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APPLICATION OF LEACHING TESTS FOR THE ASSESSMENT OF AVAILABLE HEAVY METALS FROM DOMESTIC AND INDUSTRIAL SLUDGES

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Various sludge samples from different domestic and industrial wastewater treatment plants were analyzed by Flame Atomic Absorption Spectrometry to evaluate their total and available contents of heavy metals (Cu, Cr, Ni, Pb, Zn and Fe). The EDTA and acetic acid single extraction procedures were applied to these samples with the aim to study the leaching behaviour of the metals in the different sludges and also to predict their possible mobility when these wastes are disposed on the environment and landfills. In acidic medium, a higher extraction efficiency was observed for the major part of the elements studied in the industrial sludges, except for Ni and Zn, which were also considerably released from domestic sludges. In contrast, in the presence of the EDTA complexing ligand, a more elevated mobility of metals was found in the domestic sludges and little or no metals were released from the industrial sludges. Moreover, the results of the microwave total digestions were compared, for all metals, with those obtained using a more simplified pseudototal digestion procedure (based on the EPA Method 3051, named microwave assisted acid digestion of sediments, sludges, soils and oils) and a good agreement was found between them, except for Cr and Ni in some particular samples. The between-batch precision (expressed as RSD) of both compared digestion methods was very similar and values lower than 7.7% were obtained in both cases. A certified domestic sludge material (SRM 2781) was employed to validate the two digestion procedures and no significant differences were found between the certified and experimental values for all the elements studied.

Keywords: Heavy metals; Domestic sludges; Industrial sludges; Single extractions; Total digestion; Pseudototal digestion; Mobility predictions

INTRODUCTION

The increasing production of sludges derived from the treatment of industrial and domestic wastewaters causes a new environmental problem due to their final disposal. In general, these sludges contain a large variety of constituents and their composition may vary from highly organic (domestic sludges) to basically mineral (industrial

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sludges). Likewise, depending on their origin they may contain organic and/or inorganic contaminants which are released to surface and ground waters, even when they are buried in shallow trenches [1]. For these reasons, among the possible options for sludge disposal [2,3] (agricultural fertilizer [4,5], landfilling, marine disposal, building materials [6], fuel, animal food, etc.), their use as soil conditioner or fertilizer is limited by the elevated pollutant contents, particularly heavy metals. In relation to this, the EU [7] as well as different countries (USA [8], Spain [9], Portugal [10], etc.) possess their own regulations and standards focused to the use and disposal of sewage sludge on soil or other destinations.

In order to assess the potential environmental impact of materials contaminated with metals, the determination of the total metal contents provides insufficient information, since the chemical forms (or species) of the metal in the sample matrix determine its mobilization capacity, and consequently its behaviour in the environment [11–13]. In relation to this, sequential extraction methods [14–18] and different leaching tests, especially batch single extractions [16,17,19] are the most common methods for estimating the metal mobility in soil and sediment samples. The numerous extraction techniques found in the literature and the lack of uniformity in the different procedures used do not allow the results to be compared nor the procedures to be validated. On the other hand, the scarcity of suitable reference materials in this field makes very difficult to control the quality of the measurements in this type of studies. In order to solve this problem, the European Commission through BCR Programme and its successors has conducted a series of interlaboratory studies, which were successfully concluded by the certification of soil and reference materials [20]. As a result, certified reference materials of sewage sludge amended soil [21,22] are now available for the quality control of EDTA and acetic acid extractable element contents, and also a sediment sample was certified for its extractable trace element contents following a three-step sequential extraction method [23].

The EDTA and acetic acid single extractions have been originally developed for soil analysis and they have been widely applied in this way [24–26]; however little or no works were found in the literature to have been carried out using these extraction procedures for sludge samples. In our opinion, it could be useful and interesting to apply these methods to evaluate the potential mobility of heavy metals from sludge samples under complexing or acidification processes developed in the environment, particularly when the sludges are disposed on landfill.

The aim of the present study was to investigate the leaching of heavy metals (Cu, Cr, Ni, Pb, Zn and Fe) from domestic and industrial sludges, using the EDTA and acetic acid reagents, in order to evaluate the mobilizable content of them. Given that the leaching behaviour of sludges is largely dictated by the nature of the sample [27], a second objective of this work was to find the similarities and/or differences in EDTA and acetic acid leaching behaviour of domestic and industrial sludges, which could be classified as highly organic matter containing and typically inorganic sludges, respectively.

On the other hand, it was also compared, in both types of samples, the results of the total microwave digestion with those obtained by means of a pseudototal digestion, based on the EPA Method 3051, where the sample was not completely decomposed due to no silicates dissolution. Although, technically, the pseudototal digestion is an extraction procedure, carried out with strong acids, it provides comparable results to the total digestion, particularly since the pollutants are not silicate-bound; this fact will be also proved in this work with domestic and industrial sludges.

EXPERIMENTAL

Instrumentation

A double-beam Atomic Absorption Spectrophotometer, GBC model 904 A, was used for metal determinations. Hollow cathode lamps (Cathodeon) were used as radiation source. Resonance lines employed were 324.8, 357.9, 230.0, 217.0, 213.9 and 248.3 nm for Cu, Cr, Ni, Pb, Zn and Fe, respectively. Lamp intensity and slit width were used according to the manufacturer's recommendations. Air-acetylene flow rate was 11-1 L min⁻¹ for all the elements, except for Cr where a more reducing flame was required (11-2 L min⁻¹). A domestic microwave oven (Samsung, model TDS 1713) with power values ranging from 100 to 800 W was used as microwave radiation source. A 45 mL capacity Parr reactor (model 4782) was employed for total and pseudototal digestions of the sludges. A magnetic shaker (Raypa, model AG-2) was used for the extraction. A centrifuge (Heraeus Sepatech, model Labofuge Ae) was used for a complete separation of the extracts from the solid phase. A pH-meter (Philips, model PW 9420) was used for pH adjustments in the extracts.

Reagents

All reagents employed were of high quality analytical reagent grade and all of them supplied by Merck. High purity water (Millipore Milli-Q Sytem) was used throughout. The stock solutions of metals (1000 µg/mL) were obtained by dissolving the pure metal (Cu, Zn and Fe) or the appropriate salts of the corresponding metals (Pb(NO₃)₂, Ni(NO₃)₂ and K₂CrO₄). Concentrated nitric (65%), hydrochloric (35%) and hydrofluoric (48%) acids were employed for the digestion of the samples. A domestic sludge certified reference material (SRM 2781) from the National Institute of Standard Technology (NIST) was used to validate the total and pseudototal microwave digestion methods.

The 0.05 mol/L EDTA solution was prepared as an ammonium salt solution by dissolving the appropriated amount of the salt in concentrated ammonia solution; the addition of ammonia solution had to be continued until all the EDTA dissolved; the pH was adjusted to 7 ± 0.05 by addition of a few drops of either ammonia or hydrochloric acid. The 0.43 mol/L acetic acid solution was prepared by adequate dilution of glacial acetic acid. Both extractant solutions were stored in stopped polyethylene containers.

Sample Collection and Pre-treatment

The domestic sludge samples studied were collected from two different wastewater treatment plants (Samples DS1 and DS2) that process the domestic effluents of Aveiro town (Portugal) by applying both physical-chemical and biological purification treatments. The third domestic sludge analyzed was the certified reference material SRM 2781, previously indicated. Two of the industrial sludges studied (Samples IS1 and IS2) proceeded from the wastewater treatment plant of an aluminium finishing factory (anodizing and coating) also located in Aveiro town. The last industrial sludge analyzed (Sample IS3) was collected from a wastewater treatment plant located in the industrial area of Agueda (Portugal) that accepts the effluents from different

kinds of metal finishing factories located in the area. All of the sludges were collected by multiple sampling (about 3 kg) in polyethylene containers and they were dried in the laboratory at 105°C [28,29] in a heater until constant weight. After this, the samples were ground in a porcelain mortar and then they were sieved using a nylon fibre sieve, in order to separate the fraction with particle size smaller than 90 µm. The initial sieved samples (< 90 µm) were split by means of several cycles of coning and quartering until the weight of the remaining half opposite quarters was approximately 160 g. Then, the selected portion of the samples were thoroughly mixed and homogenised on a clean polyethylene sheet with occasional mixing by hand. Finally, the prepared samples were bottled in polyethylene containers, each containing approximately 80 g, which were stored at room temperature into a dessicator.

Single Extraction Procedures

The EDTA and acetic acid single extractions were applied to all the pretreated sludge samples, including the reference material SRM 2781. Three replicates of each sample (each extractant) were obtained, all the extractions were performed in 50 mL capacity glass tubes also used for centrifugation, in order to avoid possible loss of sample.

The extractions with EDTA were carried out following the established extraction method [35], but slightly modified: approximately 2.5 g of pre-treated sludge sample were placed into a centrifuge tube and 25 mL of 0.05 mol/L EDTA solution were added; the mixture was shaken during 1 h at room temperature by means of a magnetic shaker instead of the end-over-end over shaker recommended in the protocol; a shaker speed of 60 rpm was needed to maintain the samples in suspension during the extraction. The acetic acid extracts were obtained using the following extraction conditions [35]: approximately 1 g of pre-treated sludge sample was placed into the centrifuge tube and 40 mL of 0.43 mol/L acetic acid were added; the mixture was also shaken during 16 h at room temperature as described above. In both cases, after shaking, the suspension was centrifuged for 12 min at 2500 rpm. The supernatants were quantitatively transferred to volumetric flasks of 25 and 50 mL for EDTA and acetic acid extracts, respectively. The resultant solutions were decanted in polyethylene bottles and stored at 4°C until analysis. Blank extractions were carried out in parallel for each set of analysis using the same procedure as described above.

The extraction efficiency of these leaching tests was also evaluated by calculating, for each element, the percentage of relative extraction (recovery) with respect to the total metal contents.

Total and Pseudototal Microwave Digestions

The determination of the total metal content in the sludges was carried out by completely dissolving the matrix of the sample by means of a microwave digestion procedure optimized (also for sludge samples) in a previous work [30]. In this case a little portion (0.1 g) of sample (< 90 µm) was placed into the PTFE vessel of the Parr reactor and 4 mL of nitric acid (65%), 1 mL of hydrochloric acid (35%) and 2 mL of hydrofluoric acid (48%) were added in order to decompose the siliceous material present in the sludge. The vessel was closed and then it was heated in a microwave oven during 2 min at 540 W of power. Once the sample was digested, the reactor was allowed to cool in an ice bath before it was opened. The resultant

solution was heated to dryness in order to eliminate the unreacted hydrofluoric acid and dissolved with 1 mL hydrochloric acid. Finally, it was quantitatively transferred into a 10 mL volumetric flask and make up to volume with ultrapure water. The solution was decanted and stored at 4°C in stopped polyethylene bottles until it was analyzed.

The pseudototal digestions of the sludges were carried out using the EPA Method 3051 [31] slightly modified, with respect to the ratio mass of sample/volume of acid reagent as well as to the microwave parameters employed (heating time and power). In this case, 4 mL of nitric acid (65%) and 1 mL of ultrapure water were mixed with a little portion of the solid sample (0.1 g) into the PTFE vessel of the Parr reactor. The vessel was also closed and heated in the microwave oven during 90 s at 450 W of power. After this, the reactor was cooled before opening in a similar way to the above. Then, the vessel content was centrifuged during 5 min at 2500 rpm in order to separate the supernatant from the undissolved solid phase. The solution was quantitatively transferred into a 10 mL volumetric flask and diluted to volume with ultrapure water. The storage and conservation of the sample was made as the above.

With the aim to check both total and pseudototal microwave digestion methods, a domestic sludge reference material (SRM 2781) with certified values of total metal contents and NIST reference values for acid extractable metals [32,33] was employed using the EPA Methods 3050, 3051 [31] and the NJDEP 100 Method [34]. Finally, in order to estimate the effectiveness of the pseudototal digestions with respect to the total metal content, the percentage of relative extraction (or leaching recovery) was calculated, in all samples.

RESULTS AND DISCUSSION

Analysis of Sludge Samples after Total and Pseudototal Microwave Digestions

The analytical results obtained in the studied domestic and industrial sludge samples after total and pseudototal digestions are summarized in Table I. All metals were determined by interpolating the absorbance signal in a calibration curve prepared with aqueous standards and the values obtained are given as mean of three separated determinations ($\mu\text{g/g}$).

As can be seen in Table I, and in contrast to that expected, not always domestic sludges are lower polluted than industrial sludges. Thus, in the three industrial sludges analyzed in this work, only the Sample IS3 presents, for all the elements studied, total mean contents considerably more elevated than those of the domestic sludges; the other two industrial sludges (Samples IS1 and IS2) display for the most elements (Cu, Pb, Zn and Fe) inferior metal contents to the domestic sludges. Only in the case of Cr, the values of Samples IS1 and IS2 are clearly higher than to that found in the domestic sludges and the values of Ni in these samples are similar to that obtained in Samples DS1 and DS2. The elevated Cr content found in the industrial sludges could be perfectly attributed to the use of Cr(VI) for chromation operations in the coating finishing industry, reduced to Cr(III) in the wastewater treatment plant [36]. On the other hand, it is important to stress that the total metal contents found in all the analyzed domestic sludges as well as the Samples IS1 and IS2, except Cr, does not

TABLE I Analytical results obtained in domestic and industrial sludges after pseudototal and total microwave digestions

| | Domestic sludges ($\mu\text{g/g}$) | | | Industrial sludges ($\mu\text{g/g}$) | | |
|------------------------------|--------------------------------------|----------------------|---------------------|--|-------------------|------------------------|
| | Sample DS1 | Sample DS2 | SRM 2781 | Sample IS1 | Sample IS2 | Sample IS3 |
| <i>Pseudototal digestion</i> | | | | | | |
| Cu | 194.9 \pm 6.5 | 158.8 \pm 6.6 | 590.9 \pm 7.1 | 16.07 \pm 0.27 | 17.44 \pm 0.12 | 3804.5 \pm 88.1 |
| Cr | 24.83 \pm 0.13 | 27.19 \pm 1.0 | 135.6 \pm 2.5 | 1214.6 \pm 3.8 | 744.8 \pm 12.4 | 28228.9 \pm 547.4 |
| Ni | 19.62 \pm 1.02 | 34.45 \pm 2.65 | 71.01 \pm 3.62 | 25.95 \pm 1.89 | 18.84 \pm 1.18 | 9109.4 \pm 258.9 |
| Pb | 133.9 \pm 4.2 | 60.09 \pm 1.83 | 190.3 \pm 4.05 | 52.86 \pm 1.95 | 41.52 \pm 2.82 | 1096.3 \pm 4.40 |
| Zn | 1181.4 \pm 35.6 | 786.6 \pm 16.1 | 1123.3 \pm 34.0 | 68.15 \pm 3.23 | 46.85 \pm 0.58 | 23923.1 \pm 691.2 |
| Fe | 6246.5 \pm 190.8 | 86387.2 \pm 620.5 | 24841.1 \pm 375.9 | 1436.7 \pm 35.8 | 1580.4 \pm 19.9 | 255447.9 \pm 10638.3 |
| <i>Total digestion</i> | | | | | | |
| Cu | 196.6 \pm 11.1 | 160.9 \pm 6.6 | 625.1 \pm 7.4 | 16.61 \pm 0.15 | 18.30 \pm 0.65 | 4196.6 \pm 138.1 |
| Cr | 41.19 \pm 3.0 | 40.93 \pm 2.24 | 199.3 \pm 3.1 | 1234.7 \pm 68.2 | 756.5 \pm 6.7 | 38662.3 \pm 806.7 |
| Ni | 24.31 \pm 1.19 | 37.58 \pm 1.97 | 78.90 \pm 2.11 | 36.92 \pm 1.02 | 26.60 \pm 0.93 | 9864.5 \pm 294.1 |
| Pb | 142.2 \pm 3.6 | 62.12 \pm 3.84 | 203.5 \pm 6.75 | 54.68 \pm 1.33 | 43.95 \pm 2.05 | 1134.7 \pm 7.8 |
| Zn | 1286.9 \pm 23.5 | 881.7 \pm 16.3 | 1275.2 \pm 17.8 | 71.56 \pm 2.26 | 52.67 \pm 1.00 | 25971.4 \pm 363.2 |
| Fe | 7984.9 \pm 111.3 | 86906.7 \pm 1022.3 | 28500 \pm 1200 | 1649.4 \pm 28.7 | 1859.2 \pm 23.1 | 261125.7 \pm 5948.5 |

present a pollution problem in agricultural uses, according to Portuguese environmental regulation [10].

The results of the pseudototal digestions are also listed, for all samples, in Table I. As was expected, the values were, in all cases, smaller than those obtained with the total digestion procedure. However, it is important to emphasize that for most of the elements studied in both type of samples, the results of the pseudototal digestion were comparable to the total metal contents. The most important differences between both groups correspond to Cr, in all domestic sludges and in the Sample IS3, and to Ni in the industrial sludges IS1 and IS2.

In order to establish a more rigorous comparison between both types of digestion procedures, the percentages of relative extraction between pseudototal and total digestions are shown in Figs. 1(c) and 2(c) for domestic and industrial sludges, respectively.

According to these graphics, and such as was previously indicated, it was found, for most of the elements studied in all sludge samples, a good agreement between the compared results. The percentages of relative extraction ranged from 87.2 to 99.4% for Cu, Pb and Zn in the three domestic sludges (Fig. 1(c)) and also for Ni and Fe in the Sample DS2 and in the reference material SRM 2781. The lowest extraction efficiency corresponds to Cr in all domestic sludges (66.4–68.8%) and also to Ni and Fe in the Sample DS1 (values around 80%). In the industrial sludges, the percentages of relative extraction were also elevated for the majority of the elements; values from 85 to 98.5% were found for all the elements in the three samples, except for the case of Ni in the Samples IS1 and IS2 (around 70%) and for Cr in the Sample IS3 (73%). In addition, the between-batch precision (expressed as RSD) of both compared digestion methods was very similar for all metals, with values lower than 7.7% in both cases.

In order to validate the two employed digestion methods, three replicates of the reference material SRM 2781 were dissolved using both total and pseudototal microwave digestions; the results obtained for Cu, Cr, Ni, Pb, Zn and Fe are shown

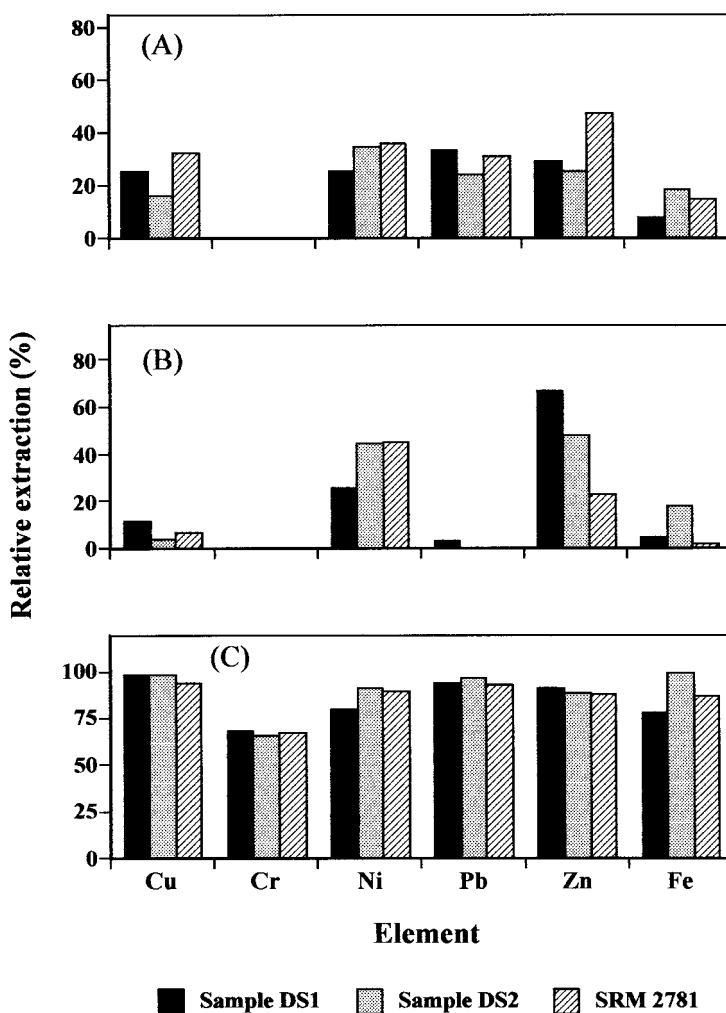


FIGURE 1 Percentages of relative extraction corresponding to the EDTA (A), acetic acid (B) and pseudototal digestion (C) respect to the total metal contents in domestic sludges.

in Table II. The statistical comparison of the experimental and certified values using the t -test ($p=0.95$) allow us to conclude that no significant differences were found between them.

By taking the above considerations into account, it is possible to say that, although with some exceptions, the results of the pseudototal digestions are in good agreement with the total metal contents. It means that in both types of sludge samples, most of the elements studied are not associated to the siliceous fraction of the matrix sample, and consequently, they are largely leached in presence of strong acids. It can be concluded that, the pseudototal digestion could be employed as a screening method to approximately estimate the total metal content in domestic and industrial sludges. In addition, it is more rapid and simplified procedure with an inferior reagents consumption.

TABLE II Analytical results obtained in the certified reference material (SRM 2781) after pseudototal and total microwave digestion

| | <i>Certified values</i> (mg/kg) | <i>Found Values</i> ^a (mg/kg) | <i>Recovery</i> (%) |
|---|---------------------------------|--|---------------------|
| <i>Total digestion</i> | | | |
| Cu | 627.4 ± 13.5 | 625.1 ± 7.4 | 99.63 |
| Cr ^b | 202.0 ± 9.0 | 199.3 ± 3.1 | 98.66 |
| Ni | 80.20 ± 2.3 | 78.90 ± 2.11 | 98.38 |
| Pb | 202.1 ± 6.5 | 203.5 ± 6.8 | 100.7 |
| Zn | 1273.0 ± 53 | 1275.2 ± 17.8 | 100.2 |
| Fe ^{b,c} | 2.8 ± 0.1 | 2.85 ± 0.12 | 101.8 |
| <i>Pseudototal digestion</i> ^d | | | |
| Cu | 601 ± 16 | 590.9 ± 7.1 | 98.32 |
| Cr | 143 ± 14 | 135.6 ± 2.5 | 94.84 |
| Ni | 72.3 ± 6.3 | 71.01 ± 3.62 | 98.21 |
| Pb | 183 ± 15 | 190.3 ± 4.1 | 104.0 |
| Zn | 1120 ± 34 | 1123.3 ± 34.0 | 100.3 |
| Fe | 24300 ± 2100 | 24841.1 ± 375.9 | 102.2 |

^aConcentrations are expressed as mean value of three determinations ± standard deviation; ^bIndicative values; ^cValues expressed as %; ^dNIST reference values from concurrent acid extractable analysis of SRM 2781 [33].

Comparison between EDTA and Acetic Acid Single Extractions in Domestic and Industrial Sludges

The EDTA and acetic acid single extractions were applied, in triplicate, for metal leaching in all the studied samples. All the measurements were carried out using the standard addition method and these results, expressed as mean of three determinations ($\mu\text{g/g}$), are displayed in Table III.

From the results of Table III it was observed that, in domestic sludges, a more extraction efficiency was achieved when EDTA was employed. So, greater amounts of Cu, Pb and Fe in all samples, and Zn in the SRM 2781 were leached using the EDTA extraction procedure; Ni and Cr were extracted in a similar way by both methods: Cr was not leached, and a similar amount of Ni was extracted in both cases. In contrast, Zn presents a particular behaviour, given that it was released more using the acetic acid procedure in the Samples DS1 and DS2, and using the EDTA in the Sample SRM 2781.

Unlikely, in the industrial sludges a bigger amount of metals were leached using the acetic acid extractions, particularly in the case of Cr, which was almost not extracted with the EDTA, and was considerably released using the acetic acid procedure. This fact could be explained by taking into account the inorganic nature of the sample as well as the influence of pH on metal leaching from industrial sludges [37]. In this case, a similar amount of Pb was extracted by both compared extraction methods.

In order to better compare the extraction efficiency of the EDTA and acetic acid extractions in both domestic and industrial sludges, the percentages of relative extraction of the single extractions respect to the total metal content were displayed in the graphics of Figs. 1 and 2(a–b) for domestic and industrial sludges, respectively.

As can be observed in these graphics, domestic and industrial sludges present a different behaviour with respect to the applied leaching tests; as it was previously indicated, a more extraction efficiency was obtained using the EDTA in domestic sludges and, in contrast, more available metals were obtained with the acetic acid in the industrial sludges. This fact could be explained by taking into account the different composition of these samples; while in domestic sludges the metals are greatly organic

TABLE III Analytical results obtained in domestic and industrial sludges using the EDTA and acetic acid single extractions

| | <i>Domestic sludges (µg/g)</i> | | | <i>Industrial sludges (µg/g)</i> | | |
|-------------------------------|--------------------------------|-------------------|-----------------|----------------------------------|-------------------|-------------------|
| | <i>Sample DS1</i> | <i>Sample DS2</i> | <i>SRM 2781</i> | <i>Sample IS1</i> | <i>Sample IS2</i> | <i>Sample IS3</i> |
| <i>EDTA extraction</i> | | | | | | |
| Cu | 50.78 ± 0.73 | 25.61 ± 1.00 | 202.7 ± 0.14 | 2.37 ± 0.06 | 2.58 ± 0.10 | 975.3 ± 41.9 |
| Cr | nd | nd | nd | 2.67 ± 0.14 | 1.65 ± 0.11 | nd |
| Ni | 6.19 ± 0.23 | 13.06 ± 0.5 | 28.57 ± 0.32 | 2.72 ± 0.08 | 2.22 ± 0.15 | 315.6 ± 14.9 |
| Pb | 47.62 ± 1.04 | 14.98 ± 0.81 | 63.35 ± 0.25 | 4.28 ± 0.02 | 3.17 ± 0.19 | 52.99 ± 1.20 |
| Zn | 374.3 ± 11.9 | 223.0 ± 3.9 | 607.7 ± 2.13 | 9.46 ± 0.81 | 5.12 ± 0.10 | 3875.4 ± 18.7 |
| Fe | 637.6 ± 24.7 | 15973.9 ± 400.3 | 4164.4 ± 102.5 | 38.66 ± 2.01 | 20.78 ± 1.42 | 133.4 ± 0.92 |
| <i>Acetic acid extraction</i> | | | | | | |
| Cu | 22.54 ± 0.56 | 6.54 ± 0.43 | 44.77 ± 0.28 | 8.66 ± 0.33 | 8.36 ± 0.29 | 1098.7 ± 73.3 |
| Cr | nd | nd | nd | 588.7 ± 17.2 | 414.4 ± 2.4 | 5473.2 ± 92.5 |
| Ni | 6.23 ± 0.37 | 16.66 ± 0.95 | 35.87 ± 0.74 | 21.77 ± 0.69 | 15.98 ± 0.03 | 3540.9 ± 64.0 |
| Pb | 4.91 ± 0.03 | nd | nd | 5.81 ± 0.01 | 5.85 ± 0.01 | 10.51 ± 0.63 |
| Zn | 858.8 ± 7.9 | 424.5 ± 7.9 | 290.7 ± 12.4 | 39.65 ± 0.69 | 26.15 ± 0.89 | 12386.1 ± 289.7 |
| Fe | 362.6 ± 8.1 | 5467.5 ± 355.6 | 561.8 ± 25.6 | 689.3 ± 19.7 | 654.8 ± 19.7 | 3596.2 ± 107.6 |

nd = not detected by FAAS.

matter-bounded [28,38], in the industrial sludges the metals are basically associated to the oxide and/or hydroxide components of the sample whose solubility highly depends on the pH of the leaching test [37,39].

When the acetic acid was employed, the extraction efficiency of metals in domestic sludges was practically insignificant for most of the elements studied, except for Ni and Zn, whose extraction efficiency varied between 25.6 and 45.5% and between 22.8 and 66.7%, respectively, depending on the sample. The rest of the elements were little or nothing leached in these samples, since the percentages of extraction were always lower than 11%, except for Fe in the Sample DS2 (value around 17%). In the industrial sludges, a considerable extraction efficiency was achieved for most of the elements studied, except for Pb in all samples (percentages lower than 13%) and for Fe in the Sample IS3. The percentages of relative extraction for Cu, Cr, Ni, Zn and Fe ranged from 35.2 to 60.1%, in the Samples IS1 and IS2; in the Sample IS3 a lower extraction efficiency was found for all the elements, except for Zn; this effect was even more notorious in the case of Fe and Cr, with percentages of extraction always lower than 14% in both cases.

In the extractions carried out with EDTA little or no metals were leached from the industrial sludges. The more significant extractions correspond to Cu and Zn with percentages around 14%, except for Cu in Sample IS3, where a higher value was found (23.2%). For the rest of the elements, the extraction efficiency was lower than 8.3% in all samples. In domestic sludges, all the elements, except Cr, were extracted when the EDTA was used; the most elevated percentages of extraction were found for Cu, Ni, Pb and Zn (values between 24.1 and 47.7%) in all samples, except for the case of Cu in Sample DS2 (around 16%). Fe was also poorly leached in these samples with values always lower than 18.4%. The between-batch precision (expressed as RSD) of the EDTA extraction procedure was lower than 5.4 and 6.8%, for all the elements studied, in the domestic and industrial sludges, respectively. In the case of the acetic acid extractions, the RSD obtained were always lower than 6.6% for all the elements, in both types of samples.

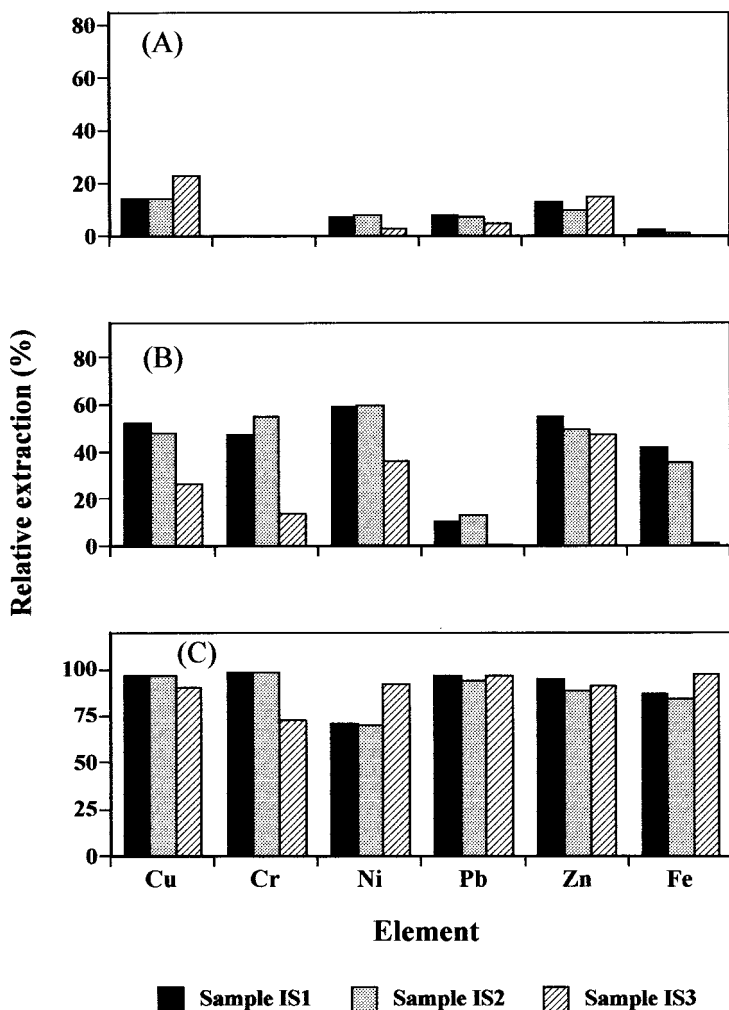


FIGURE 2 Percentages of relative extraction corresponding to the EDTA (A), acetic acid (B) and pseudototal digestion (C) respect to the total metal contents in industrial sludges.

According to the above, the results of the EDTA and acetic acid leaching tests from domestic and industrial sludges provide a relevant information about the potential mobility and availability of heavy metals to the environment. The results reported in this work allow us to conclude that the available amount of metals in these type of wastes is highly depending on the effective composition of the sludge. Therefore, it means that an experimental evaluation of easily available leaching metals in authentic wastes seems to be necessary in order to establish the best management options and assess the environmental impact of pollutants to surface and groundwater. On the other hand, the total and pseudototal metal contents obtained in the analyzed sludges indicate us that all of them, except the industrial Samples IS3 and IS1 (case of Cr), could be employed for agricultural uses by according to the Spanish [9] and Portuguese [10] regulations.

CONCLUSIONS

According to the results reported in this work, the application of EDTA and acetic acid single extractions provides a valuable information about the possible mobility and availability of heavy metals from domestic and industrial sludges under different environmental conditions.

The interest of this application is particularly useful in the determination of the leaching behaviour of pollutants from different nature sludges, in order to evaluate their environmental impact, and consequently select the best options of disposal or even the technic-economical possibilities of reuse within regulatory limits.

In the industrial sludge samples analyzed in this work, most of the present elements have a bigger potential mobility in acidic medium, with the exception of Ni and Zn, which are also considerably released from domestic sludges. It is important to emphasize that Pb is the lowest mobilizable metal in both sludges when the acidic treatment was employed. In contrast, in presence of complexing ligands in domestic sludges, the mobility of metals was more elevated and very little metal contents were released in the industrial sludges under these conditions.

On the other hand, the use of the pseudototal digestion provides, for most of the elements, comparable results to the total digestion in all samples studied, except for the case of Cr in domestic sludges and in the Sample IS3, and also for Ni in industrial sludges IS1 and IS2. It means that the pseudototal digestion could be employed as a screening method to approximately evaluate the total metal contents in sludge wastes. Moreover, it could also be defined as a fast strong acid extraction procedure with a more reduced consumption of reagents. Finally, satisfactory results were found for all the elements studied when both total and pseudototal digestions were validated by means of their application to a reference domestic sludge material (SRM 2781).

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