\circ}\text{C}$, $P=3000$ psi, pH 2, dimensionless CO₂ volume = 7.5).

cantly when the chelating agent concentration was increased from 5 ppm to 50 ppm, and then reached a steady value. When the concentration of chelating agent increased from 5 ppm to 50 ppm, the extraction efficiency with chelating agent PySH improved markedly from around 30.2% to 82.8%. Because of the acidic aqueous solution, chelating agents tend to decompose in supercritical CO₂ extraction systems, which indicates that an excess amount of chelating agents is usually required in order to achieve enhanced metal extraction efficiencies in supercritical CO₂ [34]. This increase in chelating agents was naturally accompanied by a generation of more anions available to chelate with the gallium ions in the acidic aqueous solution. However, no significant improvement in extraction efficiency was observed when the concentration of chelating agent was above 50 ppm. Increasing the concentration of chelating agent from 50 ppm to 150 ppm did not yield higher extraction efficiency; it reached a value of around 82.8–84.7%. Furthermore, the excess chelating agents blocked the outlet of the restrictor within the supercritical fluid extraction system. Therefore, a value of 50 ppm concentration of chelating agent was chosen as the optimum concentration for supercritical CO₂ extraction. All further supercritical CO₂ extraction experiments in this study were carried out at 50 ppm concentration of chelating agent.

3.6. Effect of the pH of the solution

Another critical parameter that should be considered in supercritical CO₂ extraction of metals is the pH of the solution. Metal chelate formation generally depends on the pH of the solution. In order to investigate the pH influence on the extraction efficiency of gallium (III) ions, the concentration of chelating agent was set at 50 ppm, and the pressure and temperature were set at 3000 psi and 70°C , respectively. As shown in Fig. 7, a decrease in the pH increased the extraction efficiency of gallium (III) ions for the chelating agent PySH. When the pH was varied from 2.0 to 6.0, the extraction efficiency of gallium (III) ions decreased from 82.8% to 48.2%. A previous report showed that when water is in contact with CO₂ under supercritical fluid conditions, due to the formation and dissociation of carbonic acid in water, the pH at equilibrium ranged between 2.80 and 2.95 [34]. The chelating agents, which form a stable neutral complex with metal ions at a pH of less than 3, are considered effective in supercritical CO₂. Therefore, acidic mediums are more effective than other types of mediums for metal extraction from aqueous solutions in supercritical CO₂ extraction

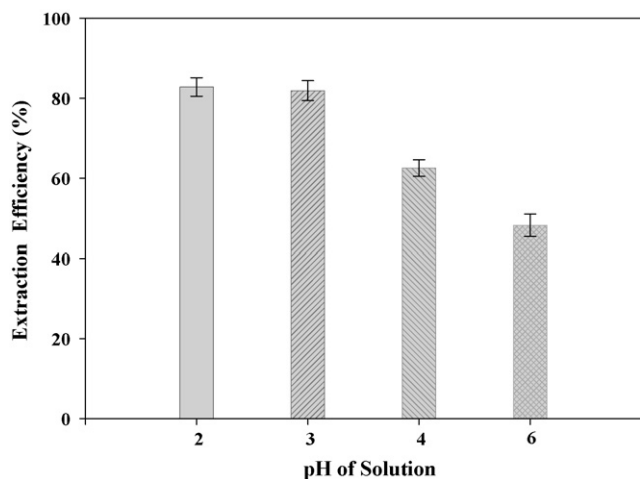


Fig. 7. Effect of the pH of the solution on the extraction efficiency of gallium (III) ions with PySH by supercritical CO₂ ($T=70^{\circ}\text{C}$, $P=2000$ psi, dimensionless CO₂ volume = 7.5, concentration of chelating agent = 50 ppm).

systems. When supercritical CO₂ extraction experiments were carried out in more acidic mediums, as well as under a high pressure state (greater than 2000 psi), the adding effects were apt to cause parts abrasion within the supercritical CO₂ extraction instrument, as well as operating considerations for security. Therefore, the optimum pH of solution for supercritical CO₂ extraction should fall in the range of 2.0–3.0.

4. Conclusion

In this study, a potential alternative separation approach to the extraction of gallium (III) ions from acidic aqueous solutions was presented. Supercritical CO₂ is often promoted as a green solvent in green chemical separation processes. With proper selection of chelating agents, our experimental data indicated that chelating agents, usually forming highly soluble metal complexes in supercritical CO₂, are very effective in the supercritical CO₂ extraction process. We have demonstrated that the PySH chelating agent achieves higher extraction efficiency in supercritical CO₂ extraction of gallium (III) ions than do the AcAcH and TTAH chelating agents. The key parameters in the extraction procedure, such as extraction pressure, extraction temperature, dimensionless CO₂ volume, the concentration of the chelating agent, and the pH of solution were also optimized in this study. It was revealed that the optimal extraction pressure and temperature for the supercritical CO₂ extraction of gallium (III) with the chelating agent PySH were 70°C and 3000 psi, respectively. A value of 7.5 was selected as the dimensionless CO₂ volume. The optimum concentration of chelating agent was found to be 50 ppm. The optimum pH of solution for supercritical CO₂ extraction should fall in the range of 2.0–3.0.

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