Study on a New Method of Extraction of Metal Ions from Solid Matrices by Supercritical Fluid

Zhao Jie CUI*, Jun Cheng LIU, Lain Cun GAO, Ying Qin WEI, Jun Zeng ZHANG

Department of Environmental Engineering, Shandong University, Jinan 250100

Abstract: 8-Hydroxyquinoline, methanol and Triton-100 were first used together in the extraction of metal ions by supercritical CO_2. In the new system, the effects of pressure, temperature and the volume of CO_2 on the efficiency of supercritical fluid extraction (SFE) were systematically investigated. The recovery under the optimum condition was only 11.38%, but if suitable concentration of methanol (v/v=5%) was added to the supercritical CO_2, the recovery was increased significantly (83.60%, RSD=4.37%, n=5). In order to further enhance the recovery Triton X-100 was added to the samples, and the results were satisfactory (96.62%, RSD=2.85%, n=5).

Keywords: Supercritical fluid extraction, chelating agent, modifier, surfactant, metal ions, solid matrices.

To date, most of the published SFE works have focused on organic compound[1], and some reports have related to SFE of metal ions[2]. Direct extraction of metal ions by supercritical CO_2 is highly inefficient. One approach of extracting metal ions by supercritical CO_2 is suggested to convert the charged metal ions into neutral metal complexes by using chelating agent in the supercritical CO_2. A variety of organic chelating agents such as thiocarbamate, β-diketones, and crown ether have been used in SFE of metal ions[3].8-Hydroxyquinoline contains double coordination atoms **(N, O^-),** so it is easy to react with Cu^{2+} and form stable neutral chelate. 8-Hydroxyquinoline was used as chelating agent in the complexation-SFE of Cu^{2+}, and we obtained satisfying results.

Experimental

Supercritical fluid extractor (made in Shandong University and Lunan Chemical Instrumental Plant), 754 model ultraviolet and visible spectrophotometer (made in the Third Analytical Instrumental Plant of Shanghai).

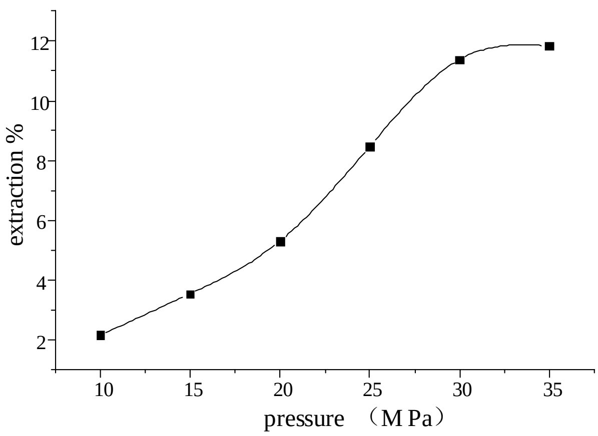
In order to find the optimum condition of the extraction of Cu^{2+}, **d**ifferent pressures, temperatures, the volumes of CO_2 have been studied. Under the optimum condition found above, the supercritical CO_2 containing 5% (v/v) methanol was used in the extraction. Then aliquot of microemulsion containing Triton X-100 was added to the samples. Finally, the metal chelates were collected in 10 ml chloroform and were determined by ultraviolet and visible spectrophotometer.

Results and Discussion

Effect of pressure on the recovery of Cu^{2+}

The efficiency of extracting Cu^{2+} at 60℃ with different pressure of CO_2 was shown in **Figure 1**. As the other condition is constant, with the increase of the pressure of CO_2 the density of CO_2 increases, and the solvent strength of supercritical CO_2 increases correspondingly, this lead to the increase of the solubility of Cu (8-Hydroxyquinoline)$_2$ in supercritical CO_2, it is beneficial to the extraction. When the pressure of CO_2 increases, the ability of supercritical CO_2 to transport Cu (8-Hydroxyquinoline)$_2$ from active sites on the surface of the matrices into the fluid phase decreases, and the losses of analytes increase due to both volatilization and the formation of aerosols. These are not beneficial to the extraction. So there are three functions in the process of extraction and they compete with each other. In the range of 10 MPa – 30 MPa, the first function is prominent. So the efficiency of extraction increases constantly, In the range of 30 MPa –35 MPa, the last two functions increase incessantly, therefore the efficiency of extraction increases very slowly.

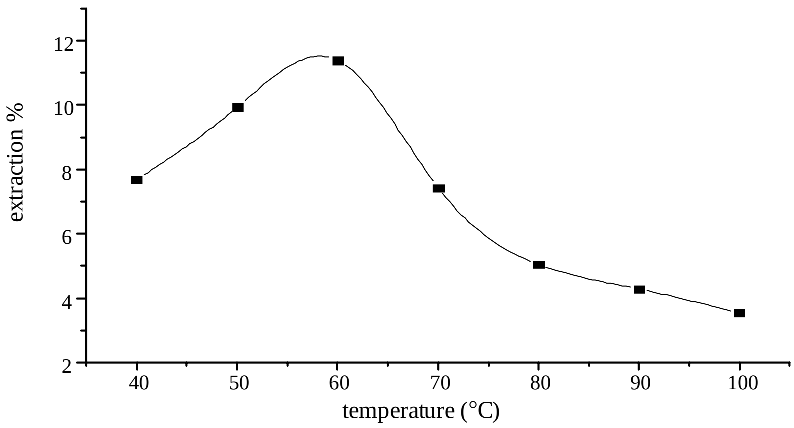
Figure 1. Effect of the pressure on the recovery of Cu^{2+} at 60℃ (The time of static extraction :20min, The volume of supercritical CO_2 used in dynamic extraction :10 ml)



Effect of temperature on the extraction of Cu^{2+}

The effect of temperature on the efficiency of extraction of Cu^{2+} is shown in **Figure 2**. As the other condition is constant, based on the rule of kinetics, the higher the temperature the more intensive the heat motion of solutes on the active sites of the matrices. It is beneficial for the solutes to overcome the adsorbing energy fortress of the matrices and to escape from the surface of the matrices into the supercritical CO_2. In the point of view of thermodynamics, when the temperature increases the saturation vapor-pressure increases correspondingly, this makes the solutes to dissolve in the supercritical CO_2 easily. When the temperature increases the density of supercritical carbon dioxide decreases, which makes the solvent strength of supercritical carbon dioxide decrease correspondingly, therefore the solubility of metal chelates in supercritical carbon dioxide decreases. The three factors compete with each other. **Figure 2** shows that the largest efficiency of extraction was obtained at 60℃. So 60℃ was selected as optimum temperature.

Figure 2. Effect of temperature on the recovery of Cu^{2+} at 30 MPa (The time of static extraction: 20 min, the volume of supercritical CO_2 used in dynamic extraction: 10 ml, the flow rate of supercritical CO_2: 1 ml/min)



Effect of volume of the supercritical CO_2 on the recovery of Cu^{2+}

When the volume of supercritical CO_2 used in the extraction increases, the balance of extraction is beneficial to move to the direction of extraction of Cu (8-Hydroxyquinoline)$_2$. But with the volume of CO_2 increases the supercritical CO_2 emited from restrictor increases, this leads to the increase of the losses of analytes due to both volatilization and the formation of aerosols, it is not beneficial to increase the recovery. The flow rate of CO_2 was fixed at 1 ml/min, 10 ml, 15 ml, 20 ml, 25 ml, 30 ml, 35 ml, 40 ml are selected as the volumes of CO_2 respectively, the result showed that in the range of 10 ml-35 ml the efficiency increases incessantly and in the range of 35 ml-40 ml the efficiency decreases slowly. So 35 ml was selected as the optimum volume of CO_2.

Effect of the modifier on the recovery of Cu^{2+}

Improved solvent characteristics and extraction efficiencies can be obtained if polar solvent such as methanol is added to the supercritical CO_2. Polar modifier is thought to aid extraction in two ways: increasing the solvent strength of the supercritical fluid as well as interacting with the analyte/matrices complex to promote rapid desorption into the supercritical CO_2. As we know CO_2 is nonpolar but Cu (8-Hydroxyquinoline)$_2$ is polar metal complex. Suitable amounts of modifier can enhance the polarity of supercritical CO_2. This increases the interaction between polar solutes and modified solvent. Methanol was chosen in our experiment because of its high solvent polarity parameter, and its ability to deactivate the active sites on the surface of solid matrices.

The results of extraction of Cu^{2+} using a commercially available SFC grade CO_2 containing 5% (v/v)methanol are summarized in **Table 1**. The methanol-modified CO_2 increases the extraction efficiency of Cu^{2+} from 11.38 % to 83.60 %.

Table 1. Effect of the modifier on the recovery of Cu^{2+} at 60℃，30 MPa (The time of static extraction: 20 min, the volume supercritical CO_2 used in dynamic extraction : 35 ml , the flow rate of supercritical CO_2: 1 ml/min)

Number	Modifier	Efficiency of extraction (%)
1	Methanol(5%)	80.39
2	Methanol(5%)	85.78
3	Methanol(5%)	83.28
4	Methanol(5%)	87.54
5	Methanol(5%)	81.02

RSD=4.37%, n=5, Average value = 83.60%.

Effect of the surfactant on the recovery of Cu^{2+}

The efficiency of extracting Cu^{2+} by supercritical CO_2 modified by methanol was further improved in the presence of a non-ionic surfactant Triton X-100. The efficiency of extracting Cu^{2+} achieved 96.62%. Triton X-100 serves the function of solubilization. It is beneficial to the dissolution of the Cu (8-Hydroxyquinoline)$_2$ in the supercritical CO_2 and desorption of Cu (8-Hydroxyquinoline) $_2$ from the active sites of the matrices to the supercritical CO_2. The result are shown in **Table 2.**

Table 2. Effect of the surfactant on recovery of Cu^{2+} at 60℃，30MPa(The time of static extraction: 20 min, the volume of supercritical CO_2 used in dynamic extraction : 35 ml , the flow rate of supercritical CO_2: 1 ml/min)

Number	Modifier	Surfactant	Efficiency of extraction (%)
1	Methanol(5%)	TritonX-100	93.09
2	Methanol(5%)	TritonX-100	95.34
3	Methanol(5%)	TritonX-100	100.01
4	Methanol(5%)	TritonX-100	96.38
5	Methanol(5%)	TritonX-100	98.26

RSD=2.85%, n=5, Average value = 96.62%.

References

1. a) M.Y. Ding. *Chinese Journal of Chromatography*, **1997,** *15*(6), 527.
1. b) L. H. Yue and C. M.Wai. *Trends in Analytical Chemistry*, **1995**, *14*(3), 123.
1. c) Y. Meguro, S. Lso, T. Sasaki and Z. Yoshida. *Anal Chem*. **1998**,70, 774.
2. a) C. M. Wai And L.H.Yue, *Talanta*, **1993**, *40*(9), 1325.
2. b) K.E.Laintz and C. M. Wai. *Anal. Chem*. **1992,** *64*, 2875.
3. a) S.F. Wang and C. W. Wai, *Anal. Chem*, **1995,** *67*, 919.
3. b) L.H.Yue, R.D.Brauer, K.E.Laintz, and C.M.Wai., *Anal. Chem*, **1993,** *65*, 2549.
3. c) L.H.Yue and C. M. Wai. *Anal. Chem*, **1994**, *66*, 1971.

Received 18 December 1998