EXTRACTION OF HEAVY METALS WITH SUPERCRITICAL CARBON DIOXIDE AND THERMODYNAMIC MODELING

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Introduction

Traditional procedures by acid solvents for removing heavy metals from soils, sludges or compost at atmospheric pressure frequently require larges quantities of solvents, which must be treated with neutralizers and disposed of. This is a great economic and environmental concern.

Recently modified supercritical fluids by complexing ligands have been used in extraction of metallic cations from solid blends and liquid solutions [1-5]. Supercritical fluid extraction (SFE) is a very efficient process compared to conventional extraction process; it is faster and its selectivity is larger.

Supercritical CO_2 is a strong solvent with high diffusivity and low viscosity and it can be discharged to environment at low temperature.

Focusing on the metal-chelate complex solubility rather than the solubility of the chelating agent itself is due to the common conception that the metal-chelate complex solubility would be the limiting factor since the chelate or ligand is organic and generally more soluble in supercritical carbon dioxide.

Thermodynamic models have been used to predict the solubility of metal-chelate complex in dioxide carbon. The equation of sate (EOS) of Peng Robinson (PR) with the van der Waals mixing rules has shown god agreements to experimental data [6,7].

In this research the extraction of metallic ion Cu^{2+} has been carried out in supercritical CO_2. The effect on extraction of methanol addition on CO_2 flow was studied. The ligand EDTA (ethylenediamine tetra-acetic acid) was used to study the static equilibrium in the metal extraction with SC CO_2.

Experimental Section

The samples were prepared with dry sand (SiO_2) as supported. The sand was spiked with a stock solution of copper ($CuSO_4 \cdot 5H_2O$ 1 M). The cation concentration was ~ 250 ppm. The samples were dried 3 h at 85 º C.

For the extraction procedure a Hewlett-Packard model SFE 7680T extractor was used. Figure 1 shows the flow diagram. The solid sample was loaded in the extraction chamber. The SC CO_2 was supplied from a tank, maintained at pressure upper 50 bars with a high pressure pump. Extraction test were carried out as a function of the pressure at constant temperature in the extraction chamber. After that the extract is dragged to a trap where solute is adsorbed and the CO_2 escapes depressurizing then the trap is rinsed with a solvent that in this case was water.

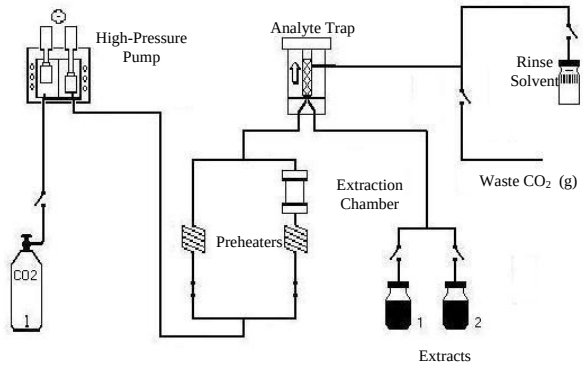

Figure 1.- Flow diagram of Supercritical Extraction experimental unit.

The CO_2 flow rate of the extraction was 1 ml/min. The pressure range was 75 to 135 bar. The chamber volume was 7 ml and temperature was maintained at 40 º C for all tests. For the dynamic tests the extraction equilibrium static stage was of 2 minutes followed by 5 minutes of flowing SC CO_2 and for static tests the time into the chamber of the SC CO_2 was of 15 minutes. The determination of Cu^{2+} was done using UV-vis spectroscopy.

The metal-chelate complex samples were prepared mixing 1 g of spiked sand with 2.1 ml of EDTA solution (0.0342 M).

Results

The extraction efficiency was defined as:

$$\%extraction = \frac{Cu \quad in \quad extract}{Cu \quad on \quad spiked \quad sand} x100$$

Figure 2 shows the copper extraction percentage (EP) as a function of pressure for dynamic tests. For pure CO_2 and CO_2 with 5% vol. of methanol the extraction efficiencies were very low, however with methanol showed a slightly better performance. A maximum for both curves can be seen at 90 bar. Upper 110 bar the gain of EP for Methanol-CO_2 flow was more marked, almost the double.

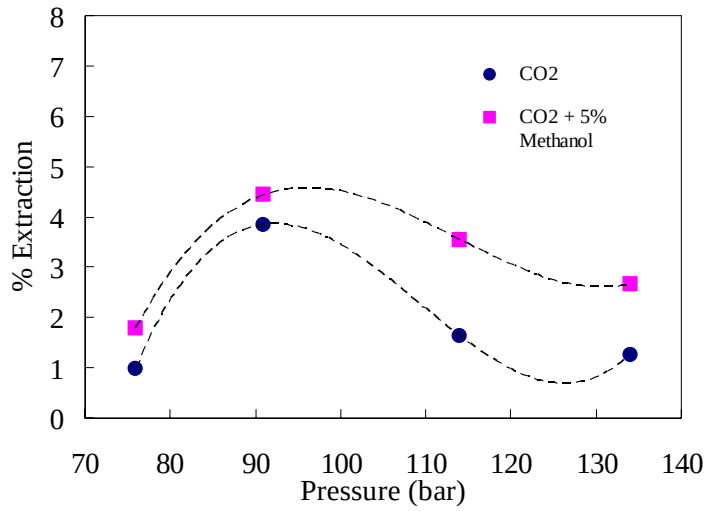

Figure 2.- Pressure effect of SFE Cu^{2+} with supercritical CO_2 at 40 C

It were detected SO_4^{-2} anions by precipitation with $Ba(C_2H_3O_2)_2$ then the copper specie was dragged by pure SC CO_2 fluid as $CuSO_4$ compound which was dissociated in their ionic species when the trap was rinsed with water. With the addition of methanol the polarity of CO_2 was modified. The mechanism of extraction for copper as a function of the pressure is not lineal. The $CuSO_4$ specie is affected for the pressure into the chamber.

For copper-ligand complex the static equilibrium behavior was almost lineal as a function of the pressure of SC CO_2 like others researches reported with other ligands [6,7]. The Figure 3 shows the solubility as a function of the pressure for Cu(EDTA) in static equilibrium with SC CO_2. The solubility was predicted with a Peng-Robinson EOS with Van der Waals mixing rules. The equilibrium equation was:

$$y_i P(\hat{\phi}_i)_{CO_2} = x_i (P_i)_{sbl} (\hat{\phi}_i)_{sbl} \exp\left[\frac{I}{RT}\int V_s dP\right] \quad (1)$$

defining:

$$PF = \exp\left[\frac{I}{RT}\int V_s dP\right] \quad (2)$$

$$y_i = \frac{(P_i)_{sbl} (\hat{\phi}_i)_{sbl} PF}{P(\hat{\phi}_i)_{CO_2}} \quad (3)$$

In equation 3 was assumed that (a) the solid is pure (x_{solid}=1), (b) the molar volumen of the solid does not change with pressure, and (c) because the pressure vapor of the solid (sublimation pressure) is very low the sublimation coefficient $(\hat{\phi}_i)_{sbl}$ can be assumed to be unity. The fugacity coefficient is predicted for PR EOS with the Van der Waals mixing rules.

$$\ln(\phi_i)_{CO_2} = \frac{B_i}{B}(Z-1) - \ln(Z-B) + \frac{A}{2\sqrt{2}B}\left[\frac{B_i}{B}\right]\ln\left(\frac{Z+2.414B}{Z-0.41B}\right) \quad (5)$$

where A, B, Bi and Z are defined by expression in the next equations:

$$a\alpha = \sum_i \sum_j y_i \sum_j y_i y_j (a\alpha)_{ij} \quad (5a)$$

$$b = \sum_i y_i b_i \quad (5b)$$

$$a_{ij} = (1-k_{ij})\sqrt{(a\alpha)_i (a\alpha)_j} \quad (5c)$$

$$a_i = 0.45724\frac{(RTc)^2}{Pc} \quad (5d)$$

$$\alpha = \left[1 + (0.37464 + 1.54226w - 0.26992w^2)(1 - Tr^{0.5})\right]^2 \quad (5e)$$

$$w = -1.0 - \log(P_r^{sat})_{Tr=0.7} \quad (5f)$$

$$b_i = 0.7780\left[\frac{R(Tc)_i}{(Pc)_i}\right] \quad (5g)$$

$$B = \frac{bP}{RT} \qquad B_i = \frac{b_i P}{RT} \quad (5h)$$

$$A = \frac{a\alpha P}{(RT)^2} \quad (5i)$$

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (5j)$$

Different works have used the PR EOS to predict the solubility data. Roggeman et al. have been estimated the critical data (Tc, Pc) from Joback's group contribution method for the solubility of an iron complex in SC CO_2 [7]. Croos et al. for copper-chelate complex solubility in SC CO_2 used critical properties and the binary interaction coefficient (k_{ij}) as fit parameters to simulate the solubility experimental data (6). The binary interaction coefficient can be taken as a constant in isothermal tests. The table 1 shows the pure component parameters that were used for simulate our experimental data showed in Figure 3.

Table 1.- Properties of pure compounds

Component	CO_2	Cu(EDTA)
T_b (K)		576.44 (1)
T_c(K)	304.13	752.31(2)
P_c(bar)	73.77	26.37 (2)
P_{vr} (Tr=0.7)		0.010634(3)
w	0.225	0.9733
V_{sol} (cm^3/mol)		1712.52*
Pvap (bar)		6.61E-9*
k_{12}		0.6772*

(1) Meissner method [8], (2) Ambrose method [9], (3) Riedel method [8] and (*) simulated parameter

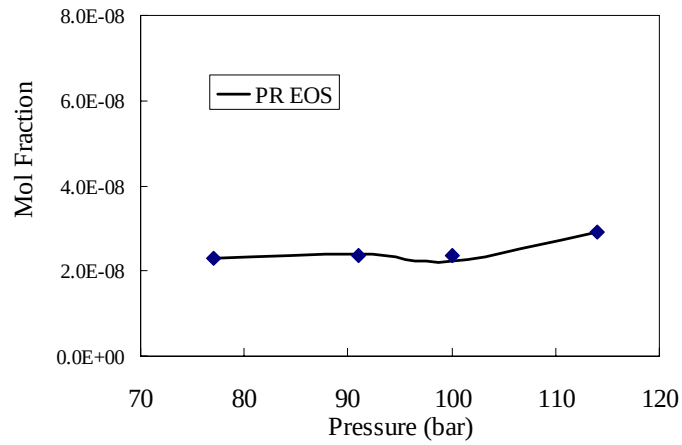

Figure 3.- Cu(EDTA) solubility in SC CO_2 at 40 º C

In Figure 3 the continue lines are the correlations by PR EOS with van der Walls mixing rules. The model fits well the experimental data. The k_{ij} parameter is very congruently reported for others similar experiments [6,7].

Conclusions

The copper extraction efficiency using SC CO_2 pure was slightly enhanced using CO_2 with methanol because the polarity of the CO_2 was modified. A thermodynamic model of PR EOS with Van der Walls mixing rules predicted very well the copper-EDTA complex solubility in SC CO_2. The molar volume of the solid (V_s) and the vapor pressure (P_{vap}) of the metal-ligand complex were found as fitting parameters together with the binary interaction coefficient (k_{ij}) that was 0.6772 for this binary system.

List of Symbols

$(\hat{\phi}_i)_{sbl}$ = Fugacity coefficient of component *i* in the solid at sublimation.

$(\hat{\phi}_i)_{CO2}$ = Fugacity coefficient of component *i* in supercritical carbon dioxide.

x_i = mole fraction of component *i* in the solid.

y_i = mole fraction of component *i* in the gas.

$(Pi)_{sbl}$ = Sublimation pressure of component *i* at T

P = Pressure

T = Temperature

V_s = Molar volume of the solid

PF = Poynting factor

Z = Compressibility factor

w = Acentric factor

P_r^{sat} = Reduced pressure at saturation

Tr = Reduced temperature

$(Pc)_i$ = Critical pressure of component i

$(Tc)_i$ = Critical temperature of component i

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