

Original Research Paper

Supercritical CO₂ Extraction of Heavy Metals Cu, Zn and Cd from Aqueous Solution using Dithizone as Chelating Agent

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Abstract: Metal ions in liquid samples can be extracted by supercritical CO₂, containing a suitable ligand. This paper presents the first experimental data for the extraction of three heavy metals Cu, Zn and Cd from aqueous samples in the presence of Dithizone as chelating agent. Extractions by supercritical CO₂ have been performed at 120 bars with 50°C used dynamic technique. After adding the CO₂ on the aqueous metal solution, the pressure and temperature were set and extraction was performed in three periodical times; 30, 60 and 120 min at constant temperature and pressure with a flow rate of CO₂ 2 mL min⁻¹. After the extraction, the CO₂ was released slowly through a restrictor. Methanol was used as a modifier (v/v) 10% and the pH value was set (10). After the extraction process, the remaining aqueous solution in the extractor was analyzed for its metal content by Atomic Absorption Spectrophotometer (AAS), determining the recovery of the metal by CO₂. During dynamic extraction noticed increased of extraction in function of time for all three metals; Cu (61.12-73.52%, RSD = 2.694, n = 3); Zn (78.33-87.00%, RSD = 1.243, n = 3) and Cd (70.60-82.40%, RSD = 2.227, n = 3).

Keywords: Supercritical CO₂, Heavy Metals, Extraction, AAS

Introduction

Chelating combined with solvent extraction is one of the most widely used techniques for pre-concentration and separation of metal ions from aqueous samples for analytical purposes Chein (1991). In many cases, solvent extraction requires the use of toxic organic liquids, generating environmental problems. The technology of Supercritical Fluid Extraction (SFE), offers the opportunity to efficiently extract both relatively non-polar analytes as well as ionic materials (such as metal ions) that can be mobilized with the addition of complexing agents Kronholm (2007). The supercritical fluid extraction SFE method is becoming popular alternative technique for the extraction of a wide range organo-metallic and inorganic analytes Wang and Marshall (1995). The high diffusivity, low viscosity and variable solvent strength as a function of density (P, T) are some of the attractive features of supercritical fluids Gere *et al.*

(1983). Their main advantage lays in the possibility of separating and drying the product by simple expansion, while the gas can be recovered, recycled and reused without the need of purification steps. The environmental benefits of using SFE in industrial processes, such as low energy consumption during operation, show their potential of replacing the far more environmentally damaging conventional organic solvents. Carbon dioxide is the most commonly used solvent as SFE, due primarily to its low critical parameters (T_c = 31.1°C, P_c = 7.38 MPa), being inexpensive, non-toxic, non-flammable, readily available and recycling capability (Seied *et al.*, 2004; Shamsipur *et al.*, 2001; Takeshita *et al.*, 2000). Direct extraction of metal ions by supercritical CO₂ is inefficient, because of the charge neutralization requirement and the weak solute-solvent interactions Cui *et al.* (2000). One approach of SFE of metals is by converting charged metal ions into neutral metal chelates using organic chelating agents. Carbon dioxide

is a non-polar gas and is suitable for solubility of non-polar substances. In order to increase the solubility of polar species in SC-CO₂, the polarity of supercritical fluid must be increased via utilization of co-solvents such as methanol, ethanol (Niehaus *et al.*, 1997; Tessy *et al.*, 2009; Ghoreishi *et al.*, 2009). Extraction of metal ions from an aqueous phase into CO₂ is influenced by the presence of carbonic acid which lowers the pH of the aqueous phase to approximately 3. While some metals are extracted efficiently at pH ~ 3 (Toews *et al.*, 1995; Niemeyer and Bright, 1998) other metal ions, cannot be efficiently extracted at such an acidic pH.

Diverse experiments for the extraction of heavy metals from different sources by using SC-CO₂ have been conducted by several researchers. Laintz *et al.* (1992) demonstrated Cu extraction from liquid and solid samples using SC-CO₂ in the presence of ligand bi's (trifluoroethyl) dithiocarbamate (FDDC). A variety of chelate agents, including dithiocarbamates, β - diketone, reagents organophosphorus compound, macrocyclic compounds and surfactants, are used for metal complexity in SC-CO₂.

The main objective of this research was to develop SC-CO₂ extraction procedure for metal ions in liquid samples and to elucidate further the parameters linked to the SFE extraction process. Complex metal ions were determined in the presence of Dithizone. The main goal was to optimize the extraction factors to give better results in qualitative and quantitative scope, without neglecting the use of statistical and instrumental analytical methods to achieve fast quantitative verification.

Materials and Methods

Reagent

ICP standard solution of Copper, Zinc, Lead and Cadmium (Fluka) were obtained. Dithizone (MERCK) was used as chelating agent. Methanol extra pure (Merck) was used as reagent of reaction and collecting agent. The reagents used were all analytical grade and of ultra-pure quality. De-ionized water is used in all experiments.

Analytical Techniques

Analytical techniques were used to monitor the outcome of experiments conducted during this study.

Atomic Absorption Spectrometry (AAS)

Flame Atomic absorption spectrometer (Solaar M6 TJA Solutions) equipped with cathode lamp "hollow" were used for determining the concentration of metals such as Cd Cu and Zn. The burner system air-

acetylene is used. Flow rate of nebulizer, 5ml min⁻¹. Wavelengths used are: Cd: 228.8 nm (0.5 nm), Cu: 324.8 nm (0.5 nm) and Zn: 213.9 nm (0.5 nm).

Calibration of the instrument was made using 1000 mg/L standard solution of these metals. All concentrations of these metals are expressed in parts per million (ppm).

Apparatuses

All experiments were carried out in a supercritical fluid extraction equipment at the Technical University of Graz, Institute of Chemistry. To carry out the objectives of this study, the supercritical extraction system shown in Fig. 1 was used. All extractions were performed using a special stainless steel cylindrical extractor vessel (50 mL). CO₂ pump, bath circulation, oven and vessels were used from company "Applied Separation". Tubes, valves and accessories were obtained from company "Nova Swiss". For the analysis of the metal ions extracted, an Atomic absorption spectrometry was used.

Procedure

During our research, we used dynamic techniques of supercritical CO₂ extraction. The extraction were performed in three time periods; 30 min, 60 min and 120 min with the flow rate 2 mL min⁻¹

The dynamic extraction procedure is described below.

From the stock standard solution was prepared 20 mL of 10 mg L⁻¹ concentration metal solution of Cu, Zn and Cd. The sample was placed in extraction cell and chelating agent (Dithizone) was added. Extractions were performed in presence of modifier Methanol 10% in basic pH value (pH = 10). Carbon dioxide was supplied from a supply tank, maintained at a pressure of approximately 53 bar. The extraction was carried under supercritical condition temperature 50°C, pressure 120 bar. The solute was extracted at a constant temperature and pressure of CO₂ in different periods of time; 30 min, 60 min and 120 min with flow rate 2 mL min⁻¹. Then the solute was removed from the extraction vessel and the vessel was cleaned with the izopropanol, to collect any solute that had precipitated within the vessel during depressurization. When the extraction was completed, solution was removed from the extraction vessel and was digested for 20 min in a microwave with HNO₃ (65%) at a temperature of 180°C. The subsequent solutions were analyzed with AAS (atomic absorption spectrometry). The extraction efficiencies were calculated based on the amount of the metal ion in the aqua sample before and after the extraction.

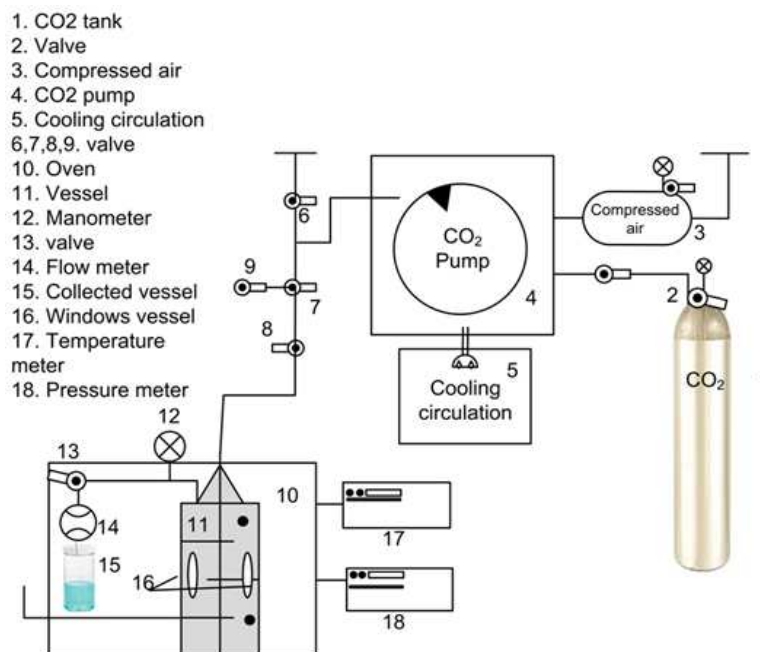


Fig. 1. Apparatus for extraction with SC-CO₂

Results and Discussion

The results of our research are presented in tables and charts as follows.

The use of supercritical fluid for extraction of various substances found wide applications recently. This method is now used to determine the total contents of (organo-metallic) complex compounds. Recently SFE technique was used by Liu *et al.* (1994). In preliminary experiments, organo-metallic mercury compounds were extracted with super-critical fluid using CO₂ as solvent and 5% to 10% methanol as modifier and the extraction rate was 64-89%. Authors Chein *et al.*, (1993) during their research concluded that metal ions can be extracted with SFE using CO₂ in the presence of suitable ligands. They have reported the application of SFE for the extraction of Cu²⁺, Cd²⁺, Zn²⁺ and Hg²⁺ in the presence of ligand lithium bis (trifluoroethyl) dithiocarbamate (LiFDDC). Negatively charged ligand (FDDC-) reacts with metal ions to form neutral chelate complexes which are soluble in CO₂.

In the scientific literature to our knowledge there were no data concerning the use of Dithizone as a ligand during the extraction of heavy metals with supercritical CO₂. However scientists have studied chemical properties of Dithizone. Fischer and Leopoldi, (1937) postulates that all metal dithizonates can exist in so-called keto-forms, in which the hydrogen atom of one phenylimino-group is replaced by metal (as II). Such complexes form preferentially in acid or neutral solution, but in basic solutions or with a deficiency of dithizone,

they pass over into "enol" complexes (as I or III) derived from the "thiol" form of the reagent by the loss of two hydrogen atoms (Fig. 3).

Irving *et al.* (1949) have studied dithizone as an acid and they have found the first dissociation constant. They also concluded that the extraction of metal-dithizone complex is influenced by pH value.

The extraction of metal-dithizone complexes during our research is done in pH values (pH = 10). Based on the results in Table 2, during dynamic extraction is noticed increasing of extraction in function of time. This increase is linear in terms of pressure 120 bar and temperature 50°C (Fig. 2). Our results agree with the results of other authors regarding the effect of time. According to literature data Osamu *et al.* (2012) the solubility of TBP-HNO₃ complex in supercritical CO₂ gradually increased as a function of time from 20min to 80 min and the recovery fraction for M TBP-HNO₃ complex was (20 min = 1.8*10⁻⁵; 80 min = 7.6*10⁻⁴). This is also reflected in our case for the metal-dithizone complexes.

Researchers Fengying *et al.* (2014) have studied the effect of pressure and temperature on the extraction efficiency. Undoubtedly pressure plays a very important role in this process. Based on the ideal gas law:

$$PV = nRT \quad (1)$$

n - is the amount of substance and can be defined as equal to $\rho V/M$ and the equation can be formulated as:

$$p = \rho RT / M \quad (2)$$

When the temperature and molar mass are constant, the pressure is directly proportional to the density. SCF-CO₂ density increases with pressure. Authors Seifried and Guigard, (2003) have measured the solubility of Cu (TTA)₂ in SCF-CO₂ in different pressures and have found that the solubility ranges in values; 0.99*10⁻⁶, 2.45* 10⁻⁶, 3.62*10⁻⁶ and 3.66*10⁻⁶ mol/mol at pressure 102 bar, 129 bar, 147 bar and 157 bar at the same temperature 40°C. During our study we have measured the efficiency of extraction in fixed pressure (120 bar) (Table 1).

Temperature is another important factor in the process of extraction heavy metals with super-critical CO₂. In thermodynamic terms, when the temperature increases, the saturated vapor-pressure increases correspondingly, the solutes dissolve in the supercritical CO₂ easily, but on the other hand the increase in temperature reduces the density of CO₂ which means also reduces CO₂ dissolving ability. According to the author mentioned above, the most efficient extraction temperature was obtained at 60°C. During our experiment the extraction temperature was obtained 50°C (Table 1).

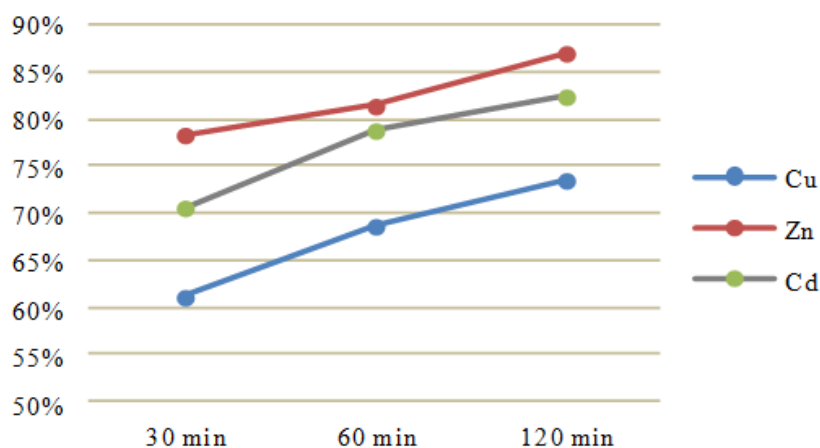


Fig. 2. Graphical presentation of the extraction percentage of Zn, Cu and Cd in different time periods in 120bar and 50°C

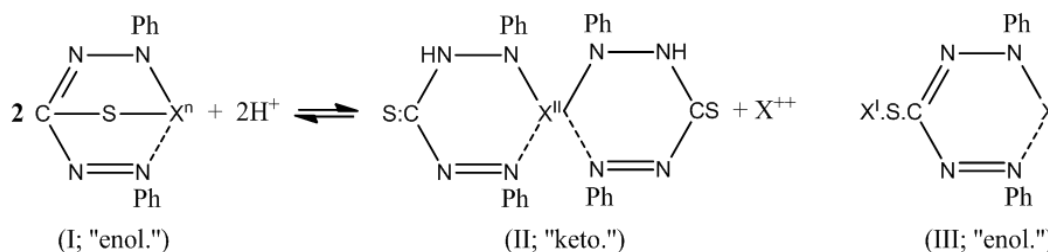


Fig. 3. Metal dithizonates complexes forms, depending on the pH value of the solution

Table 1. Pressure-temperature-modifier-time (P-T-M-T) conditions applied during SFE of M-Dithizone complexes

Metal M = Cu, Zn, Cd	Modifier	Ligand volume 0.01 M	P (bar)	T (C°)	Dynamic extraction time
M	Methanol 1 mL	Dithizone 1 mL	120	50	30 min
M	Methanol 1 mL	Dithizone 1 mL	120	50	60 min
M	Methanol 1 mL	Dithizone 1 mL	120	50	120 min

Table 2. The mean percent recoveries of Cu, Zn and Cd from the SFE using Dithizone as chelating agent

Metal/time	Cu% Recovery [%RSD]	Zn% Recovery [%RSD]	Cd% Recovery [%RSD]
30 min	61.12[2.732]	78.33[1.253]	70.60[2.134]
60 min	68.65[1.447]	81.40[1.833]	78.80[1.193]
120 min	73.52[2.694]	87.00[1.243]	82.40[2.227]

Conclusion

Dithizone was used as chelating agent in this experiment of extraction of Cu, Zn and Cd from aqua samples. The extraction efficiency, which is expressed as % extraction at three different operation time (30 min, 60 min and 120 min), varies from (61.12 to 73.52 for Cu%; 78.33 to 87.00 for Zn%; 70.60 to 82.40 for Cd%) in fixed value of pressure and temperature ($P = 120$ bar and $T = 50^{\circ}\text{C}$).

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Author's Contributions

Jeton Halili has performed the experiments, analyzed the data and gave the conclusions, discussed the results, implications and commented on the manuscript at all stages. Altin Mele has developed the concept and designed the experiments, supervised the analysis and edited the manuscript. Tahir Arbnesi has developed the analytical tools that enabled the experiments. Ilir Mazreku help with experiments.

Ethics

This manuscript and research is original work carried out by the principal author and his supervisory committee. The authors declare that this manuscript was not submitted/accepted elsewhere for publication and free from all ethical issues.

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