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Subcritical and supercritical fluid extraction of heavy metals from sand and sewage sludge

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Abstract: Demetalization of Pb, Ni, Zn, Cu and Cr heavy metal ions from sea sand and real samples of sewage sludge by subcritical water and supercritical carbon dioxide was investigated. Experimental parameters such as temperature, pressure, extraction time in the static and dynamic mode and sampling were optimized in order to determine the suitable conditions for high removal of metals. The best extraction efficiencies were obtained using acetyl acetate as a chelating agent in both subcritical water and supercritical CO₂ extractions for real and artificial samples. Samples collected from extraction system using both subcritical water and supercritical carbon dioxide were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The highest recoveries obtained from real samples for Cr, Cu, Ni, Pb and Zn were 77.25, 95.1, 84.82, 94.92 and 98.39 %, respectively, using the chelating agent in the subcritical water extraction.

Keywords: subcritical water; supercritical carbon dioxide; demetalization; heavy metal extraction; sewage sludge; sea sand.

INTRODUCTION

Metal waste contamination is a big threat for the environment and human health.^{1–4} There are several methods for monitoring and clean up metal contaminated soils.^{5,6} Traditional extraction methods, such as BCR, Tessier, *etc.*, have been used for decades, but these methods are time consuming and environmentally unacceptable.^{7–10} In addition, analytical difficulties are encountered when employing sequential extraction methods. In addition, these methods involve the use significant amounts of environmentally unacceptable chemicals.

Previous research showed that in order to obtain higher recoveries of selected metal ions, the use of nitric acid-modified water as an extraction solution is the most effective.¹¹ The acid is stronger than water in solubilizing metals

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from sewage sludge and various matrixes. Enhancing the nitric acid concentration has a positive effect on the extraction recoveries. Nevertheless, it was shown that concentrations higher than 4 % caused clogging of the extraction system, including tubes, filters and valves.^{12,13} Morales-Muñoz *et al.* tested various HNO₃ acid concentrations as an extraction solvent modifier in order to optimize the method and obtain the best recoveries. They obtained that the optimum value was 1 %.¹⁴ Therefore, a solution of 1 % nitric acid was used in the study. Thus, an initial experiment that was performed with 1 % nitric acid for optimizing the method and blank experiments confirmed that concentrations higher than 1 % introduced difficulties and decreased recoveries.

Subcritical water extraction (SbWE) and supercritical carbon dioxide extraction (SCE) are promising alternatives to conventional solvent extraction, as not only do they remove heavy metals, but also the morphology and structure matrix is retained.

Carbon dioxide and water are an environmentally acceptable solvent due to their low cost, and non-toxic and non-flammable nature and solubility characteristics, which are changeable by varying the temperature and pressure. Therefore, the SbWE is the efficient technique which nowadays constantly applied by researchers for its beneficial properties such as the solubility capability, mass transfer properties, diffusion coefficient etc.¹⁵

In the recent years, the vast majority of supercritical fluid extractions have focused on the use of supercritical carbon dioxide (scCO₂) to extract metals as some metal complex, because carbon dioxide has low toxicity and is environmentally acceptable.¹⁶

Subcritical water, which is usually sufficient to produce the desired physico-chemical properties, exhibits moderate polarities and suitable solvent properties at temperatures between 100 and 374 °C and high enough pressure to maintain the water in the liquid state.^{16,17} The dielectric constant of water, which is a measure of polarity, decreases dramatically when it is heated under sufficient pressure to maintain the liquid state.^{18,19} For example, dielectric constant (ϵ) of water is 80 at ambient temperatures, but decreases to ≈ 30 at 250 °C.¹⁹ Thus, water at high temperature behave as a non-polar solvent; hence, it can be employed to extract organometallic compounds. At ambient conditions, low polarity organic compounds are poorly soluble in water, but increasing the temperature increases the solubility of non-polar organic compounds. Thus, low polarity organic compounds could be dissolved in supercritical water ($T > 647$ K and $p > 22.0$ MPa), but unfortunately its reactive and corrosive nature makes supercritical water impractical for analytical applications, due to the high temperature and pressure.²⁰ Hawthorne *et al.* used water as an extraction solvent to extract polycyclic aromatic hydrocarbons (PAH) at subcritical and supercritical conditions.¹⁸ Likewise, Akinlua *et al.* used subcritical water for trace metal

extraction from petroleum source rock.²¹ Many organic complexing agents have been used in previous studies of supercritical fluid extraction and pressurized hot water extraction (PHWE) of heavy metals.^{22–25}

The solubility of metal ions in the fluids is crucial. However, by converting charged metal ions into neutral metal chelates using organic chelating agents, this solubility can be enhanced.^{26–32} Thus, the selection of suitable agents is critical in the chelating-SCE of metal ions.³³ Acetyl acetonate (AcAc) and its metal chelates dissolve in subcritical water and supercritical CO₂.^{34,35}

Although various methods including different additives widely applied for the extraction of heavy metals, few data are available for the extraction of sewage sludge with subcritical water or supercritical carbon dioxide using the beta diketone AcAc.^{36,37}

Thus, AcAc was used as a chelating agent in the present study, which was aimed at the development of a fast, a cheap and an environmentally friendly method for the demetalization of soils using subcritical water and supercritical CO₂ extraction methods. The heavy metals (Cu, Cr, Ni, Pb and Zn) were extracted from an artificial sample and a CRM (Certificated Reference Material) sewage sludge sample in the presence and absence of the metal chelating agent AcAc.

EXPERIMENTAL

Chemicals and apparatus

The certificated sewage sludge reference material (LGC 6181, Laboratory of the Government Chemist (LGC), Teddington, Middlesex, TW11 0LY, UK) contains Cu(NO₃)₂, Cr(CIO₄)₃, Ni(NO₃)₂, Pb(NO₃)₂ and Zn(NO₃)₂ in certain quantities obtained from LGC. Standard metal salts, *i.e.*, Cu(NO₃)₂, Cr(CIO₄)₃, Ni(NO₃)₂, Pb(NO₃)₂ and Zn(NO₃)₂, and sea sand (extra pure), which were used for the artificial experiments, were obtained from Merck. Ultra-pure HNO₃ was purchased from Sigma-Aldrich. Chelating agent (acetyl acetonate) was procured from J. T. Baker. Ultra-pure water (18 MΩ cm), which was used in the SbWEs and dilution procedures, was obtained from a Millipore Milli-Q Advantage A10 system.

All extractions were performed using a special stainless steel cylindrical extractor (100 mm × 5 mm i.d.). Both ends of the column were covered with 0.45 μm mesh size filters for the prevention of particulates. A solution of 1 % nitric acid was used as the extraction solvent for the SbWE experiments, while neat CO₂ was used for the supercritical CO₂ extraction (SCE) experiments. The experimental set-up as shown in Fig. 1 was used for both the SbWE and supercritical CO₂ extraction experiments. The fluids were delivered in the constant pressure mode at a specific value using a Teledyne ISCO 260 D series pump.

An Agilent 7500ce ICP-MS instrument (Tokyo, Japan), equipped with a collision/reaction cell in the form of octopole reaction system (ORS), was used for the analysis of Cu, Cr, Ni, Pb and Zn metal ions in the extracted samples. The utilized argon gas was of spectral purity (99.998 %). The external standard calibration method was applied to all determinations, using Li, Sc, Ge, Y, In, Tb and Bi internal standard mixture (in 2 % HNO₃ matrix). National Institute of Standards and Technology (NIST) single element reference standards were used to construct ten-point calibration curves.

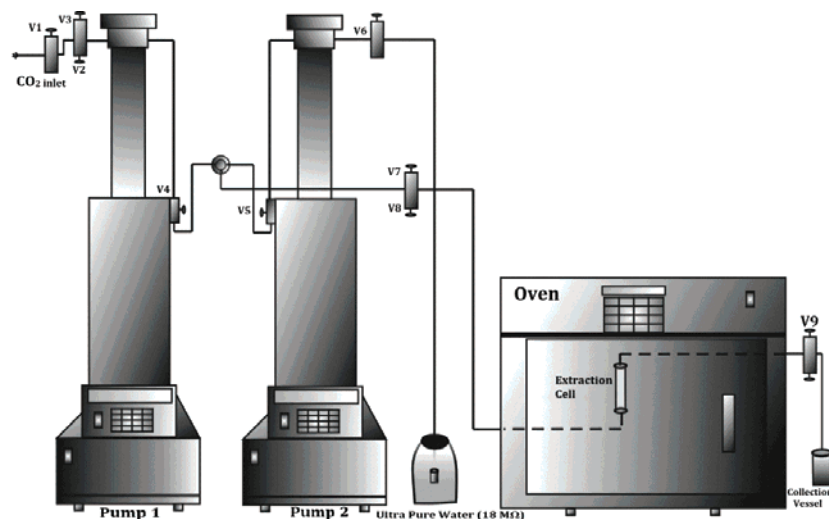


Fig. 1. Schematic diagram of extraction system (V1: CO₂ tube filling valve, V2 and V3: pressure regulation valve, V4: pump 1 filling valve, V5 and V6: pump 2 filling valve, V7 and V8: fluid transfer valve, V9: emptying/collecting valve).

The ICP-MS instrument was operated under the following parameters; RF power 1500 W, plasma gas 15 L min⁻¹, auxiliary gas flow at 1 L min⁻¹, nebulizer pump 0.1 rps, measurement time 0.5 s, make-up gas 0.13 L min⁻¹.

Pre-tests of sampling

For determining trace metal residue derived from the chemicals and apparatus, extra pure sea sand was used as a blank. Initial experiment was performed with subcritical water and supercritical carbon dioxide and the metals of interest were not detected in collected solutions.

Procedure

The artificial samples were prepared by adding 400 µL of a 500 ppm concentrated metal salt solution to 1.000 g of sea sand. Likewise, 1.000 g of sewage sludge was used for the CRM samples. The sample was placed in extraction cell and 200 µL of the chelating agent (acetyl acetate) was added and covered by glass wool. The extraction cell was screwed on, and the cell was placed into the oven and pressurized with fluid (water in SbWE and carbon dioxide in SCE). After static mode extraction (30 min), the exit valve was opened and during dynamic mode extraction, the extracts were collected in ultra-pure water modified by 1 % HNO₃. 5 mL of water was used in the SbWE and 200 cm³ of CO₂ was used in the SCE for each experiment. Acetyl acetate (AcAc) was used as a chelating agent. Experiments were performed in the presence and absence of the chelating agent under the same extraction conditions. Each experiment was repeated three times under the same conditions and the average recovery and standard deviation values were calculated. SCE experiments were performed at 90 °C, 120 bar; 80 °C, 110 bar and 70 °C, 100 bar. The SbWE experiments were also performed at 110 °C, 70 bar; 120 °C, 80 bar and 130 °C, 90 bar in the constant pressure mode.

RESULTS AND DISCUSSION

In order to optimize the SCE and SbWE methods, Pb^{2+} was used as a reference metal. The parameters affecting both SCE and SbWE, namely, the amount of chelating agent, the extraction time and the optimum pressure–temperature, were investigated in order to attain the best recoveries. It was observed that density, which can be varied by changing the temperature and pressure, is one of the most influential factors affecting the extraction step and its increase had a positive effect on the recovery of the analytes. The other influential factor affecting the extraction is the addition of chelating agent on the samples, especially for the SCE. It was found that the recovery of Pb^{2+} increased by using the chelating agent AcAc and with increased temperature–pressure (Table 1).

TABLE I. Removal of Pb^{2+} added to sea sand by SCE or SbWE in the absence (a) or presence (b) of AcAc; initial amount: 500 ppm

SCE					SbWE				
<i>p</i> bar	<i>t</i> °C	CO ₂ density ⁴¹ g mL ⁻¹	a	b	<i>p</i> bar	<i>t</i> °C	Water density ⁴² g/mL	a	b
100	70	0.248	16.8±2.6	46.7±4.5	70	110	0.95407	76.6±1.1	95.3±0.9
110	80	0.258	17.2±1.4	52.6±2.2	80	120	0.94680	79.5±0.9	96.3±0.8
120	90	0.264	20.1±1.8	57.4±3.8	90	130	0.93918	83.6±1.3	97.6±1.2

Extraction of artificial Pb^{2+}

Artificial extractions of Pb^{2+} from sea sand were performed by SCE and SbWE at selected temperature with and without AcAc and the obtained recoveries were compared with each other. Artificial extractions of Pb^{2+} from sea sand were performed by SCE at 70 °C, 100 bar ($d_{CO_2} = 0.248$ g mL⁻¹); 80 °C, 110 bar ($d_{CO_2} = 0.258$ g mL⁻¹) and 90 °C, 120 bar ($d_{CO_2} = 0.264$ g mL⁻¹) and by SbWE at 110 °C, 70 bar ($d_{H_2O} = 0.95407$ g mL⁻¹), 120 °C, 80 bar ($d_{H_2O} = 0.94680$ g mL⁻¹) and 130 °C, 90 bar ($d_{H_2O} = 0.93918$ g mL⁻¹) both with and without AcAc. The recoveries are given in Table I. It was observed that enhancing the density of CO₂ and decreasing the density of water, especially using the chelating agent, increased the extraction yields.

SCE of artificial samples and CRM samples

Effective extractions of the selected metals were performed by SCE from CRM samples and the best result was obtained at 90 °C, 120 bar ($d_{CO_2} = 0.264$ g mL) for each metal with AcAc (Table II). In the absence of the chelating agent, the extraction yields were not good enough for efficient demetalization. The highest recovery was obtained for Pb^{2+} (50.2±2.4) at 90 °C, 120 bar with the chelating agent (Table II). It was observed that an enhanced density mostly scaled up the recoveries and that without the chelating agent no satisfactory yield was obtained. Solubilities of the organo-metallic compounds played a key role in

determining the extraction efficiencies. Dissolution and extraction of the insoluble metal compounds from CRM samples depended on the chelation ability of the chelating agent.²⁸ Using AcAc, enhanced the recoveries for each metals and enhanced temperature–pressure improved the yields.

TABLE II. Removal of metals from artificial and CRM samples by SCE in the absence (a) or presence (b) of AcAc; initial amount: 100 ppm

Ion	a			b		
	100 bar, 70 °C	110 bar, 80 °C	120 bar, 90 °C	100 bar, 70 °C	110 bar, 80 °C	120 bar, 90 °C
Extraction yields of metals from artificial samples, %						
Cr ³⁺	9.3±0.9	9.9±1.4	10.0±1.2	31.0±1.2	37.4±2.6	40.2±2.3
Cu ²⁺	8.9±1.4	10.7±1.8	11.6±1.5	31.9±2.4	40.0±2.8	45.4±2.5
Ni ²⁺	12.4±1.6	17.3±1.7	18.1±2.1	27.6±2.9	43.6±2.7	47.5±4.3
Pb ²⁺	13.6±0.8	15.6±1.1	18.60±1.2	41.4±1.3	45.1±1.8	50.2±2.4
Zn ²⁺	13.1±0.3	14.1±0.5	15.1±1.0	45.2±0.9	47.1±1.3	48.2±5.4
Extraction yields of metals from CRM samples, %						
Ion	a			b		
	100 bar, 70 °C	110 bar, 80 °C	120 bar, 90 °C	100 bar, 70 °C	110 bar, 80 °C	120 bar, 90 °C
Cr ³⁺	6.2±0.9	7.1±0.9	7.9±1.3	27.9±2.8	28.2±2.9	28.6±2.0
Cu ²⁺	9.2±2.7	9.3±1.5	10.6±2.1	26.2±1.7	32.1±2.0	35.8±1.8
Ni ²⁺	10.6±3.1	12.5±1.8	13.2±1.4	22.5±4.5	35.6±1.6	39.4±0.9
Pb ²⁺	9.5±1.4	10.9±2.8	12.3±2.0	36.4±0.3	42.1±0.8	45.3±0.4
Zn ²⁺	9.6±2.7	11.8±2.0	12.6±1.9	31.2±1.0	40.8±2.9	42.1±1.1

The direct extraction of metal ions using neat supercritical CO₂ without the addition of a chelating agent is extremely inactive because of the necessity of charge neutralization and the weak solute–solvent interaction. Whereas, when the metal ions are chelated with organic ligands, they become quite soluble in scCO₂. Similarly, direct extraction of metal ions by subcritical water without the addition of the chelating agent is highly inefficient in comparison with extraction using a chelating agent.^{38,39} Generally, higher yields were obtained in the extraction of sea sand samples compared with CRM samples for almost all metals because of the solute–solute and solute–matrix interactions which caused reduced yields in the CRM samples.²³ The matrix composition plays an important role in the efficiency of the extraction of heavy metals by supercritical and subcritical fluids. The artificial metals are held on the surface of the sea sand crystals during artificial sample extractions.²⁸ The difference between the results of Pb extraction yields (%) in Tables I and II for the single element (57.4 %) and multi mixed element (50.2 %) suggests that extraction of this metal from CRM was dependent on the chemical form and matrix interaction. Therefore, the

extraction of Pb from sea sand was facilitated compared to CRM. Thus higher recoveries could be obtained in the extraction of artificial samples.

SbWE of artificial samples and CRM samples

The extraction yields shown in Table III clearly demonstrated that SbWE was a more effective method than SCE method. The highest recoveries obtained from real samples for Cr, Cu, Ni, Pb and Zn were 77.25, 95.1, 84.82, 94.92 and 98.39 %, respectively, when the chelating agent was employed. The lowest recovery was obtained for Cr (52.4 ± 2.6) at 110 °C, 70 bar ($d_{H_2O} = 0.95407 \text{ g mL}^{-1}$) in the absence of the chelating agent. It was found that the efficiency of SbWE was increased in the presence of the ligand.

TABLE III. Removal of metals from artificial and CRM samples by SbWE in the absence (a) or presence (b) of AcAc

Extraction yields of metals from artificial samples, %							
Ion	Initial amount ppm	a			b		
		70 bar, 110 °C	80 bar, 120 °C	90 bar, 130 °C	70 bar, 110 °C	80 bar, 120 °C	90 bar, 130 °C
Cr ³⁺	100	52.4±2.6	54.8±1.8	56.5±2.3	78.1±2.3	79.4±1.9	83.6±4.5
Cu ²⁺	100	62.6±1.9	63.4±2.4	67.8±2.9	93.5±1.4	96.4±1.7	96.8±1.4
Ni ²⁺	100	58.7±2.5	58.5±2.2	69.4±3.4	85.1±1.8	86.3±2.7	90.6±1.2
Pb ²⁺	100	69.2±3.2	71.8±1.5	74.9±2.9	93.5±1.4	94.6±0.7	96.6±0.7
Zn ²⁺	100	72.9±2.9	74.7±2.6	72.5±1.8	97.9±1.6	98.1±0.6	96.4±0.9
Extraction yields of metals from CRM samples, %							
Ion	Initial amount ppm	a			b		
		70 bar, 110 °C	80 bar, 120 °C	90 bar, 130 °C	70 bar, 110 °C	80 bar, 120 °C	90 bar, 130 °C
Cr ³⁺	78	69.4±5.4	60.6±4.5	64.7±3.4	71.2±12.6	73.2±9.4	77.2±4.9
Cu ²⁺	354	73.7±1.3	80.2±1.7	86.7±1.6	84.2±2.6	90.2±3.8	95.1±3.4
Ni ²⁺	45	64.9±4.6	72.6±5.9	73.6±6.7	81.0±6.2	82.3±10.3	84.8±12.0
Pb ²⁺	105	80.4±2.5	85.7±3.1	86.6±4.1	92.0±7.7	92.9±4.4	94.9±7.0
Zn ²⁺	1100	86.4±0.5	89.4±1.8	83.8±2.0	96.7±0.5	98.4±1.8	94.7±4.6

The reduced viscosity, efficient surface tension properties of subcritical water and diffusion coefficients of solutes in subcritical water allow for favorable mass transfer properties. Changing the temperature–pressure had a large effect as it altered the physicochemical properties of analytes and fluids. Thus, SbWE could be performed in the demetalization of various matrixes.⁴⁰

The chelating ligand formed stable organometallic complexes with the metal ions. The organometallic complex dissolved readily in the subcritical water. Thus, the extraction of the heavy metals was simplified *via* their conversion to ligand–metal complexes.

High extraction yields were obtained in the SbWE extraction of the CRM samples both with and without the chelating agent (Table III). However greater

recoveries were obtained using AcAc. The matrix interaction that caused reduced yields in the SCE was not effective in the SbWE. Thus, the extraction yields showed that SbWE was more effective than SCE. There were only small differences in the yields when the SbWE was performed at different temperatures. Hence, temperature was less influential than the chelating agent (AcAc) in improving the yields during SbWE.

CONCLUSIONS

The effective conditions for elevated recoveries of heavy metals from real and artificial samples were investigated. It was observed that subcritical water is a more effective fluid compared to supercritical CO₂ for the extraction of heavy metals from various matrixes, although SbWE requires more harsh conditions than SCE. The density of supercritical CO₂ increased and that of water decreased with increasing temperature–pressure. Thus, the diffusivity of subcritical water, and the solvation and penetrating power of both improved and higher recoveries were obtained at elevated temperature–pressure in SbWE and SCE

The most popular environmentally friendly techniques, SCE and SbWE, for the extraction of trace metals, such as Pb, Ni, Zn, Cu and Cr, from sewage sludge and sea sand using the chelating agent AcAc were compared. It was shown some amounts of the metals could be extracted by SCE and almost the total amount of metals present in the samples could be extracted by SbWE from sea sand and real samples in a short time compared to traditional methods, such as BCR and Tessier.

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ИЗВОД

СУБКРИТИЧНА И СУПЕРКРИТИЧНА ФЛУИД ЕКСТРАКЦИЈА ТЕШКИХ МЕТАЛА ИЗ ПЕСКА И ОТПАДНОГ МУЉА

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Испитивана је екстракција јона тешких метала Pb, Ni, Zn, Cu и Cr из морског песка и реалних узорака отпадног муља помоћу субкритичне екстракције водом и суперкритичне угљен-диоксидом. Оптимизовани су експериментални параметри као што су температура, притисак, време екстракције у статичком и динамичком режиму и узорковање, ради одређивања погодних услова за уклањање метала. Највећа ефикасност екстракције са реалним и синтетичким узорцима је добијена коришћењем ацетил-ацетоната као хелирајућег агенса, у оба типа екстракција, субкритичној водом и суперкритичној угљен-диоксидом. Узорци добијени после екстракције анализирани су применом индуктивно спрегнуте плазме са масеном спектрометријом (ICP-MS). Највише вредности процента приноса, добијене за реалне узорке, за Cr, Cu, Ni, Pb и Zn, износиле су

77,25, 95,1, 84,82, 94,92 и 98,39 %, са хелирајућим агенсом, субкритичном екстракцијом водом.

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