EXTRACTION OF PB-DIETHYL DITHIOCARBAMAT COMPLEX BY LIQUID CO$_2$ IN LIQUID-VAPOR EQUILIBRIUM CONDITIONS

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ABSTRACT

The interest of soil remediation technology of more stringent environmental control has focused the studies in the field of extraction by supercritical fluids and liquid gases under liquid-vapor equilibrium conditions. In this work liquid CO$_2$ extraction of Pb is studied. "Jennings" autoclave with a sokslet system inside is used to perform all the extraction experiments. Extraction conditions have been 294-296K and a pressure of 55-65 atm, lower than CO$_2$ supercritical parameters. Diethyl dithiocarbamat, which has high solubility in liquid CO$_2$, is used to react with lead forming a well soluble complex compound in liquid CO$_2$ as well. Extraction kinetic was studied performing a fractional extraction process under the liquid-vapor equilibrium. The solubility of Pb(DDC)$_2$ was found to be 0.3912*10^{-6}mol/l. Lead amount in the obtained extracts is determined using SF ditizon chloroform technique.

Keywords: heavy metals, soil remediation, liquid CO$_2$ extraction, SFE

PËRMBLEDHJE

Interesi për zhvillimin e teknologjive të reja në përmirësimin e cilësisë së tokave duke respektuar parimet e mbrojtjes së mjedisit ka nxitur studimet në fushën e ekstraktimit të ndotjeve me SFE dhe gaze të lëngështuar. Në këtë punim është studiuar ekstraktimi i Pb-së me CO$_2$ në gjendje të lëngët. Për ekstraktim është përdorur autoklava e tipit Jennings e pajisur me një aparat tip "sokslet". Kushtet e ekstraktimit janë mbajtur 294-296K dhe presioni 55-65 atm, pak nën parametrat e gjendjes mbikritike të CO$_2$.

Si kelatues i Pb-së është përdorur dietil-ditiokarbamati i cili ka tretshmëri të lartë në CO$_2$ të lëngët në gjendje të lirë dhe në formë të kompleksuar me Pb.

Kinetika e ekstraktimit u studjua duke zbatuar një proces ekstraktimi të fraksionuar në kushtet e ekuilibrit lëng-avull. Tretshmëria e Pb(DDC)$_2$ në CO$_2$ të lëngët ka rezultuar (0.3912±0.067)*10^{-6}mol/l. Përmbajtja e Pb-së në ekstraktet e fituara u përcaktua me metodën SF kloroform-ditizon.

INTRODUCTION

Heavy metals have been recognized as elements of considerable environmental significance because of their highly toxic properties and unfavourable ecological consequences. Heavy metals enter the environment naturally (erosion, fire, and volcanic processes), and are also released as

a result of human activities (combustion, smelting, mining, chemical industry, agriculture, corrosion, military activities).

Pollution of soil can disturb the delicate balance of physical, chemical and biological processes that is necessary for the maintenance of soil fertility. When soils are polluted by metals there is a possibility of transfer of heavy metals to surface and ground waters and inhibition of microbial enzyme activity and reduction of the diversity of soil, flora and fauna populations. Metals may be transferred to man by consumption of contaminated plants or indirectly by consumption of grazing animal's meat or milk. To minimize the impacts, it is necessary to remediate these contaminated soils. Soil remediation technologies that exist are physical methods (thermal desorption, soil vapor extraction, mechanical separation, reactive walls/barriers, etc.), chemical methods (soil washing/flushing, solidification/stabilization, dehalogenation, solvent extraction, chemical reduction/oxidation), biological methods (bioremediation, phytoremediation, land flaming, bioreactors), (United Nations 2000) but only some of them can be applied to metal contaminated soils [11]. Recently, the interest to introduce remediation technology of more stringent environmental control using cleaner solvents and processes has focused the researches on the field of extraction by supercritical fluids [3, 7, 8, 10, 11] and liquid gases under liquid-vapor equilibrium conditions [4-6, 9]. It is a promising remediation technology that may be used to replace established ones. Carbon dioxide is the substance of choice for extraction technology because of its moderate critical parameters (Tc = 304.2 K; Pc = 72.9 atm) (Fig1). CO_2 is non-flammable, non-toxic, and non-reactive and does not leave any residue. It is also relatively inexpensive and available in pure form. It is an excellent extraction medium for non-polar and moderately polar species, and with careful ligand design, it can be used for analytical and process scale metal extraction from solution and solid phases. In general, the dissolution of a metal in liquid CO_2 requires neutralization of the metal charge
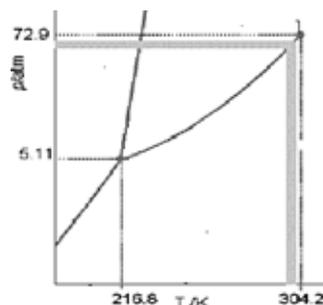
Fig 1 Pressure-temperature diagram of carbondioxide

ion by ligand complexation. In this way, many chelating agents such as dithiocarbamates and hydroxamic acids have been utilized to extract metal ions such as Hg, Cu and Fe into liquid-CO_2 [3, 11]. Depending on the type of soil and chelating agents the amount of Cu removed from the soil material using supercritical fluid extraction was determined to be from 25% until 54%. In the case of liquid CO_2 extraction under liquid-vapor equilibrium conditions the lower extraction effectivity should be expected. In our previous work [13] it is shown that extraction of Hg from contaminated sand using liquid CO_2 has been around 13%. In this work we show that the complexation with dithiocarbamates followed by extraction with liquid-CO_2 under gas-liquid equilibrium conditions, can be used for developing a clean, eco-friendly chemistry to remove Pb from polluted sites. Also the solubility of $Pb(DDC)_2$ in liquid CO_2 under the specified conditions of the experiments is determined.

Experiment
Apparatus and materials

The Jennings-type apparatus [1-6, 9, 14] for CO_2 extraction has been used (Fig.2). The high pressure part of the apparatus consists of a cylindrical autoclave from stainless steel with closures at bottom and top. The top closure contains the cooling finger and the high pressure tubes. In the cylinder walls a sapphire window is placed to observe the condenser, the siphon and the flask. The inner extraction apparatus is built completely by glass. It consists of an extraction flask with a siphon for periodical removal of the extractant and a separate glass vessel serving as reservoir
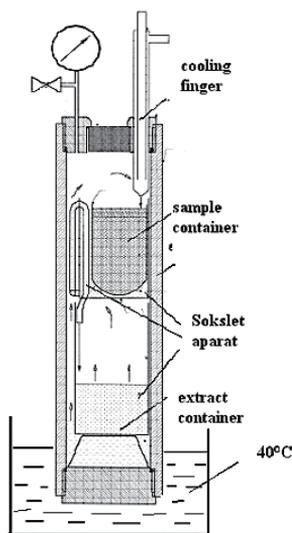
Fig 2. The Jennings-type apparatus for CO2 extraction

for evaporating extractant and for the storage of the extract. CO_2 of 99.97% purity was transferred as a liquid from the storage vessel to the autoclave. The amount was controlled by weighting the whole autoclave on normal scales. The CO_2 content in autoclave was around 230g equal to the free volume of the flask with siphon filled with sample. The apparatus operates in the two phase region below the critical temperature of the gas which is easily detected and controlled by the operating pressure (294-296K; 55-65atm). The bottom of the apparatus was kept in a water bath at 313K in order to ensure the evaporation of extractant.

Extraction of lead was performed by applying successively extraction processes (Tab 1), in the presence of sodium diethyl dithiocarbamat as chelating agent using pure CO_2 in each process. The extracts obtained from each process were saved as they were received in room temperature in excicator. All extracts were analyzed for lead content using Dithizon spectrometric method.

Results and discussion

Lead was extracted from the pure salt $Pb(NO_3)_2$. In stead of the soil sample 2g of lead nitrate was inserted into the autoclave and 4 extraction processes were performed. The amount of chelating agent was calculated to be in excess relating the total amount of Pb. Because of DDC has a good solubility in liquid CO_2 in its free state, a new amount of 0.5g was added before each extraction to ensure its excess during each process.

Tab.1 Extraction of Pb from the salt $Pb(NO_3)_2$

Nr. of procces	DDC (gr)	Time (min)	Pb (µg)	Pb (µg/min)
1	2	20	81.07±1.99	4.05
2	+0.5	48	135.11±6.11	2.81
3	+0.5	82	138.17±4.23	1.68
4	+0.5	67	113.13±2.60	1.69

In Tab. 1 it is shown this experimental set up. Based on the amount of Pb extracted in each process it is calculated the amount of Pb extracted per minute in each process. The diagram of Pb extracted is shown in fig. 3.
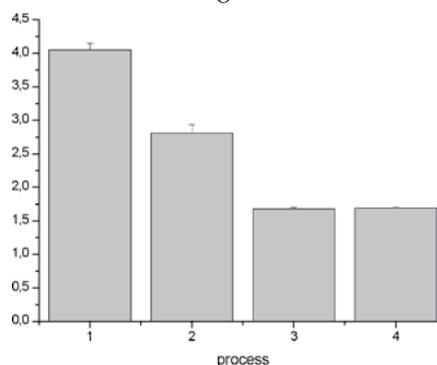
Figura 3. The diagram of Pb successively extracted from $Pb(NO_3)_2$

The higher amount of lead was extracted during the first process and was continuously decreased. The kinetic of extraction is shown in fig. 4. The rate of extraction was decreased from 4µg/min to 1.68µg/min after approximately 70 min extraction process.

Tab.2 Solubility of $Pb(DDC)_2$ in liquid CO_2 in 295K

Nr.of experiment	Pb (gr)	DDC (gr)	Nr. of cycles	Pb-extracted (µg)	Solubility mol/l
1	0.001	2	3	30	0.460*10-6
2	0.1	2	3	20	0.300*10-6
3	0.2	2	3	27	0.413*10-6

The decrease of the extracted lead amount from one process to the following one is justified by the partitition coefficient of Pb-DDC between liquid-vapor phases into the autoclave. In each process pure CO_2 can be used only in the first cycle. The second cycle works with CO_2 richer with Pb-DDC complex and so on. It means that the
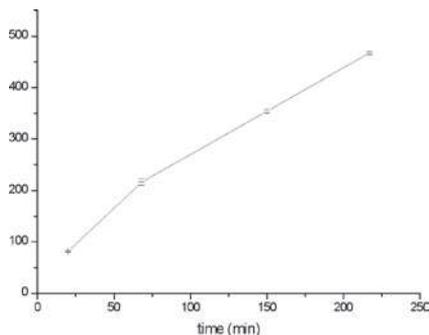
Figura 4. Extraction kinetic of Pb from the salt Pb(NO₃)₂

increasing of the extraction time (or the number of cycles during the process), should be followed by the decrease of the extraction efficiency. This is an important conclusion that the extraction of Pb should be done through a large number of processes with a low number of cycles each. If ones would study carefully the results represented in Tab.1 it is observable a disagreement between the amount of lead extracted during the second and fourth process. During the fourth process which was longer than the second one the extracted lead amount was lower instead of the contrary would be expected. This could be justified if we suppose that during the fourth process the amount of chelating agent have not been in excess.

Several experiments were carried out to determine the solubility of $Pb(DDC)_2$ in liquid CO_2 under the specified experimental conditions. In tab 2 are presented the results obtained from three experiments where Pb was extracted from different amount of pure lead nitrate. The experimental conditions were precisely maintained equal. Based on the density of the liquid CO_2 in the experimental temperature and pressure (d=0.73 g/ml) and the amount of CO_2 used (315ml), the solubility corresponds to be $(0.3912\pm0.067)*10^{-6}$ mol/l.

Conclusions

In this study liquid CO_2 was used to extract lead from its pure salt $Pb(NO_3)_2$. The results obtained based on the kinetic of extraction indicate good possibilities to develop other soil remedia-tion technologies using liquid CO_2.

Inorganic form of lead is possible to be extracted from the contaminated soils after chelating process with dithiocarbamat which have good solubility in no polar solvent such as CO_2 in liquid state. The extraction efficiency would be increased with the increasing of the number of shorter extraction process. The solubility of $Pb(DDC)_2$ in liquid CO_2 in 295K was 0.3912*10-6 mol/l.

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