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APPLICATION OF SUPERCRITICAL FLUIDS TO THE REACTIVE EXTRACTION AND ANALYSIS OF TOXIC HEAVY METALS FROM ENVIRONMENTAL MATRICES–SYSTEM OPTIMISATION

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ABSTRACT

The extraction of Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} utilising supercritical fluid carbon dioxide containing dissolved organophosphorus reagents is shown to be feasible. Using the solubility parameter concept and investigation of a variety of physical parameters favourable extraction conditions of 60 °C and 400 atm pressure were determined. Cyanex 302 was found to be the most favourable ligand in terms of stability and ability to complex a range of metal ions. A soil containing substantial amounts of Pb^{2+} and Cd^{2+} was studied using SFE and the technique was found to reduce the levels of leachable metal ions to near US EPA regulatory levels.

INTRODUCTION

Supercritical fluids (SF) have been finding increasing use as extraction solvents due to the increased restriction on the use of solvents, particularly chlorinated solvents, resulting from environmental legislation (1). Carbon dioxide has been the solvent of choice due to its low toxicity, relatively low cost and convenient critical properties. For the extraction of organic compounds, SF CO_2 has been found to be a particularly useful solvent at both analytical and process scales (2,3). The SF extraction (SFE) of metal ions had been considered unfeasible, due to high polarity of these species, until recently. In a process similar to that of solvent extraction, SF CO_2 containing dissolved chelating agents has been shown to be an effective solvent for the extraction of metal ions from either solid or liquid matrices (4).

Although a number of studies have now demonstrated the feasibility of metal extraction using SF, optimisations of extraction procedures have not yet been presented. Compared to the use of SFE for organic compounds, the extraction of metals presents a number of additional difficulties. The SF must be able to dissolve both ligand and metal complex in quantities sufficient to achieve extraction in a reasonable time scale. The ligand must be able to access and react with the metal within the sample matrix. Finally, the metal complex formed must be transported in the SF without significant decomposition, such that metal loss cannot occur. These relevant parameters are illustrated in Fig. 1.

Typically in SF processes, a solvent gas, such as CO_2 is contacted with a solid or liquid phase at high pressure and temperature (5). Slight changes in temperature or pressure of the system can cause large changes in the density of the solvent and consequently in the ability to solubilize heavy nonvolatile compounds from the liquid or solid phase (6). By manipulation of the system pressure, a nonvolatile compound can be extracted and also following a pressure let down, generally to a pressure below the fluids critical pressure, the material can be com-

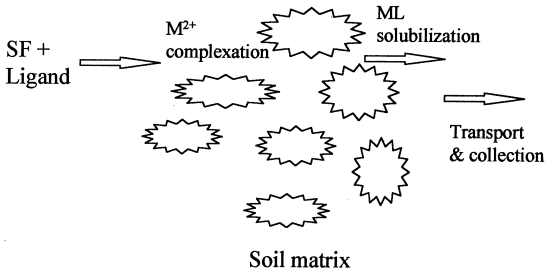

Figure 1. Schematic of processes involved in the SFE of metals from solid environmental matrices, such as soil.

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pletely precipitated. In this communication, we present the optimisation of a SFE system for the extraction and recovery of heavy metals from solid environmental samples. The solvating capability of SF CO_2 is compared to that of conventional solvents at a variety of physical conditions. The ability to extract metals directly from soil is demonstrated. The physical parameters for the optimisation of the SFE extraction procedure utilizing commercially available extraction reagents are shown.

EXPERIMENTAL

Reagents - *bis* (2,4,4-Trimethylpentyl)dithiophosphinic acid (Cyanex 301 from Cytec Industries Inc., West Paterson, NJ), *bis* (2,4,4-trimethylpentyl) monophosphinic acid (Cyanex 302, Cytec), *bis*- (2,4,4-trimethyl pentyl)phosphinic acid (Cyanex 272, Cytec) and di(2-ethylhexyl)monothiophosphorous acid (D2EHTPA from AG Bayer, Germany) were used as supplied. Kelex 100 (obtained from Ashland, U.K.) was purified by column chromatography using chloroform as an eluant and vacuum distillation, yielding a clear pale brown liquid. Gaseous carbon dioxide (Air Products, SFE/SFC grade) and methanol (MeOH) modified carbon dioxide (Air Products, SFE/SFC grade) were used as received. Nitric Acid (Fisher) was used as supplied. Metal ion stock solutions were prepared from the metal nitrate salts and dissolved in purified water. The zinc Cyanex 302 complex was prepared in the reaction of $Zn(NO_3)_2.6H_2O$ and Cyanex 302. To the solution of Cyanex 302 in methanol, $Zn(NO_3)_2.6H_2O$ dissolved in a small amount of water was added and a white precipitate was formed. The solid was filtered and washed with methanol.

Instrumentation used - SF CO_2 was supplied via a syringe pump (model 260D, ISCO, Lincoln, NB). The pump head was cooled with a circulating water bath (5° C) to liquefy the gaseous CO_2. The experiments were performed with PEEK extraction cells (9 mL, ISCO, Lincoln, NB) placed in an extractor (SX2-10 ISCO, Lincoln, NB). At the oven exit a silica capillary restrictor (20 cm, 50 μm) was used to maintain a constant pressure and SF flow though the extraction cell. For analysis of the extracted samples, a Perkin-Elmer 2380 atomic absorption spectrometer was used.

Procedures - Static extraction experiments were performed in the following manner: solid samples were prepared by spiking 50 μL of a mixture of Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} stock solution (5000 ppm of each metal) on to prewashed filter papers (Whatman 42, 1 cm by 2 cm in size, washed with ultrex nitric acid and rinsed in deionised water) or washed sea sand (Fisher). The samples were placed in the extraction cell followed by glass wool, with the ligand placed at the top. The extraction cell was placed into the oven and pressurized with SF CO_2 for 20 minutes of static extraction followed by opening an exit valve and 20 minutes

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of dynamic extraction. After 20 minutes the inlet valve was closed and the cell depressurized slowly via the capillary restrictor. The extracts were collected in a small volume of chloroform (~10 mL). When the extraction was completed, the sample matrix was removed from the extraction cell and treated with 20 mL of 1 M nitric acid, which was subsequently analysed by atomic absorption spectroscopy, determining the amount of metal remaining in the extraction cell after completion of the extraction procedure. The amount of metal remaining in the cell was used to determine the 'extraction efficiency' (% extraction), as follows:

$$\%\ extraction = \frac{metal\ spike/\mu g - metal\ remaining/\mu g}{metals\ spike/\mu g} * 100\%.$$

The effectiveness of this procedure for removing all remaining metal ions from the sample matrix was established by analysis of unextracted samples, and it was observed that quantitative recovery of the metals was possible. The 'collection efficiency' was determined by evaporation of the samples collected in chloroform and the residue treated with hot 1 mL concentrated nitric acid and then diluted to 20 mL, with deionised water. The concentration was then determined by atomic absorption spectroscopy. The % collected was determined as follows:

$$\%collection = \frac{metal\ collected/\mu g}{metals\ spike/\mu g} * 100\%$$

The solubility of the zinc Cyanex 302 complex was determined using a procedure outlined elsewhere (7).

A soil sample (~ 100 g) obtained from Kellogg, Idaho, was dried, ground and thoroughly mixed using a mechanical shaker. About 0.5 g of the soil was placed in an extraction cell containing a small volume of sand and the remaining void volume of the cell was filled with sand. Experiments were performed at 200, 300 and 400 atm, for 20 minutes static extraction and 20 minutes dynamic extraction time. For each extraction 200 mg of Cyanex 302 was added to the extraction cell. This extraction procedure was repeated five times at any given condition. Extracts were collected in chloroform (about 10 mL). The chloroform was evaporated after collection, and the residue was digested with 2 mL of concentrated HNO_3 for 2 hr and then diluted with deionized water to 22 mL total volume. Samples were analyzed for Pb^{2+} and Zn^{2+} by atomic absorption spectroscopy. For the soil residue, a TCLP equivalent* (Toxicity Characteristic Leaching Procedure) was performed in order to determine the unextracted leachable metals.

* An equivalent of the US EPA TCLP procedure was used since only 0.5 g of soil was available for treatment and the volumes of leachate were scaled down in proportion to the sample. Also, as pointed out by the US EPA, the use of a 0.5 g sample does not provide large enough volume to act as a representative sample for a soil matrix and thus introduces limitations into the above comparisons.

RESULTS AND DISCUSSION

SF CO_2 Compared to Conventional Solvents

In conventional solvent extraction (SE), a convenient means of expressing the solvating capability of the solvent has been to utilise the solubility parameter concept. The solubility parameter concept has also been applied to the solvating power of SF CO_2 and this enables comparison between the two solvent types to be made in a semiquantitative manner. The solubility parameter of a SF can be varied by altering the physical conditions to which the SF is subjected. Hence, in terms of system optimisation, we can make predictions as to the conditions under which SF CO_2 will behave similar to conventional solvents. One means of representing the solvent power of the SF has been presented by Giddings, *et al.* (8), where the solid solute is treated as a sub-cooled liquid and the Hildebrand parameter, δ, is used. The solubility behaviour of analytes in SFs can be semiquantitively related to the δ (δ_{SF}) of the SF,

$$\delta_{SF} = 1.25 P_c^{1/2} \left(\frac{\rho_f}{\rho_1} \right) \quad (1)$$

where P_c = critical pressure of the solvent, ρ_f = is the reduced density of the SF, ρ_l the reduced density of the fluid in the liquid state, which is close to 2.66. Hence, the δ_{SF} is directly proportional to the density of the SF. In general, the larger the δ_{SF} value, the more soluble a solute is at any given temperature. The δ_{SF} of SF CO_2 under the varying conditions of this study are shown in Fig. 2. It is observed that changing the physical conditions of the SF CO_2 greatly influ-

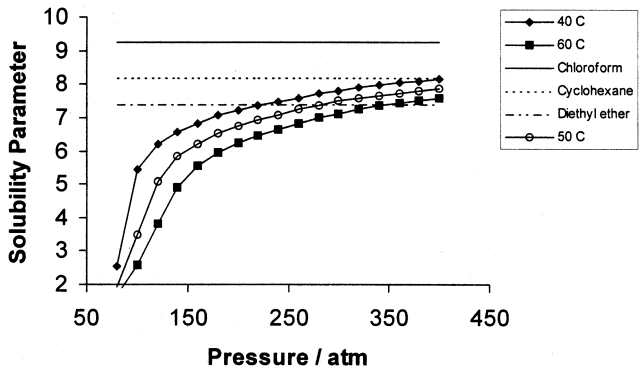

Figure 2. Solubility parameter of CO_2 at varying conditions compared to conventional solvents (at 25 °C and 1 atm).

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ences the solvating ability of the fluid. Also shown are the solubility parameters (at 25 °C and 1 atm pressure) of a number of conventional solvents and that under certain conditions, SF CO_2 can approach or exceed the solvent power of these. This illustrates that by application of suitable physical conditions to the SF CO_2, it is possible to obtain a solvent with properties similar to those utilized in conventional extraction processes. It appears from the above that if properties approaching those of a conventional organic solvent are to be attained by the SF CO_2, then conditions of pressure greater than 150 bar and temperatures in the range 40 °C to 60 °C should be utilised. Higher temperature appears to decrease the solvating power of the SF CO_2 at any given pressure, but in practice this decreased solvating effect may be offset by the increased extraction kinetics at the higher temperature.

Potential Ligands for Extraction in SF CO_2

Analysis by Smart *et al.* utilising the regular solution concept indicates that ligands substituted with alkyl chains containing approximately 8 carbon groups, preferably branched will be the most favourable for achieving effective extractions (9). The Cyanex and D2EHPTA families of ligands are found to fit the criteria and were chosen for this investigation. Also, ligands containing aromatic substituents will have poor solubilities in SF CO_2 as illustrated by Smart *et al.* (10).

Ligand Purity

The purity of the ligands used in this study, in terms of the amounts of Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} ions, was determined and the results are shown in Table 1. From the values obtained it is estimated that the effect of the 'background' concentration of metals in these ligands will have an insignificant effect upon the results of extractions at the metal concentration levels utilized in this study.

Table 1. Amounts of Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} Ions in 350 mg of Free Ligands Prior to Carrying Out Extractions

Ligand	Cu^{2+} (ppm)	Pb^{2+} (ppm)	Zn^{2+} (ppm)	Cd^{2+} (ppm)
Kelex 100	0.028	0	0.058	0.016
Cyanex 301	0.067	0	0.054	0.020
Cyanex 302	0.056	0.020	0.072	0.006
Cyanex 272	0.037	0	0.066	0.007

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Table 2. Percent Extracted (% Ext.) and % Collected (% Coll.) of Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} Ions from Sand, Spiked with and without Nitric Acid Solutions, Using SF CO_2 and Dissolved Extractants. A 350 mg Portion of Ligand was Used in Each Case the Results Represent the Mean Value Obtained from Duplicate Runs Under Each Condition Studied

Ligand	Acid added	Cu^{2+} % Ext.	Cu^{2+} % Coll.	Pb^{2+} % Ext.	Pb^{2+} % Coll.	Zn^{2+} % Ext.	Zn^{2+} % Coll.	Cd^{2+} % Ext.	Cd^{2+} % Coll.
Kelex 100	None	96	*	0	0	0	2	0	0
Cyanex 301	None	95	90	85	85	90	86	99	76
Cyanex 302	None	98	96	83	86	88	88	96	79
Cyanex 272	None	3	4	0	2	89	82	0	2
D2EHTPA	None	94	96	92	88	86	85	96	85
Cyanex 302	10 μL 1 M	94	90	93	83	92	91	98	83
Cyanex 302	10 μL 0.1 M	96	94	93	88	91	90	99	88
Cyanex 302	10 μL 0.01 M	96	88	93	76	90	77	99	79

* Analysis procedure was found to be unreliable for the recovery of metals from the Kelex-100 samples.

Extraction of Heavy Metals from Inert Matrix

For the extraction of metal ions from sand, it is observed that high extractions and recoveries are attained for all species, as is shown in Table 2. The extraction tends to occur with efficiencies in the range of 80% to 100%. The recoveries are usually slightly lower (up to 10 %) which may be accounted for by sample loss in the extraction system and minor losses in the analytical procedure utilized. The affinity of these ligands for heavy metals has been extensively reported, in solvent extraction (SE) and more recently in SFE (9,11). The thiophosphinic acid ligands show high affinity for heavy metals and are particularly useful in the SE of these metals from acidic solutions. This behaviour is reflected in this study, where the SFE is found to occur with high efficiency both in the presence and absence of acid in the sample. Using Kelex 100, selective extraction of Cu^{2+} is observed, again correlating with the use of this ligand in SE. Although the ligands D2EHTPA, Cyanex 302 and Cyanex 301 shown equivalent performance in terms of SFE, the Cyanex 302 was found to be the most stable and convenient ligand for use in SF and was chosen for further investigation.

The amount of ligand available for complexation with the metal ions is important as shown in Fig. 3. As the amount of ligand is decreased, the amount of metal ion extracted decreases. However, reasonable extraction efficiencies can be

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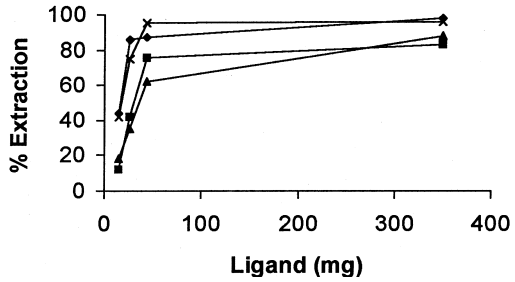

Figure 3. The effect of Cyanex 302 used on the % extraction of ◆ Cu^{2+} ■ Pb^{2+} ▲ Zn^{2+} **6** Cd^{2+} from sand using SF CO_2 at 60 °C and 300 atm. The extractions were carried out for 20 minutes static and 20 minutes dynamic. The results represent the mean value of duplicate determinations.

obtained using smaller amounts of ligand than used in most of this study, indicating that the ligand at 350 mg is very much in excess. Two criteria must be satisfied with respect to ligand in the SF system: (a) that there is a quantitative amount of ligand to complex all of the metal ions in the sample and (b) that the ligand can access the metal sample. Condition (b) is thought to be the rate limiting aspect in terms of extraction into SF CO_2, since the metal ions are present at low concentrations and potentially difficult to access. For extraction of larger quantities of metal ions, however, it is essential that the ligand be in excess. This can be achieved by either using a SF stream containing dissolved ligand or using repeated extractions.

The effect of extraction time was observed by varying the amount of time required for the static stage of the extraction process. These results are shown in Table 3. It is observed that the static phase of the extraction process plays little part in increasing extraction efficiencies. This indicates that the rate of metal ion complexation is not rate limiting under the conditions of this study. However, when the time for static and dynamic portions of the extraction are decreased to 5 min, it is observed that the % extraction values are similar to the 20 extraction values but the % collection values are less. This may be caused by the poor transport of the metal complexes in the SF CO_2 phase and that some loss by deposition in the SFE system occurs. At longer dynamic extraction times, the deposited metal complex can be redissolved and transported from the system.

With differing pressures of the extraction system, it was observed for all 4 metal ions studied, using the Cyanex 302 ligand, that the efficiency of extraction increases with increasing pressure as shown in Table 4. With increasing pressure from 200 atm to 300 atm little benefit is observed in terms of extraction efficien-

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Table 3. Percent Extracted and % Collected of Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} Ions from Sand, Using SF CO_2 and Cyanex 302 at 60 °C and 300 atm by Varying Static and Dynamic Times

A 350 mg Portion of Ligand was Used in Each Case. The Results Represent the Mean Value Obtained from Duplicate Runs under Each Condition Studied

Ligand	Cu^{2+} % Ext.	Cu^{2+} % Coll.	Pb^{2+} % Ext.	Pb^{2+} % Coll.	Zn^{2+} % Ext.	Zn^{2+} % Coll.	Cd^{2+} % Ext.	Cd^{2+} % Coll.
20 min static / 20 min dynamic	98	96	83	86	88	88	96	79
5 min static / 5 min dynamic	96	84	90	79	90	90	99	85
0 static / 20 min dynamic	94	84	91	82	93	92	99	87

cies. The effect of temperature on the extraction of Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} ions is illustrated in Table 4. At 200 and 300 atm, little temperature effect is observed. At 100 atm very low collection efficiencies are obtained and are much smaller than the extraction efficiencies. This indicates that at the low pressures, the ligand is transported into the extraction cell forming the metal complex which is partially transported from the extraction cell but is not completely transported from the extraction system. Similar observations for the extraction of metal β-diketone

Table 4. Percent Extracted and % Collected of Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} Ions from Sand with Neat SF CO_2 with Cyanex 302 at Different Temperatures and Pressures, Using 20 min Static and 20 min Dynamic Extraction Times

T/°C	P/atm	Cu^{2+} % Ext.	Cu^{2+} % Coll.	Pb^{2+} % Ext.	Pb^{2+} % Coll.	Zn^{2+} % Ext.	Zn^{2+} % Coll.	Cd^{2+} % Ext.	Cd^{2+} % Coll.
0	100	83	4	45	3	15	2	94	3
40	200	92	87	93	75	91	79	99	77
40	300	96	93	92	81	95	84	99	80
50	100	68	2	54	3	32	2	78	1
50	200	95	92	94	78	87	78	99	78
50	300	95	93	94	80	82	79	99	79
60	100	69	2	55	0	42	1	80	2
60	200	93	85	83	77	77	82	99	87
60	300	98	96	83	86	88	88	96	79

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complexes using SF CO_2 have been reported (12). Low complex solubility and metal complex instability can result in losses of metal in the extraction system and poor mass balance when comparing extraction versus collection efficiencies.

Solubility of Zn Cyanex 302 Complexes in SF CO_2

The solubility of the Zn Cyanex 302 ligand was measured at varying conditions and the results obtained are shown in Table 5. The most favourable condition, in terms of maximising the solubility of the ligands was observed to be a temperature of 40 °C and 200 atm. The trend with respect to pressure is expected, in that, with increasing pressure the solvating power of the SF is increased due to an increase in the density of the SF CO_2. Trends in solubility in SF CO_2 with increasing temperature at constant pressure are a function of two competing parameters, solvating power of the fluid and volatility of the solute. For the zinc cyanex 302 complex, it appears that the solvating power of the fluid dominates, since solubility decreases slightly with increasing temperature. However, in terms of extraction, the slight decrease in solubility with increasing temperature may be offset by increases in the kinetics of extraction. The observed trends, in terms of solubility of the metal complexes, qualitatively correlate with the solvating power predicted by use of the solubility parameter concept, as discussed above.

Solubility measurements at subcritical conditions (25 °C) indicate that the zinc cyanex complex is soluble when the CO_2 is in the liquid state.

Extraction of Leachable Metals from Environmental Samples

The extraction of heavy metals from environmental samples using the above optimisation data was investigated. A heavy metal contaminated soil obtained

Table 5. Solubility of Zn Cyanex 302 in Subcritical and SF CO_2

	Solubility (g / L)			
	25 °C	40 °C	65 °C	80 °C
60 atm	*	*	0.044	0.044
90 atm	0.188	0.066	0.044	0.044
120 atm	0.244	0.222	0.111	0.066
150 atm	0.755	0.466	0.311	0.222
200 atm	0.588	0.855	0.555	0.300

* Solubility below detection limit of technique used.

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Table 6. Soil Data for Lead and Zinc Content Prior to and after SFE Using Cyanex 302 Ligands

	Pb (mg / Kg Soil)	Zn (mg / Kg Soil)	Pb / ppm in Leachate	Zn / ppm in Leachate
Total Metal	13896	9367		
Leachable Metal Prior to SFE (TCLP)	1479.2	1015.8	73.9	50.8
Leachable Metal after SFE (300 atm, 'dry') (TCLP)	850.9	966.2	40.8	46.4
Leachable Metal after SFE (300 atm, 'wet') (TCLP)	323.1	535.2	16.2	26.8
Leachable Metal after SFE (400 atm, 'wet') (TCLP)	247.7	642.1	12.4	32.1
TCLP limit			5.0	N/A

from the Coeur d'Alene mining district near Kellogg in northern Idaho was studied. The major contaminants from this area are lead and zinc, and hence, the extraction of these metals was studied. The samples were subjected to a number of repeated extraction procedures using conditions of 200 atm, 300 atm, and 400 atm, and 60 °C. Approximately 0.5 g of sample was extracted in each case, and each extraction was allowed to proceed for 20 minutes static and 20 minutes dynamic. A representative sample of the soil was characterised for the presence of lead and zinc by both complete digestion, yielding total metal content, and by the US EPA TCLP, yielding 'leachable' metal content. The results obtained showed that the amounts of leachable Pb were reduced to 12.4 ppm, in the leachate, at conditions of 400 atm with soil 'wet' prior to extraction; this approaches the EPA's TCLP limit for this element (Table 6). These results indicate that the SFE process will yield a soil with a much lower content of leachable metal. The results of the repeated SFE are shown in Fig. 4. Increasing the pressure for the extraction significantly increases the amount of both lead and zinc recovered. Initially, large amounts of metal are extracted followed by a much slower extraction of the metals for subsequent extractions. This indicates that the extraction is limited by the rate of reaction of the ligand with the metal rather than the solubility of the metal complex in the SF CO_2. Extraction profiles of this type have been observed for the removal of organic compounds from environmental matrices, such as soils. The extraction profiles for the extraction of Pb^{2+} and Zn^{2+} were found to be very similar, indicating that the rate of extraction is not controlled by chemical specificity,

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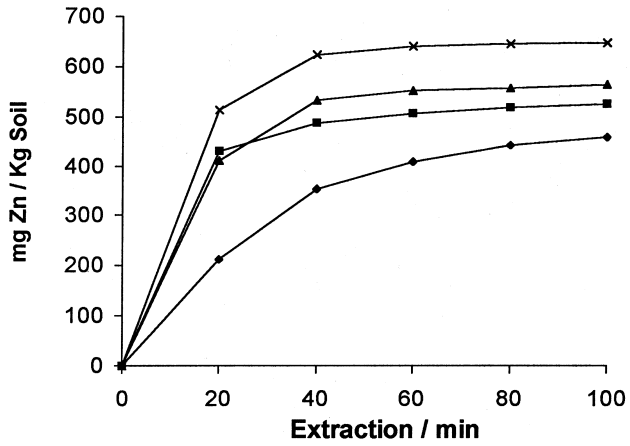

Figure 4a. Extraction of Zn from contaminated soils using SF CO_2 with Cyanex 302 ligand at 60 °C and varying pressures and moisture additions. 0.5 g Cyanex per extraction procedure. 'Wet' samples were obtained by additon of 10 μL H_2O to soil prior to first extraction. ◆ 200 atm, dry sample; ■ 300 atm, dry sample; ▲ 300 atm wet sample; ✖400 atm wet sample.

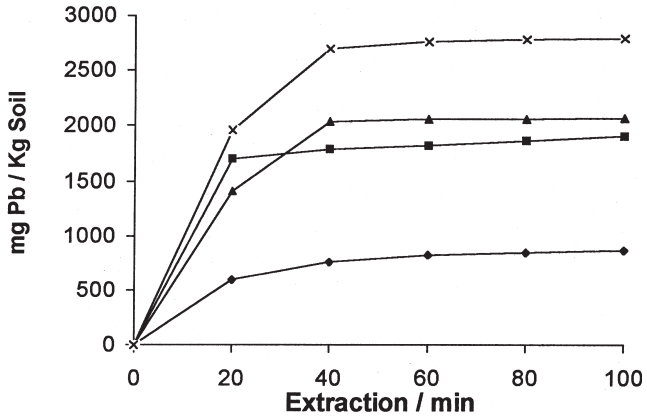

Figure 4b. Extraction of Pb from contaminated soils using SF CO_2 with Cyanex 302 ligand at 60 °C and varying pressures and moisture additions. 0.5 g Cyanex per extraction procedure. 'Wet' samples were obtained by addition of 10 μL H_2O to soil prior to first extraction. ◆ 200 atm, dry sample; ■ 300 atm, dry sample; ▲ 300 atm wet sample; ✖400 atm wet sample.

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but by access to the sites containing the metal ions. Hence, the matrix of the soil plays a large role in determining the amounts of metal extracted. This effect will be studied in more detail in a later publication.

CONCLUSIONS

Using SFE, heavy metals can be extracted nearly quantitatively from soils, using a range of organophosphorus reagents. The most favourable reagent was found to be Cyanex 302 and this ligand was utilised in the extraction of Pb and Zn from a contaminated soil sample. The levels of these metals in the soil were greatly reduced, to levels close to the US EPA TCLP regulatory requirement for a non-contaminated soil.

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