

THE EVALUATION OF THE DITHIZONE PERFORMANCE AS A COMPLEXING REAGENT FOR SUPERCRITICAL CO₂ EXTRACTION OF HEAVY METALS FROM AQUEOUS SOLUTIONS

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Abstract. Heavy metal ions in liquid samples, apart from classical methods of extraction, can also be efficiently and environmentally friendly extracted by the use of supercritical CO₂, containing a suitable complexing agent - ligand. This study represents the experimental data for the extraction of three heavy metals (Cu, Zn and Cd) from aqueous samples in the presence of dithizone as a ligand. The extractions by supercritical CO₂ were accomplished at p=120 bars with t=50°C through the use of the dynamic technique. After the CO₂ addition to the aqueous solution containing corresponding heavy metal ions, the pressure and temperature were set and extraction was performed in three different time periods: 30, 60 and 120 min (t=const., p=const. with a CO₂ flow rate of 2 mL min⁻¹). Once the extraction was stopped, the CO₂ was released slowly through a restrictor. Methanol was used as a modifier (v/v) 10% and the pH value was set to 10. After the accomplishment of the extraction process, the leftover aqueous solution in the extractor was analyzed for its metal content by the use of the Atomic Absorption Spectrophotometer (AAS). The overall performance of the use of the dithizone as a ligand in all three cases of heavy metal ions enhanced greatly the extraction efficiency of these ligand/metal species.

Key words: Supercritical CO₂, Atomic Absorption Spectrophotometer (AAS), heavy metals

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1. INTRODUCTION

The extraction and separation of metal ions from an aqueous phase using the supercritical CO₂ (SC-CO₂) is emerging as a promising “green” technology. Compared with the conventional solvent extraction, supercritical fluid extraction (SFE) is relatively fast and environmentally friendly. Environmental applications, such as the extraction of heavy metals or radionuclides from contaminated soil or metal removal from industrial waste water, have been a major focus in recent years [1], [2]. The solubility of metal-organic compounds in supercritical fluids (SF) has been the matter of several publications and reviews [3], [4-6]. Systematic studies of the effect that the ligand has on the solubility of these compounds in SC-CO₂ have been published for metal-diketonates [7, 8] and metal dithiocarbamates [9, 10]. The effect that the metallic center and its valence have on the solubility of different metal acetylacetonates in SC-CO₂ has been also studied [11]. Scientist have also studied the effect of gas pressure on the phase behavior of metal-organic compounds [12]. The objective of our study was first to

measure the solubility of metal dithizone complexes in SC-CO₂ and finally we were interested in examining whether the metal ions (Cu²⁺, Zn²⁺ and Cd²⁺) could be extracted from an aqueous solution using the dynamic extraction technique with SC-CO₂. Dithizone is a well-known and widely used ligand as photometric reagent [13]; it forms complexes with various metal ions (Figure 1). So far, no data is available on the usage of dithizone as a ligand for the extraction of heavy metals with SC-CO₂.

Irving and Andrew [14] have studied dithizone as an acid, and they have found the first dissociation constant. They have also concluded that the extraction of a metal-dithizone complex is influenced by pH value. Based on the literature data [15], higher extraction efficiency for metal ions was observed in the pH range from 8-10.

2. EXPERIMENTAL

The extractions were performed in three different time periods: 30min, 60min and 120min with the CO₂ flow rate of 2ml/min at supercritical conditions (p=120 bar and T=50 °C). In each case, the solution to be

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** This definition does not prejudice the position of status in accordance with UNSC Resolution 1244 and the International Court of Justice on Kosovo's Declaration of Independence

extracted contained either Cu (II), Zn (II) or Cd (II) ions.

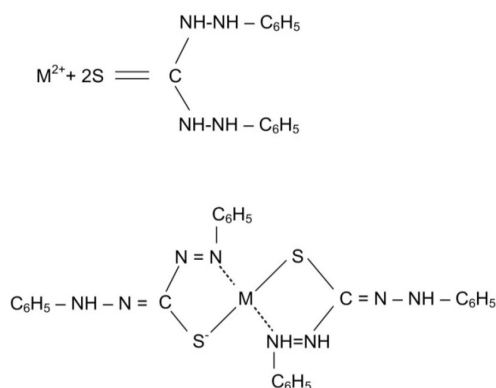


Figure 1. Reaction of metal ions with dithizone to form a metal-dithizone complex

The desired values of temperature and pressure were set in the temperature and pressure indicator controller, respectively. After filling the extractor (Fig. 1) with 20ml of 10mg/L metal solution of Zn (II), Cu (II) and Cd (II) ions, the chelating agent (dithizone) was added. Extractions were performed with the addition of a modifier (methanol 10% at pH=10). The pH value was maintained through the addition of several drops (3-5 drops) of NaOH (1M). Carbon dioxide was introduced from cylinder (~ 53 bar). During extraction, liquid CO₂ was pumped by opening the suction valve 2 and valves 7 & 8 in the discharge line of the pump. After reaching the desired temperature and pressure, experiments were performed in dynamic mode. A metering valve (13) was always heated during the extraction to obtain the desired flow. Measurement of the flow rate was done by the flow meter (14). After the extraction, the solution was removed from the extraction vessel and was digested for 20 minutes in a microwave with 65% HNO₃ at a temperature of 180°C. The subsequent solutions were analyzed with AAS (atomic absorption spectrometry). The extraction efficiencies (EE) were calculated based on the amount of the metal ion in the aqua sample before and after the extraction (Eq. 1):

$$EE(\%) = [C_{\text{(after extraction)}}/C_{\text{(before extraction)}}] * 100 \quad (\text{Eq. 1})$$

All experiments were carried out in the SFE equipment shown in Figure 2. The experimental setup consisted of a CO₂ tank, pumps, an extractor vessel, an oven, valves, a flow meter, a pressure and temperature controller. The CO₂ pump, bath circulation, oven and vessels were supplied by "Applied Separation" company. Tubes, valves, and accessories were obtained from "Nova Swiss" company. For the analysis of the extracted metal ions, AAS was used.

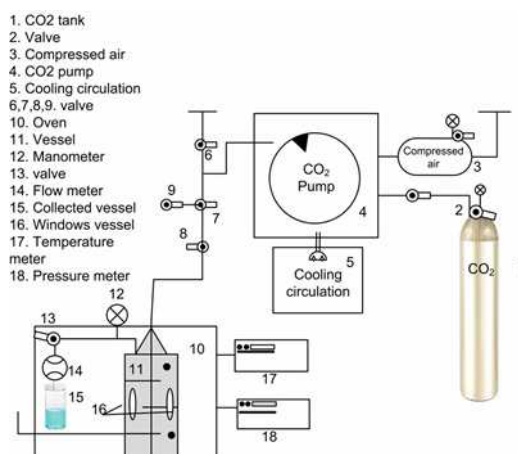


Figure 2. Apparatus for extraction with SC-CO₂

3. RESULTS AND DISCUSSION

As expected, the extraction performance increased with time (Table 1). This increase is linear in terms of pressure and temperature. When the extraction time is increased from 30 to 120 minutes, EE for the copper ions is increased up to 12.4%, for zinc ions 8.67% and 12.2% for cadmium ions. The EE would further increase with time because the equilibrium wasn't established yet, but due to the fact that the increase of time for practical purposes increases the cost for the extraction process, we chose the maximum experimental time at 120 min. From the results (Figure 3), as the EE for all of the studied metal ions is higher than 60 % in the first 30 min of extraction, this means that the process of extraction can be performed using this extraction time because this lowers the cost for this process.

The pH value in the aqueous phase during the extraction process could have decreased (approximately to pH=3) due to the solubility of the pressurized CO₂ and the formation of carbonic acid. On the other hand, metal-dithizone complex is unstable in an acidic environment. The increase of the pH value of the solution was achieved through the addition of NaOH.

Other parameters in this study include the effect of the modifier in the efficiency of the extraction. Based on our results, the modifier (methanol) increases the rate of extraction.

Table 1. The mean percent recoveries of Cu, Zn and Cd from the SC-CO₂ using dithizone as the chelating agent

Time	Cu% Recovery [%RSD]	Zn% Recovery [%RSD]	Cd% Recovery [%RSD]
30min	61.12[2.732]	78.33[1.253]	70.60 [2.134]
60min	68.65[1.447]	81.40[1.833]	78.80 [1.193]
120min	73.52[2.694]	87.00[1.243]	82.80 [2.227]

Methanol was chosen in this experiment due to its high polarity and the ability to facilitate the transfer of

analyte from an aqueous solution to the CO₂ phase and to increase the polarity of the CO₂ phase.

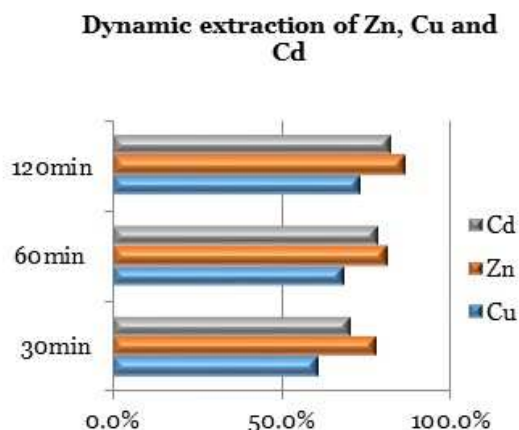


Figure 3. Extraction percentage of Zn, Cu and Cd in different time periods at 120bar and 50°C

4. CONCLUSIONS

SFE of Cu (II), Zn (II) and Cd (II) ions was studied by using dithizone as the chelating agent in this work. The study was conducted by the use of dynamic SC-CO₂ extraction techniques. The use of modifiers (MeOH), T and P were studied for achieving the best extraction efficiency. In this context, the extraction efficiency, which is expressed as a percentage of extraction at three different operation times (30, 60 and 120 minutes) varies (from 61.12 to 73.52 for Cu%; 78.33 to 87.00 for Zn% and 70.60 to 82.80 for Cd%) in fixed values of pressure and temperature (P=120 bar and T = 50°C).

From the obtained results, as expected for dithizone ligand, the best extraction efficiency was obtained at pH=10. The addition of methanol as a modifier further enhanced the extraction efficiency of the process.

In conclusion, the use of SC-CO₂ can be considered to be a very suitable method for the extraction of heavy metal complexes.

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