SUPERCRITICAL FLUID EXTRACTION OF MOLYBDENUM FROM AQUEOUS SOLUTION USING TRIOCTYLAMINE

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ABSTRACT

Dynamic extraction experiments with supercritical carbon dioxide were carried out on sulfuric acid solutions containing molybdenum at concentrations of 10^{-3} M and 10^{-2} M. The temperature, pressure and CO_2 flowrate are respectively set at 40°C, 25 MPa and 0.5 ml.min^{-1}. Trioctylamine, known for having a strong affinity with molybdenum in solvent extraction from sulfuric acid medium, was chosen as complexing agent. Solubility of trioctylamine is measured prior to extraction experiments. Extraction efficiency is calculated from the initial amount of metal taken into the reaction vessel and the remaining amount after extraction. More than 99% of the molybdenum are extracted from sulfuric acid solutions. However, it was difficult to recover molybdenum in the collection vessel because of the metal complex low solubility in supercritical carbon dioxide. Some selectivity studies were performed using iron and zirconium as impurities. Trioctylamine proved to be more selective towards molybdenum than iron. However, no selectivity was observed between molybdenum and zirconium.

Keywords: Molybdenum, sulfuric solution, trioctylamine, supercritical CO_2

1. INTRODUCTION

The aim of this study is to recover molybdenum from sulfuric effluents using supercritical carbon dioxide instead of organic solvents. Carbon dioxide is known to have many attractive properties such as being easily recyclable, inexpensive, non toxic, non flammable, chemically inert and abundant [1]. As carbon dioxide is a nonpolar molecule, a complexing agent addition is necessary to neutralize the charge on the metal ions and enhance its extraction [2]. According to literature, the extraction of molybdenum using complex formation with ligands in supercritical carbon dioxide has not been studied so far [3]. Trioctylamine (TOA), known for having a strong affinity with molybdenum in solvent extraction from sulfuric acid medium [4], is chosen as complexing agent. In this study, solubility of TOA is first measured at 40°C and different pressures. Then, dynamic extractions with supercritical carbon dioxide are carried out on sulfuric acid solutions containing molybdenum at concentrations of 10^{-3} M and 10^{-2} M. Selectivity of the extractant is studied using iron and zirconium as impurities.

2. MATERIALS AND METHODS

2.1 Materials

Trioctylamine (molecular weight: 353.68 g.mol^{-1}) with purity > 93% was purchased from Merck Millipore. Liquid CO_2 with purity of 99.7% was supplied by Air Liquide. Glass wool from Dominic Dutscher is used to reduce dead volume and to increase surface contact in the pressurized reactor containing the extractant and the collection vessels. Sulfuric acid solutions are prepared by dissolving ammonium molybdate tetrahydrate, ferric sulfate, zirconium sulfate and ammonium sulfate. Acidity is adjusted with 1 N H_2SO_4. Dodecane, ammonium carbonate 0.5 M and nitric acid 2wt% are used as collection solvents.

2.2 Apparatus and procedure for solubility measurement

Complexing agent solubility needs to be first determined before carrying out extraction experiments in order to better understand its behaviour under different operating conditions. An experimental set-up combining dynamic and gravimetric method has been developed to measure extractant solubility in supercritical CO_2. The apparatus is mainly composed of a CO_2 pump, an oven, a pressurized reactor, collection vessels and a thermal mass flowmeter (Figure 1). The high-pressure reactor is a titanium cell with filters at its top and bottom which can be easily weighted. It is filled with 10 mL of TOA and glass wool. Temperature of the oven is set at 40 ± 1°C. When the temperature reaches 40°C in the reactor, carbon dioxide is introduced in the apparatus until the desired pressure. During experiment, supercritical carbon dioxide flows continuously through the reactor at a low flowrate (accuracy: ±2%) to ensure that equilibrium is attained. The pressure is adjusted with a manual back-pressure regulator. Carbon dioxide flow is depressurized in the collection vessels allowing separation of solute from carbon dioxide. CO_2 goes through a second collection vessel to collect the remaining TOA in CO_2. Its flow is measured with a thermal mass flowmeter (accuracy: ±1%).
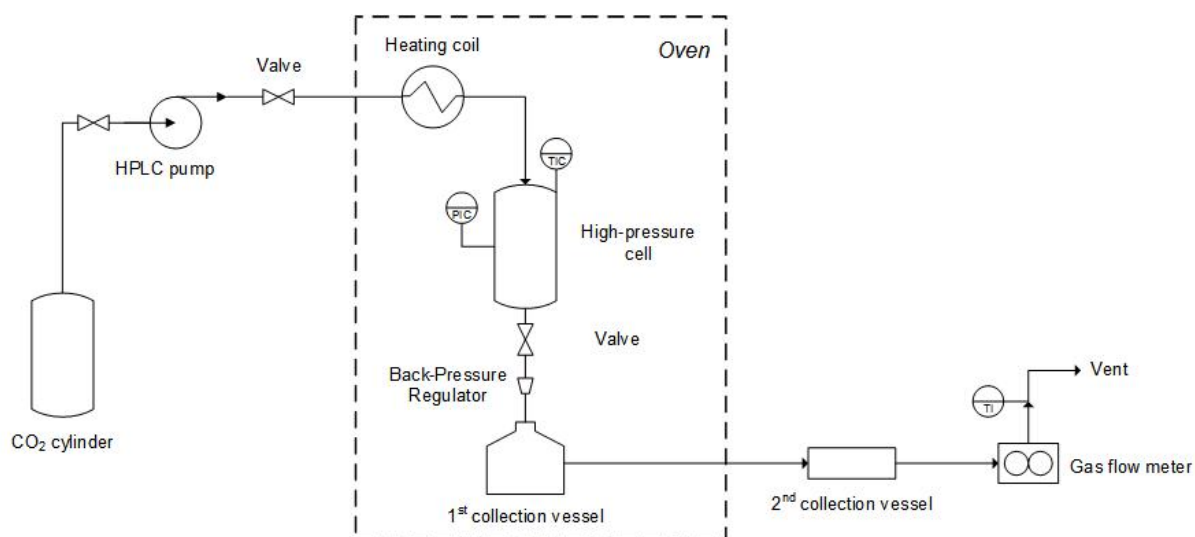

Figure 1: Experimental set-up for measuring solubility in supercritical carbon dioxide

Solubility is determined by weighing the quantity of TOA recovered in the collection vessels. The amount of TOA recovered during depressurisation is not taken into account as it is not possible to discern recovery of TOA residues in the tubes from physical transfer of TOA from the reactor. Solubility in molar fraction is calculated using Equation 1,

$$S(mol.mol^{-1}) = \frac{m_s / M_s}{m_s / M_s + m_{CO2} / M_{CO2}} \qquad (1)$$

where m_s, m_{CO2}, M_s, M_{CO2} are the amount of TOA recovered in the collection vessels (g), the amount of carbon dioxide measured by the flowmeter (g), the molecular weight of TOA and the molecular weight of carbon dioxide respectively (g.mol^{-1}).

The mass balance deviation is also calculated, according to Equation 2.

$$Deviation\ (\%) = \frac{\Delta m_{reactor} - \Delta m_{collection\,vessel}}{\Delta m_{reactor}} \times 100 \qquad (2)$$

where $\Delta m_{reactor}$ and $\Delta m_{collection\ vessel}$ are respectively the weight loss in the high pressure reactor and the weight gain in the collection vessel. The amount of TOA recovered during depressurisation is taken into account in the mass balance deviation.

2.2 Apparatus and procedure for dynamic extraction

An apparatus has been developed to carry out dynamic extraction. It is slightly different from the one used for solubility measurement as it is composed of two high-pressure reactors and an automatic back-pressure regulator. 5 to 15 mL of TOA are first introduced in the first vessel with some glass wool. 20 mL of aqueous solution containing metal ions at 10^{-3} M or 10^{-2} M are introduced in the extraction vessel (volume: 60 mL). After introduction of reactants, the temperature is set at 40°C in the oven. When the temperature reaches 40°C in both reactors, carbon dioxide is delivered with the HPLC pump until the pressure in both reactors reaches 25 ± 0.2 MPa. Carbon dioxide flowrate is then set at 0.5 mL.min^{-1} during the experiment. Different collection solvents (dodecane, ammonium carbonate, nitric acid 2%) are put in the collection vessel to solubilize the metal complex formed between molybdenum and TOA.
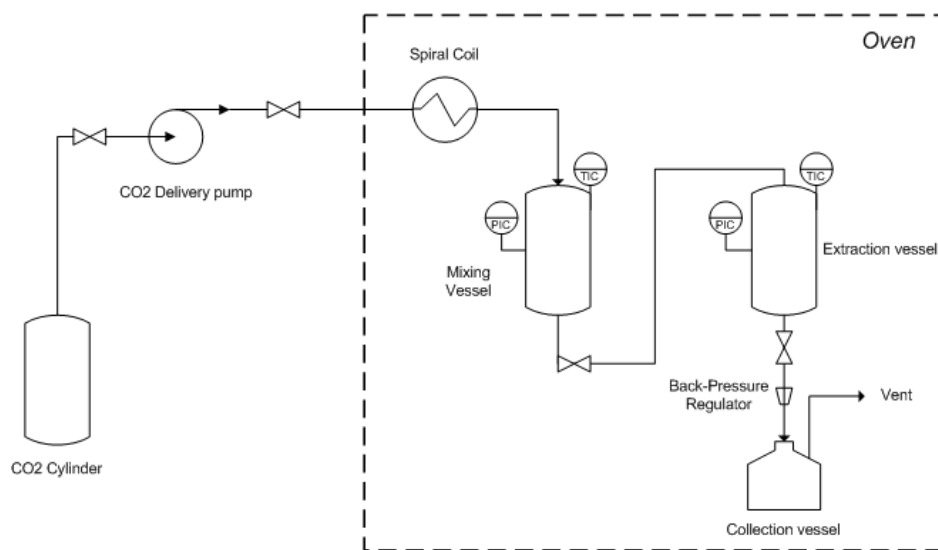

Figure 2: Experimental set-up for supercritical CO$_2$ extraction

After the extraction procedure, metal ions contained in the aqueous solution in the extraction vessel are analysed by ICP-AES (Thermo Icap 6000). The extraction efficiency is calculated using Equation 3.

$$Extraction(\%) = \frac{[E]_{initial} \times V_{initial} - [E]_{final} \times V_{final}}{[E]_{initial} \times V_{initial}} \quad with \ E = Mo, Zr, \ Fe \qquad (3)$$

where $[E]_{initial}$, $V_{initial}$, $[E]_{final}$ and V_{final} are respectively the initial concentration of the extracted element, the initial volume of the solution, the final concentration of the extracted element and the final volume of the solution.

After analysing the collection solvents by ICP-AES, it is possible to calculate the collection efficiency by Equation 4.

$$Collection \ (\%) = \frac{[E]_{collection} \times V_{collection}}{[E]_{initial} \times V_{initial}} \quad with \ E = Mo, Zr, \ Fe \qquad (4)$$

where $[E]_{collection}$, $V_{collection}$, $[E]_{initial}$ and $V_{initial}$ are the concentration of the recovered element in the organic phase, the volume of the recovered organic phase in the collection vessel, the initial concentration of the extracted element and the initial volume of the solution respectively.

3. RESULTS

3.1 Solubility measurement

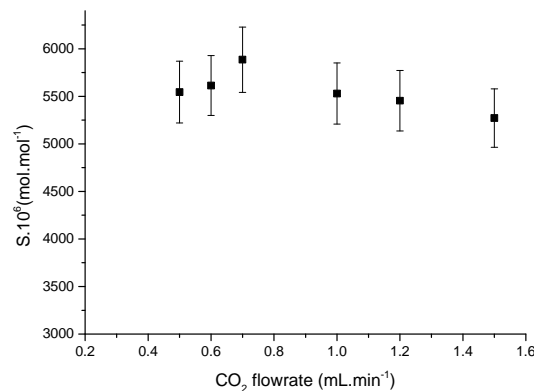To ensure that the equilibrium has been reached, solubility is measured at several flowrates.

Figure 3: TOA concentration measured in supercritical CO_2 with a CO_2 flowrate from 0.5 to 1.5 mL.min^{-1}, P = 20.0 MPa and T = 40 °C

Figure 3 shows that concentrations obtained at a flowrate between 0.5 and 1.5 mL.min^{-1} are rather constant which means that equilibrium is reached at these flowrates.

In this study, the uncertainty of a solubility measurement which includes repeatability and accuracy is generally ± 6 %. Repeatability calculated on the solubilities at 20.0 MPa, 40°C and a flowrate of 0.5 mL.min^{-1} is ± 5%. For each solubility value, the accuracy is generally ± 3%.

Table 1 presents the solubility values of TOA and the mass balance deviation obtained for pressures from 10 to 30 MPa. All solubility measurements were performed at a temperature of 40°C and a flowrate of 0.5 mL.min^{-1}. Solubility values of the literature are also indicated for comparison. The mass balance deviation is generally lower than 10 % which is an acceptable value.

Table 1: TOA solubility in supercritical CO_2 at 40°C under different pressures

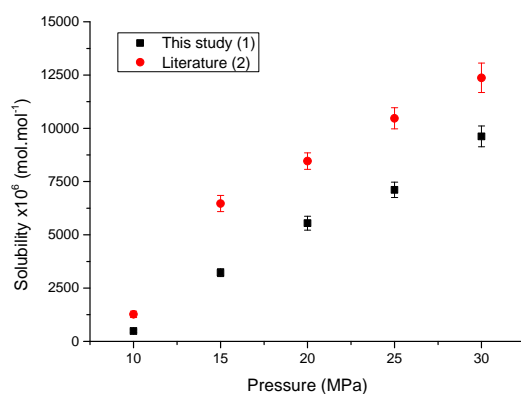| Pressure (MPa)	$S.10^6$ (mol.mol^{-1})	Mass balance deviation (from eq.2) (%)	$S.10^6$ (mol.mol^{-1}) [5]
10	481±56	9.6	1270±150
15	3224±188	6.4	6470±380
20	5545±324	5.3	8460±390
25	7111±362	5.8	10470±500
30	9622±490	7.7	12370±690

Figure 4: TOA solubility in supercritical CO_2 at 40°C and different pressures

As shows by Figure 4, the solubility of TOA increases with pressure. Experimental solubility values are significantly lower than the literature solubility values [5] irrespective of the flowrate. In the literature, two high-pressure reactors were used instead of one in our case. It might be interesting in further studies to measure TOA solubility using two reactors in order to understand this difference and see if it reduces the mass balance deviation. It is also important to notice that the literature data available come from a unique publication.
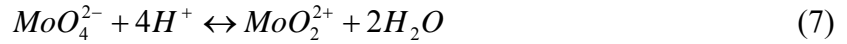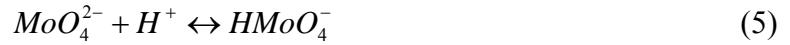
3.2 Extraction experiments
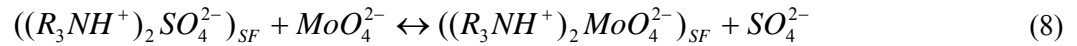
3.2.1 Extraction reaction

As an anion exchanger, TOA needs to be preequilibrated with sulfuric acid during 30 minutes to form TOA sulfate. The organic phase containing TOA sulfate is separated from the aqueous phase and introduced in the mixing vessel (See Figure 2).

$$2R_3NH_{org} + H_2SO_4 \leftrightarrow ((R_3NH^+)_2SO_4^{2-})_{org} \tag{4}$$
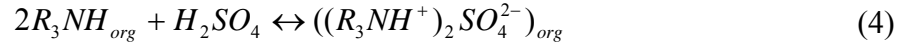
The speciation of molybdenum is not very well known. Molybdenum could exist under different species. According to Basualto [6], the following equilibria of molybdenum (VI) species are considered for a pH <4.

$$MoO_4^{2-} + H^+ \leftrightarrow HMoO_4^- \tag{5}$$

$$HMoO_4^- + H^+ \leftrightarrow H_2MoO_4 \tag{6}$$

$$MoO_4^{2-} + 4H^+ \leftrightarrow MoO_2^{2+} + 2H_2O \tag{7}$$

Under our operating conditions (pH<2), the following extraction equilibria are supposed to describe the chemistry of our system.

$$((R_3NH^+)_2SO_4^{2-})_{SF} + MoO_4^{2-} \leftrightarrow ((R_3NH^+)_2MoO_4^{2-})_{SF} + SO_4^{2-} \tag{8}$$

$$((R_3NH^+)_2SO_4^{2-})_{SF} + 2HMoO_4^- \leftrightarrow 2(R_3NH^+, HMoO_4^-)_{SF} + SO_4^{2-} \tag{9}$$

3.2.2 Extraction results

The operating conditions for all extraction experiments are: P = 25 ± 0.2 MPa, T = 40 ± 1 °C, CO_2 flowrate (6 MPa, 0°C) = 0.5 mL.min^{-1}.

3.2.2.1 Extraction of molybdenum in supercritical CO_2

Extraction experiments are carried out on sulfuric solutions containing [Mo] = 1.10^{-3} M. Other characteristics of the solution are: pH = 1.8, [H+] = 0.1 M, [S] = 0.5 M. 20 mL of this solution are introduced in the extraction vessel. 5 mL of TOA sulfate are introduced in the mixing vessel.

Table 2: Mo extraction efficiencies with TOA in SC-CO$_2$.

Extraction time (hr)	TOA sulfate/Mo molar ratio*	Extraction efficiency (%)	[H$^+$] ± 5% (mol.L^{-1})	Collection solvent
3	17.2	100±12	0.01	
4	22.9	99±10	0.05	Dodecane
6	34.3	99±11	0.04	

*The molar ratio of TOA sulphate over molybdenum was calculated from the solubility value of sulphate TOA measured at the extraction operating conditions: $S.10^6 = 201 \pm 74$ mol.mol^{-1}.

Molybdenum is completely extracted from the aqueous solution after 3 hours of dynamic extraction. Protons are consumed during the experiment which could mean that a part of TOA is acidified during experiment despite the preequilibration. After acid digestion of dodecane and ICP-AES analysis, molybdenum was not found in the collection vessel. The recovery efficiency is less than 1% for the three experiments. The complex between molybdenum and TOA does not seem to be soluble in supercritical CO_2.

3.2.2.2 Selectivity study in presence of iron and zirconium impurities

Selectivity experiments are carried out on sulfuric solutions containing $[Mo] = 1.10^{-3}$ M and $[Fe] = 0.9.10^{-3}$ M. Other characteristics of the solution are: pH = 1.9, $[H^+] = 0.1$ M, $[S] = 0.5$ M. 20 mL of this solution are introduced in the extraction vessel. 5 mL of TOA sulfate are introduced in the mixing vessel.

Table 3: Extraction efficiencies and selectivities of Mo and Fe with TOA in SC-CO_2.

Extraction time (hr)	TOA sulfate/Mo molar ratio	Extraction efficiency (%)		$[H^+]\pm 5\%$ (mol.L^{-1})	Collection solvent
		Mo	Fe		
0.5	3.5	100±10	12±1.2	0.02	Ammonium carbonate 0.5 M
1	6.9	99±9.5	14±1.3	0.01	Nitric Acid 2wt%
6	41.6	99±11	20±2.2	0.02	Ammonium carbonate 0.5 M

The molybdenum contained in the solution is totally consumed after 30 minutes of dynamic extraction. Molybdenum is preferentially extracted over iron regardless of the extraction time but iron extraction efficiency increases over time and TOA sulfate/Mo ratio. Similarly to the previous experiments on aqueous solutions containing only molybdenum, acidity decreases after extraction. Protons are probably consumed by TOA. Instead of dodecane, ammonium carbonate 0.5 M and nitric acid 2wt% are used to recover the metal ions. Unfortunately, after ICP-AES analysis of the collection solvents, less than 1% of molybdenum is recovered for all experiments.

Two extraction experiments were performed on 20 mL of an aqueous solution containing $[Mo] = 1.10^{-3}$ M, $[Zr] = 0.9.10^{-3}$ M, pH = 1.9, [H+] = 0.1 M, [S] = 0.5 M. Considering the last results, the extraction time is reduced to 1 hr. In the first experiment, TOA was preequilibrated with sulfuric acid. In the second experiment, no preequilibration was done. 5 mL of TOA sulfate are introduced in the mixing vessel. The results figured in Table 4.

Table 4: Extraction efficiencies and selectivities of Mo and Zr with TOA in SC-CO_2.

Elements	Extraction efficiency (%)		$[H^+] \pm 5\%$ (mol.L-1)
	Mo	Zr	
with TOA preequilibration	100±10	99±7.1	0.06
without TOA preequilibration	100±7.1	100±6.5	0.01

According to the results, preequilibration has no influence on the extraction efficiency. It is also observed that TOA has no selectivity towards molybdenum in presence of zirconium. Protons are totally consumed during extraction in both cases as observed in the previous experiments.

3.2.2.3 Extraction of molybdenum in supercritical CO_2 with an excess of extractant

One dynamic extraction is carried out on a solution containing $[Mo] = 1.10^{-2}$ M, pH = 1.8, $[H^+] = 0.2$ M, $[S] = 0.5$ M. 15 mL of TOA without further preequilibration with sulfuric acid. After an extraction time of 5 h, up to $100 \pm 10\%$ of molybdenum was extracted from the aqueous phase. In addition, organic phase was recovered not only in the collection vessel but also in the extraction vessel. An organic layer of 5 mL was found above the remaining aqueous solution. After acid digestion and ICP-AES analysis of this organic layer, $91 \pm 6.5\%$ of the molybdenum was found in the extraction vessel. Only $12 \pm 0.9\%$ of molybdenum was recovered in the collection vessel. This proves that the metal complex between molybdenum and TOA sulfate is not enough soluble in supercritical carbon dioxide to be recovered in the collection vessel.

CONCLUSION

A continuous flow apparatus was developed for measuring solubility of trioctylamine in supercritical CO_2. A CO_2 flowrate lower than 1.5 mL.min^{-1} should be used in order to be at equilibrium. Dynamic extraction experiments with supercritical carbon dioxide were carried out on sulfuric acid solutions containing molybdenum. An extraction efficiency of $100 \pm 12\%$ for molybdenum was obtained after three hours of dynamic extraction. The selectivity study showed that trioctylamine is more selective towards molybdenum than iron. However, no selectivity was observed between molybdenum and zirconium. For all extraction experiments where 5 mL of TOA sulfate were used, molybdenum was not recovered in the collection vessel. Even in large excess of extractant, the complex formed between molybdenum and trioctylamine is not enough soluble in supercritical carbon dioxide to be properly recovered in the collection vessel. Other extractants which meet the requirement that both extractant and metal complex are soluble in supercritical carbon dioxide are currently studied.

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