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Juncheng Liu[a]; Wei Wang[b]; Zhengwu Wang[a]; Ganzuo Li[a]; Buxing Han[c]
[a] Institute of Colloid and Interface Chemistry, Shandong University, Jinan, China [b] Department of Chemistry, Jinan University, Jinan, China [c] Center for Molecular Sciences, Chinese Academy of Science, Institute of Chemistry, Beijing, China

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COMPLEXATION-SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF COPPER IONS FROM SOLID MATRICES WITH THENOYLTRIFLUOROACETONE AND MODIFIERS

Juncheng Liu,[1,2] Wei Wang,[3] Zhengwu Wang,[1]
Ganzuo Li,[1] and Buxing Han[2,*]

[1]Institute of Colloid and Interface Chemistry,
Shandong University, Jinan 250100, China
[2]Center for Molecular Sciences, Institute of Chemistry,
Chinese Academy of Science, Beijing 100080, China
[3]Department of Chemistry, Jinan University,
Jinan 250002, China

ABSTRACT

The method of chelant thenoyltrifluoroacetone complex copper ions combined with supercritical fluid extraction (SFE) was used to extract Cu^{2+} from solid matrices. The influences of pressure, temperature, and total volume of CO_2 used in the extraction on the recovery of Cu^{2+} were studied systematically in the 40–100°C range at pressures up to 35 MPa. In order to improve recovery of Cu^{2+}, three modifiers of different polarities (methanol, dichloromethane, and toluene) were tested, respectively. All the modifiers can improve the efficiency of the extraction, with methanol being the most efficient. Most of the Cu^{2+} (recovery $= 97.3\%$, R. S.

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*Corresponding author. Fax: +86-10-62559373; E-mail: hanbx@infoc3.icas.ac.cn

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D = 2.88, $n = 4$) can be recovered from the solid matrices at suitable conditions.

Key Words: Complexation; Copper ions; Modifier; Recovery; Supercritical fluid extraction

INTRODUCTION

Complexation combined with solvent extraction is one of the most widely used techniques for preconcentration and separation of metal ions from solid and liquid samples (1,2). These solvent extraction procedures, however, are usually time-and labor-intensive. In addition, solvent extraction requires large amounts of organic solvents and often poses environment problems. In recent years, supercritical fluid extraction (SFE) of metal ions has elicited significant interest, (3–8) because it is an environmental friendly process. Compared with conventional solvent extraction, SFE has many advantages. For example, this process is relatively fast, the selectivity can be controlled by pressure, temperature, and suitable cosolvent, and the solvent of supercritical fluids can be captured easily after decreasing pressure. Moreover, the solvent residue in the product is negligible. Carbon dioxide is most commonly used in SFE, because it is inexpensive, nontoxic, nonflammable, nonpolluting, and has favorable critical constants ($T_C = 31.1°C$, $P_C = 7.38\,MPa$).

Most metal ions exhibit negligible solubility in a low dielectric medium such as CO_2. Therefore, direct extraction of metal ions by supercritical CO_2 is impossible. However, if metal ions are bound to suitable organic ligands, their solubility in the supercritical CO_2 will increase significantly. It is generally known that β-diketones are useful chelating agents in coordination and analytical chemistry (9,10); fluorinated β-diketones such as thenoyltrifluoroacetone (TTA) are especially useful for the conventional solvent extraction of various metal ions (11,12). The solubility parameter of CO_2 is calculated using the heat of vaporization and the molar volume is $4–5\,cal/cm^3$ in the liquid state at temperatures between 0 and 25°C, which is similar to that for fluorinated materials (13). Hence, fluorine-containing ligands usually form CO_2-philic metal chelates and thus are effective reagents for metal ion extraction into supercritical CO_2.

Modifiers (usually less than 5%) are often used, which serve the functions of increasing the polarity of supercritical CO_2 and making the metal chelate desorb from the surface of solid matrices easily. As such, they have been used extensively in SFE to increase the extraction efficiency (14–17).

In this work, the extraction of Cu^{2+} from the surface of samples of silica gel prepared was studied systematically. It will be demonstrated that supercritical carbon dioxide with 5% methanol can extract Cu^{2+} successfully in the presence of fluorinated β-diketones chelating agents TTA.

EXPERIMENTAL SECTION

Reagent and Materials

CO_2 with a purity of 99.995% was supplied by Beijing Analytical Instrument Factory in China. Thenoyltrifluoroacetone (A. R. Grade) was obtained from Beijing Chemical Reagent Company in China. $CuCl_2 \cdot 2H_2O$ (A.R. Grade) was supplied by Jinan Chemical Reagent Company in China. Silica gel of 100–120 mesh was purchased from Shanghai Chemical Reagent Factory in China. Ethanol, methanol, dichloromethane, and toluene were A.R. grade, and were supplied by Beijing Chemical Reagent Company of China.

Apparatus

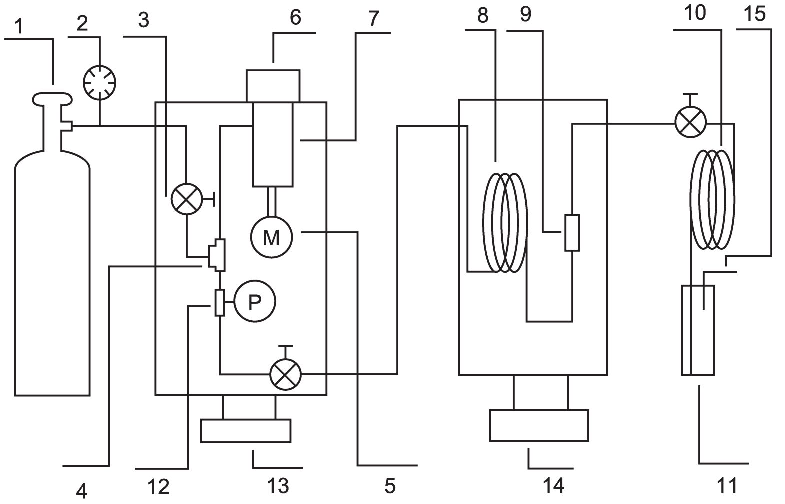
The schematic diagram of SFE is shown in Sch. 1. In this system CO_2 was delivered using a high-pressure pump controlled by computer. The extractor consists of on/off valves connected to a 2.5 mL extraction cell. The extraction cell was placed in an oven where the temperature was controlled by a computer. Fused-silica tubing (50 μm i.d. and 20 cm in length) was used as the back pressure restrictor for the extraction fluid. The SFE system allowed static and dynamic extraction to be performed by the use of the on/off valves.

Preparation of Solid Sample

In order to study the optimum conditions for the extraction of Cu^{2+} systematically, simulated copper samples were prepared. A known amount of $CuCl_2 \cdot 2H_2O$ reacted with TTA in ethanol solution. The molar ratio of $CuCl_2 \cdot 2H_2O$ to TTA was 1:2. Then the Cu $(TTA)_2$ solution was spiked on the surface of silica and the ethanol was removed by vacuum in the vacuum oven.

Extraction Procedures

The different pressures, temperatures, total volumes of CO_2 used, and modifiers of supercritical CO_2 were studied in order to find the optimum



Scheme 1. Schematic diagram of the SFE apparatus. (1) CO_2 steel cylinder, (2) pressure gauge (3) high pressure on/off valve (4) tee-joint, (5)electric machinery, (6) cooling equipment, (7) SB-2 injection pump, (8) preheating pipe (9)extraction cell (10) restrictor, (11) collector, (12) pressure sensor, (13) the system of controlling pressure, (14) the system of controlling temperature, (15) vent.

conditions for the extraction of Cu^{2+} from the surface of the silica. A 1.700 g silica sample which consists of 4.221×10^{-4} g Cu^{2+} was packed into the extraction cell, which was then installed in the system as shown in Sch. 1. The air in the system was removed by vacuum. The system was stabilized at desired temperature for 2 hr. The system was charged with the desired CO_2 and stabilized statically for 10 min. Dynamic extraction was then initiated. The flow rate of liquid CO_2 from the injection pump (at 20°C and the experimental pressure) was 1 mL/min. The extracted metal chelate was collected in the collector with ethanol and concentration of the solution was determined by UV–Vis. spectrophotometer (Third Analytical Instrumental Plant of Shanghai, China), The main absorption peak of Cu $(TTA)_2$ was at 347.2 nm with ethanol as the reference solution. The amount of the extracted metal chelate was easily calculated on the basis of the concentration and mass of the solution in the collector.

The Method of Analysis

The concentration of metal chelates obtained by the complexation-SFE was determined by ultraviolet and visible spectrophotometry. The main absorption peak of Cu $(TTA)_2$ was at 347.2 nm with ethanol as the reference solution. The calibration equation obtained is $Y = 0.06855 + 0.05439X$ where Y is the absorbance and X is the concentration of copper in 10^{-4} g/L, and the regression coefficient is 0.99962.

RESULTS AND DISCUSSIONS

The efficiency of metal ions extraction from solid matrices using chelating method depends on several factors including the solubility of metal chelates in supercritical CO_2, the ability of desorption of metal chelates from the surface of the solid matrices, and the total volumes of supercritical CO_2 used in the extraction. Both pressure and temperature affect the solubility of metal chelates in supercritical CO_2. Addition of modifiers is a useful method of increasing solubility of metal chelate in supercritical CO_2. Thus, effects of temperature, pressure, total volume of CO_2 used, the structure, and polarity of modifier on the recovery of Cu^{2+} were systematically studied.

Effect of Pressure on Extraction of Cu^{2+}

The fluid pressure is an essential parameter in SFE because the fluid density is directly related to the applied pressure. As the other conditions were fixed, the density of CO_2 increased with the increase in the CO_2 pressure, and the solubilizing ability of supercritical CO_2 increased correspondingly, leading to the increase in the solubility of metal chelate in supercritical CO_2, which is beneficial for the extraction. However, as the density tended to reach its maximum value, additional pressure did not increase density. So the solubility of metal chelate in supercritical CO_2 also approached a limit as suggested by Fig. 1. The recovery of Cu^{2+} at 60°C at different pressure of CO_2 is shown in Fig. 1. The volume of liquid CO_2 used was 6 mL. A value of 25 MPa was selected as optimum pressure.

Effect of Temperature on Extraction of Cu^{2+}

Temperature also had a large effect on the recovery of SFE. The effect of temperature on the extraction of Cu^{2+} is shown in Fig. 2. As other conditions are fixed, the higher temperature promotes metal ion-chelate desorption from the active sites of the matrix. This may be viewed as displacement on preferential desorption of the ions from the actives sites by supercritical CO_2 at higher temperature. In addition, with increase of temperature, the saturated vapor pressure increased correspondingly, which made solutes dissolve into

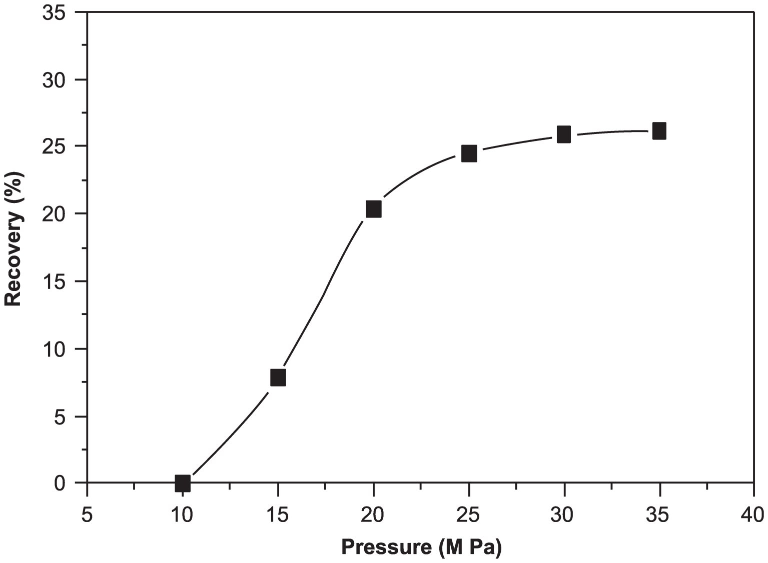


Figure 1. Effect of pressure on the recovery of Cu^{2+} at 60°C.

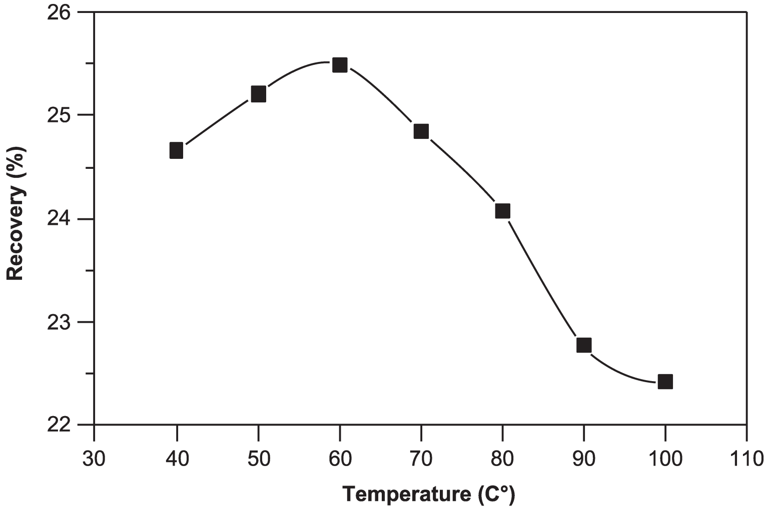


Figure 2. Effect of temperature on recovery of Cu^{2+} by supercritical CO_2 at 25 MPa.

supercritical CO_2 more easily. Moreover, when temperature increased, the density of supercritical CO_2 decreased, which made the solubilizing ability of supercritical CO_2 decrease, therefore, the solubility of metal chelate in supercritical CO_2 is expected to decrease. The effect of temperature on the recovery of Cu^{2+} at 25 MPa is shown in Fig. 2. The volume of liquid CO_2 used was 6 mL. Figure 2 shows that the most efficient extraction was achieved at 60°C.

Effect of Total Volume of CO_2 Used in the Extraction on the Recovery of Cu^{2+}

The effect of the total volume of CO_2 on the efficiency of the extraction of Cu^{2+} at 60°C and 25 MPa is shown in Fig. 3. When the total volume of CO_2 of supercritical CO_2 increased, the balance of extraction shifted to favor extraction of metal chelate. With the increased volume of CO_2, the amount of CO_2 emitted from the restrictor increased, leading to a further loss of metal chelate in the collector. This is due to both the solute volatilization and formation of aerosols, which were not beneficial to increase the recovery. In the range of 3–18 mL the efficiency increased significantly, and in the range of 18–21 mL the efficiency increased slowly, so 18 mL was selected as the optimum total volume of CO_2.

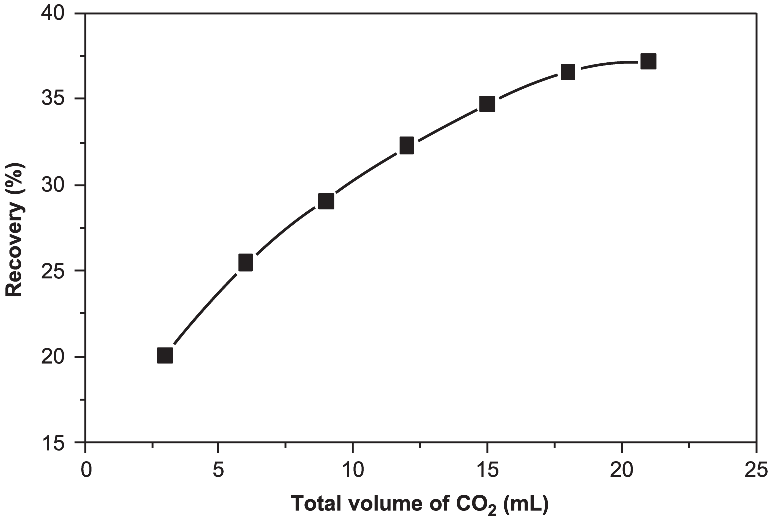


Figure 3. Effect of total volume of CO_2 used on the recovery of Cu^{2+} at 60°C and 25 MPa.

Table 1. Effect of Modifiers on the Recovery of Cu^{2+} at 60°C and 25 MPa

Number	Modifier (5% v/v)	Efficiency of Extraction (%)
1	CO_2	26.1
2	CO_2 + methanol	86.8
3	CO_2 + dichloromethane	64.9
4	CO_2 + toluene	62.6

Effect of Modifiers on Extraction of Cu^{2+}

Adding modifiers to CO_2 is an effective method to improve the extraction efficiency. In this study, methanol, dichloromethane, and toluene were used as the modifiers, which have different structures and polarities. All the experiments were conducted at 60°C, at 25 MPa. The volume ratio of CO_2 to modifiers was 95:5. The volume of the CO_2 used was 6 mL in each experiment. The results are shown in Table 1. The recovery of Cu^{2+} can be enhanced significantly by the modifiers and methanol was the most efficient, as can be known from Table 1. Modifiers affect the extraction in two ways: by increasing the solubilizing ability of the supercritical CO_2 as well as promoting desorption of metal chelates from solid matrices. Cu $(TTA)_2$ is polar metal chelate and CO_2 is nonpolar. Modifier serves the function of increasing both the polarity of supercritical CO_2 and desorption of the metal chelate.

On the basis of the study, four identical extractions under optimum conditions were carried out. The results showed that at 60°C and 25 MPa, most of the metal chelate (recovery = 97.3%, R. S. D. = 2.88, $n = 4$) could be extracted using 18 mL CO_2 with methanol (5% v/v) as modifier.

CONCLUSION

TTA can be used as chelating reagent for extracting Cu^{2+} from the surface of silica by using supercritical CO_2. The effects of temperature, pressure, total volume of CO_2 used, and modifiers of different structures and polarity on the recovery of Cu^{2+} have been studied. Most of the Cu^{2+} can be extracted under the reported optimum conditions. The technique established in the study offers a potential method to extract Cu^{2+} from environmental solid samples.

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