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The applications of inorganic and organic acids for the treatment of heavy polluted sewage sludge and the evaluation of the remaining metal with sequential chemical extraction

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ABSTRACT

Sludge is classified as difficult solid waste that requires special arrangements for disposal because of its noxious properties. The acid extraction method is characterized by fast removal of metals. Following this, this paper examined how the concentration and the contact time of the acids affect the removal of metals from the sludge. The sludge was further treated with HNO_3, HCl and CH_3COOH in different concentrations and different contact times. 5%, 10% 15%, 20% and 30% v/v of HNO_3, HCl and CH_3COOH for 10, 20 and 30 min of contact time were applied. The final result indicates that a sufficient metal amount, about 60%, is removed by the application of HNO_3 (using 20% v/v HNO_3), 50% is removed by the application of HCl (using 20 v/v HCl) and 30% is removed by the application of CH_3COOH (using 20% v/v CH_3COOH). Also, this paper presents the result of the sequential chemical extraction procedure (SCEP) which was applied in order to observe the partitioning of Cd, Cu, Cr, Fe, Ni, Pb and Zn. SCEP was applied as well in the treated samples in order to observe where the remaining metals load. The final results indicated that the remaining metal is further stabilized.

*Keywords***:** Sewage sludge; Organic acid; Inorganic acid; Acid extraction; Metals speciation; Sludge management

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1. Introduction

Environmental problems associated with sewage sludge disposal have prompted strict legislative actions over the past years. At the same time, the upgrading and expansion of wastewater treatment plants have greatly increased the volume of sludge generated. The sludge is classified as difficult solid waste that requires special arrangements for disposal because of its noxious properties. Land application of sludge may be the least energy consuming and the most cost-effective means of sludge disposal or utilization. However, much of the sludge originating from urban wastewater treatment is contaminated with heavy metals [1–6]. Theses metals may be leached from the sludge and enter the ecosystem, the food chain and finally the human population. Also the determination of total concentration of heavy metals cannot provide useful information about the risk of bioavailability, toxicity and the capacity for remobilization of heavy metals in the environment [7–9]. Zinc, copper, nickel, lead and chromium are the principal elements limiting sludge recycling to agricultural land. Their potential

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accumulation in human tissues and bio-magnification through the food-chain cause both human health and environmental concerns. These considerations are usually based on total heavy metal content in sludge. However, it is now widely accepted that the determination of total elements does not give an accurate estimation of the potential environmental impact. This is the case because it is becoming more and more apparent that both bioavailability and toxicity are critically dependent on the chemical form of heavy metals [10].

The most common treatment methods of sludge are landfill, composting, incineration, agricultural use. All these methods have some potential environmental impacts. Landfill may cause emissions of CH_4, CO_2, odors and also produces leaching of salts, heavy metals and persistent organics to groundwater. Also landfill and the uncontrolled use of sludge in agriculture leads accumulation of the hazardous substances in soil and toxic substances in food chain. Incineration is a very promising treatment method due to the fact that the volume of raw material is limited, however it presents environmental impact if the incineration is not controlled like emission of SO_2, NO_x, CO_x, dioxins, heavy metals, etc. The final disposal of sewage sludge on landfills, or on soils as a nutrient for agriculture increases heavy metal contamination in groundwater and in soils, respectively [2,11]. Heavy metals entering a wastewater treatment system may originate from a large variety of industries, from street runoff, from infiltration through leaking systems and from residential populations. Consequently, application of sludge to lands may involve the risk of environmental pollution because of heavy metals contained in the sludge [12]. In the future, reuse of sewage sludge will increase with expansion of sewerage works and advanced sewage treatments [12]. Several physical, biological and chemical reagent metal removing systems have been tested. Among them acid extraction may be the most extensively studied method, [2,12–14].

Unlike organic pollutants, heavy metals are persistent environmental contaminants that cannot be destroyed [15]. Thus, removing heavy metals from sludge before composting is a necessity for achieving more sustainable sludge treatment. Currently, there are a few clean-up techniques for removing heavy metals from sludge, including chemical extraction [16], thermal treatment [17], bioleaching treatment [18], cementation and ion exchange [19]. Chemical extraction of heavy metals has received extensive attention due to its simple operation, short extraction time and high removal efficiency. Extraction efficiency of heavy metals depends on pH, temperature, contact time, and type of extracting agent. Previous studies showed that low pH, high temperature, and long contact time can improve heavy metal extraction [20]. Various inorganic acids (HNO_3, HCl and H_2SO_4) [21], organic acids (oxalic and citric acid) [20], and strong complex agents (NTA and EDTA) [22] have been proposed as effective extracting agents. Nevertheless, high extraction efficiency requires a large number of dosages, which results in high processing costs and difficulty in pH adjustment of the sludge compost. Thus, it is necessary to reduce the dosages of extracting agents. Previous studies have shown that ultrasound, as an assisted extraction method, can efficiently release heavy metals from sludge and shorten extraction time [23,24]. Thus, ultrasound may be regarded as an efficient tool to enhance extraction efficiency of heavy metals together with the use of extracting agents.

In this study dewatered anaerobically stabilized primary sewage sludge was collected from the wastewater treatment plant in Psittalia in the Greater Athens area and was studied in order to determine the removal of heavy metals due to the acid treatment in different concentrations and contact times, as well as the metal species before and after acid treatment using inorganic and organic acids.

2. Materials and methods

At Psittalia approximately 850,000 $m^3 d^{-1}$ of mainly municipal wastewater along with industrial wastes are subjected to primary treatment, producing approximately 300 $t d^{-1}$ of anaerobically stabilized primary sewage sludge (ASPSS). This has been collected from the Psittalia wastewater treatment plant. A portion of the samples was dried at 105°C, homogenized and stored at 22°C in plastic bags of 25 kg in dark place.

For the characterisation of the sludge, an aliquot was analysed for moisture content, pH value, conductivity, total Kjeldahl nitrogen (TKN), total phosphorus ($P\text{-}PO_4$), organic matter (OM), total organic carbon (TOC) content and heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) concentrations.

The determinations of moisture content, pH and conductivity value, OM and TOC, TKN, were performed according to the Soil Analysis Standard Methods [26]. The total phosphorus was determined by a digestion technique and a turbid metric method. For the total metal concentration, a known quantity (1 g) of sample was digested with 10 ml of concentrated HNO_3 according to Zorpas [27]. After the completion of the digestion the samples were vacuum filtered and the filtrate was used for the determination of heavy metal concentration by flame atomic absorption spectroscopy using a Perkin Elmer 2380 spectrophotometer.

In order to study the metal species in the sludge samples, a sequential chemical extraction procedure was used for the partitioning of these metals into five fractions (exchangeable, carbonates, reducible, organic and residual fraction) as described by Tessier and modified by Zorpas [27–30]. According to this scheme, heavy metals are associated with five fractions: exchangeable (extracted by 1 M CH_3COONa), bound to carbonates (extracted by 1 M CH_3COONa), bound to iron and manganese oxides (extracted by 0.04 M $NH_2OH.HCl$ in 25% v/v CH_3COOH), bound to organic matter (extracted by 0.02 M HNO_3 and 30% w/v H_2O_2) and residual (extracted by 40% w/v HF, c. HNO_3 and 0.2 M NH_4NO_3).

In order to examine the removal of heavy metals from the primary sewage sludge, HNO_3, HCl and CH_3COOH acids were used in different concentrations and contact times, specifically, 5%, 10%, 15%, 20% and 30% v/v for 10, 20 and 30 min contact time. The samples were treated at room temperature and the ratio between sludge and acid was 1:2. The samples were vacuum filtered and the filtrates were used for the metal determination by flame atomic absorption spectroscopy using a Perkin-Elmer 2380 spectrophotometer. It is important to know that all the experiments were carried out in ambient temperature.

3. Results and discussion

The water content, pH, conductivity, total phosphorus, organic mater and total organic carbon and total Kjeldahl nitrogen are given in Table 1. The water content was almost 70%. The pH values of the dry sludge sample were about 7. The total phosphorus and the TOC content were found in high levels due to the fact that the main loads of the treated wastes were municipal.

The concentrations of heavy metals are shown in Table 2.

Table 3 shows the concentrations of heavy metals after the nitric acid treatment. As it is observed in Table 3, by increasing the concentration of nitric acid and the contact time the leachability of heavy metals is increased. It was also observed that Cd, Cr and Zn are removed in high concentrations (almost 70%) in respect to the contact time in 10%, 15% and 20% of nitric acid.

Table 1
Characteristics of an-aerobically stabilized primary sewage sludge

Parameters	Mean values of 20 samples	
Moisture, %	69.50	+/– 1.70
pH	7.05	+/– 0.03
Conductivity, mS/cm	1.002	+/– 0.005
Total phosphorous (P-PO_4), mg g^{-1}	12.35	+/– 0.03
Organic matter, %	44.50	+/– 1.50
Total organic carbon, %	25.20	+/– 1.20
Total Kjeldahl nitrogen, %	1.85	+/– 0.05

All values in dry matter except moisture, significantly different at $p < 0.05$

Table 2
Metals concentration in primary sewage sludge

Metals (mg g^{-1})	Mean values of 20 samples	
Cd	0.002	± 0.0001
Co	0.563	± 0.003
Cr	0.552	± 0.004
Cu	0.258	± 0.002
Fe	5.089	± 0.020
Mn	0.150	± 0.002
Ni	0.041	± 0.001
Pb	0.326	± 0.005
Zn	1.739	± 0.010

All values in dry matter

Table 3
Metal removal from P.S.S in % (dry samples) in different concentration of nitric acid and contact time and in respect to the total amount of each metal

%v/v HNO_3	Contact time (min)	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
5	10	18.3	29.0	22.7	30.2	29.8	25.7	29.7	15.6	40.0
	20	23.3	33.5	32.7	35.5	34.8	32.6	39.1	28.9	40.4
	30	26.7	39.7	50.9	40.7	37.3	40.0	40.3	29.5	50.2
10	10	20.0	29.2	34.0	30.2	32.1	32.5	34.1	28.2	46.4
	20	35.0	38.8	51.4	38.9	41.2	42.8	41.7	38.0	53.9
	30	51.7	44.6	71.4	45.9	49.4	50.1	43.6	36.7	63.4
15	10	51.7	30.2	50.9	33.1	37.9	37.8	37.1	36.5	49.0
	20	60.1	42.5	60.9	40.1	42.4	43.0	45.1	41.8	60.6
	30	68.3	53.8	69.5	55.8	49.9	48.1	50.9	39.8	71.1
20	10	56.7	39.0	66.8	38.4	44.1	42.8	40.3	29.2	53.2
	20	58.3	55.1	73.6	54.1	45.7	46.7	48.9	33.2	65.8
	30	68.3	63.7	74.1	64.5	59.5	60.1	57.7	40.0	71.9
30	10	57.5	64.0	66.8	4.01	45.3	44.1	42.3	35.1	53.5
	20	59.4	59.2	75.2	55.3	45.8	48.3	49.0	34.3	69.2
	30	68.5	64.1	75.3	65.0	60.9	63.0	58.9	45.1	74.1

Significantly different at $p < 0.05$

Table 4 indicates that the application of HCl in 20% v/v (30 min of contact time) has the ability to remove more than 50% of heavy metals except Pb which is removed in 40%. Specifically, 20% v/v of hydrochloric acid (and for 30 min contact time) has the ability to remove 68% of Cd, 65% of Zn, 63% of Cr, 62% of Cu, 55% of Ni, 53% of Co, and almost 50% of Fe and Mn.

Comparing the application of CH_3COOH (Table 5) with the HCl and HNO_3, it can be said that acetic acid gave unsatisfactory results. It is obvious that only Cr and Cu were removed more than 30% (33 and 35% respectively). The removal of heavy metals by using acetic acid in reduction series is the following: Cu > Cr > Mn = Fe > Zn > Pb > Ni > Cd.

Table 4
Metal removal from P.S.S in % (dry samples) in different concentration of hydrochloric acid and contact time and in respect to the total amount of each metal

%v/v HCl	Contact time (min)	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
5	10	15.2	10.3	15.1	12.6	15.0	14.2	14.3	19.5	22.4
	20	21.3	24.5	23.2	35.4	25.6	20.4	21.0	16.3	25.3
	30	23.7	33.5	30.2	40.2	28.3	22.3	30.9	14.6	36.0
10	10	18.3	29.0	28.0	14.3	29.8	25.7	29.7	45.6	28.0
	20	23.3	33.5	35.7	53.6	34.8	32.6	39.1	60.9	30.4
	30	26.7	39.7	38.9	55.1	37.3	40.0	40.3	55.5	40.2
15	10	20.0	29.2	35.6	15.7	32.1	32.5	34.0	28.2	46.4
	20	35.0	38.8	50.1	60.2	41.2	42.8	41.7	42.0	53.9
	30	51.7	44.6	53.1	61.0	49.4	50.0	43.6	36.7	63.4
20	10	51.7	30.2	40.1	20.9	37.9	37.8	40.1	36.5	49.0
	20	60.0	42.5	60.2	61.7	42.4	43.0	51.1	45.8	58.6
	30	68.3	53.8	63.1	62.4	49.9	48.1	55.9	39.8	65.1
30	10	52.3	35.1	41.1	25.9	40.1	39.1	55.2	50.6	57.4
	20	60.3	44.3	68.0	68.3	51.1	50.3	62.2	49.3	63.2
	30	69.3	55.9	68.3	70.0	55.9	55.0	64.3	45.3	67.5

Significantly different at $p < 0.05$

Table 5
Metal removal from P.S.S in % (dry samples) in different concentration of acetic acid and contact time and in respect to the total amount of each metal

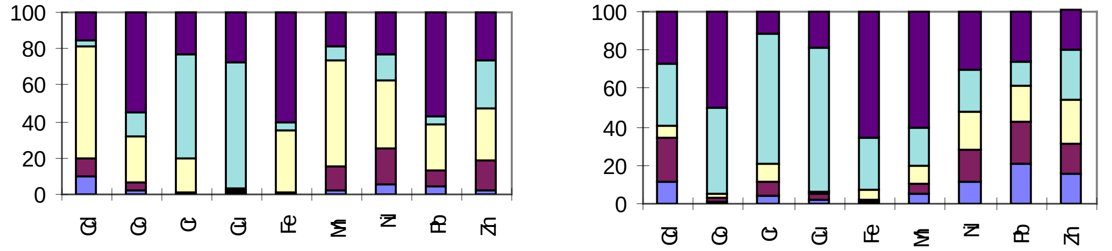
%v/v CH_3COOH	Contact time (min)	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
5	10	0.5	0.6	0.2	0.6	0.6	0.7	0.5	1.2	9.0
	20	1.1	2.5	1.2	1.3	2.1	1.5	1.1	3.6	9.6
	30	1.9	5.5	5.2	4.5	2.5	3.3	1.9	4.1	10.3
10	10	1.2	4.1	2.5	3.2	2.4	4.1	1.2	6.3	10.5
	20	2.3	7.2	8.5	5.1	4.1	7.2	2.3	7.5	13.3
	30	3.7	10.9	10.2	11.3	9.5	9.3	3.7	7.9	16.1
15	10	2.1	13.9	18.1	20.9	15.0	10.1	5.1	7.2	11.0
	20	4.2	18.6	22.3	24.6	22.1	15.4	9.9	11.2	15.8
	30	5.5	20.8	25.1	26.8	26.8	18.8	12.3	13.0	17.0
20	10	2.3	14.0	19.3	20.0	15.3	14.0	12.1	12.5	11.5
	20	5.4	26.4	25.4	26.4	25.3	26.4	15.0	14.2	19.3
	30	6.1	28.1	29.3	32.1	29.1	29.1	17.1	16.9	21.1
30	10	2.5	24.1	22.7	24.1	22.1	23.0	15.1	16.1	15.6
	20	5.8	24.5	28.4	28.5	28.5	26.5	16.8	17.3	26.9
	30	7.2	25.6	33.1	35.6	29.6	29.6	16.9	21.8	28.7

Significantly different at $p < 0.05$

Especially those metals seem to be removed in high concentration in 10% v/v of HNO_3 for Cd and Cr and in 10–15% v/v of HNO_3 for Zn. However, for most metals the satisfactory removal concentrations were after 20 min and for 20% v/v of HNO_3. Acid treatment for a long time does not affect the increase of the metal leachability, while at the same time we can have a contrast result. That phenomenon can be explained by the increase of pH during the contact time and maybe the metal re-precipitation. The maximum metal concentration removal in respect to the concentration of the nitric acid and contact time are as follows: Cd, Ni, Pb for 15% v/v of HNO_3, Cd, Co, Cr, Cu, Mn, Fe, Zn for 20% v/v of HNO_3 Similar results have been found with the use of hydrochloric acid 30% v/v and contact time 30 min [31]. Also, according to some studies carried out before, the use of sulphuric acid (1 N H_2SO_4 for 1 h contact time) seems to remove Cd, Cr, Fe, Ni and Zn in 75 % while Cu and Pb is about 30% [31]. Also, the use of the ethylene diamine tetra acetic acid (EDTA), gave a slightly higher removal [32]. Jenkins et al. [32] identified that using inorganic acids (1 N H_2SO_4) the most difficult metal to solubilise for any of the sludges was Cu (only about 1% removed) followed by Cd and Pb. This suggested that part or all of the Cu in the sludges exist as an organic complex and that the organic metal bond strength is greater than Cd and Pb (1). In general, Jenkins and Scheybeler [32] found out that for a contact time of 24 h, the maximum removal efficiencies for Cd, Cr, Fe, Ni and Zn were found to be about 70% and for Pb was only 13%. Lo and Chen [16] using sulphuric acid (H_2SO_4) at 4 h contact time (for the removal of metals from urban and industrial sludges in Taiwan), found that Cd and Zn were the most readily solubilised metals with removal >95%. Veeken and Hamelers [33] using both organic and inorganic acids found that both citric and oxalic acids had increased heavy metals extraction (70% and 60% respectively, for Cu; 90% and 70%, respectively, for Zn) while with the application of HNO_3 38% and 65%, respectively for Cu and Zn were the removal. Marchioretto et al. [34] by using HNO_3 HCl for the removal of metals found that the maximum metal removal efficiency was 80% of Cr, 80% of Cu, 100% of Pb, 60% of Ni, and 80% of Zn.

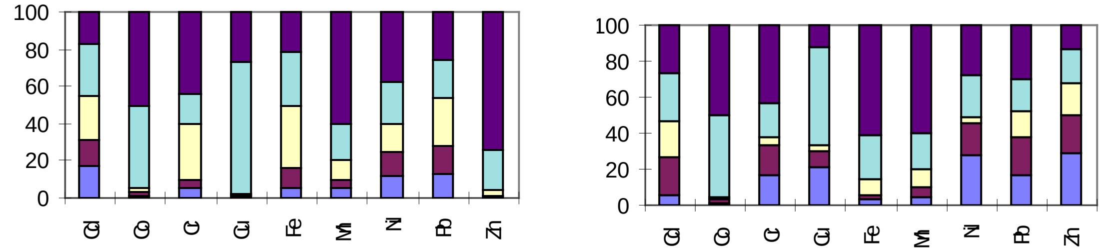
Heavy metal extraction with inorganic and organic acids using inorganic acids, Jenkins and Scheybeler [32] assessed the removal of metals from sludges obtained from a central wastewater treatment plant in California, USA. The types of sludge used in the experiment were primary sludge (PS) containing 2.92% solids; digested primary sludge (DPS) containing 4.66% solids; waste activated sludge (WAS) containing 0.68% solids; and digested waste activated sludges (DWAS) containing 1.54% solids. The sludges were dosed with sulfuric acid (1 N H_2SO_4) to effect metal solubilization. The results indicated that the most difficult metal to extract for any of the sludges was Cu (only about 1% removal), followed by Cd and Pb. This suggested that part or all of the Cu in the sludges exists as an organic complex and that the organic-metal bond strength is greater than Cd and Pb [34]. In general, the experiment showed that if the pH is decreased to about 2 for contact time of 24 h, the maximum removal efficiencies for Cd, Cr, Fe, Ni and Zn were found to be about 70% or greater. Removal efficiency for Pb was less at only 13%. Preliminary estimates indicated that about 0.5 metric ton of acid would be required for each dry metric ton of sludge solids for metal removal of more than 50% of Cd. Based on US $52.27/metric ton H_2SO_4, the total cost for acid treatment of PS and DPS at maximum metal removals was determined to be US $25.88 and US $37.08/dry metric ton, respectively. Using hydrochloric acid (HCl) as an extracting agent to remove metals from a waste activated sludge sample obtained from a treatment plant in Wisconsin, USA, Wozniak and Huang [1] determined the variables affecting the metal removal efficiency. They observed variations in metal removal with pH, sludge solids concentration, individual metals, and time of extraction. They found that solubilization increased with increasing time, up to approximately 12 h, and with lower values of pH and sludge solids. The rate of metal extraction was also found to be related to the possible metal species present. Up to 15% of nickel and chromium extracted was solubilized almost immediately after acid addition, indicating dissolution of inorganic precipitates. The initial removals of other metals such as Cd, Cu, Pb and Zn, which were less than 10%, indicated the presence of these metals in organometallic complexes. At approximately pH 2, as much as 100% Zn removal was attained. The removal efficiencies for other metals were 92.5% for Cd, 88% for Ni, 73% for Cu, 65% for Pb and only 24% for Cr. Logan and Feltz [35] also used HCl to observe the effect of aeration, cadmium concentration and solids contention acid extraction especially of Cd from an anaerobically digested sludge obtained from a municipal wastewater treatment plant in Ohio, USA. The average solid content of the sludges used was 3.3%. They found that extended aeration for at least 14 d was necessary for the oxidation of organic and inorganic forms of Cd prior to acid extraction, and that aeration during acid extraction was sufficient to maintain the metal in the extractable form. At pH 2 and leaching time of 18 h, an average of 76% of Cd was removed. Other metals removed were Zn (77%), Mn (75%), Ni (70%), and Cu (26%). Not much removal was attained for Fe (15%), Pb (4%), Cr (2%), and Al (1%). Lo and Chen [16] explored the removal efficiencies of heavy metals from urban and industrial sludges in Taiwan using sulfuric acid (H_2SO_4) at 4 h contact time and twice the stoichiometric dose (one stoichiometric dose equals one equivalent acid per one equivalent of metals). The thickened aerobic digested sludge was taken from a municipal treatment plant in Taipei City, while the anaerobic digested sludge was taken from an industrial district wastewater plant in the north of Taiwan. Results of acid extraction indicated that better removal efficiencies were obtained at pH 1.5 or 2. For the municipal sludge, Cd and Zn were the most readily solubilized metals with removal >95%. For the industrial sludge, the removal percentages of Cd, Cr and Ni were >97%. The remaining amount of most metals in the decontaminated sludge was within the US EPA 1993 standards for sludges used in agriculture. Using both organic and inorganic acids, Veeken and Hamelers [33] conducted an acid leaching study on the removal of heavy metals from anaerobically digested sewage sludge with 20% dry matter (DM) collected from a municipal sewage treatment plant in the Netherlands. The metal extraction was performed at a pH range of 2–6 for 0.1 M oxalic acid; 0.1 M citric acid; and nitric acid (HNO_3) at room temperature. Only two heavy metals (Cu and Zn) and competing metals (Ca and Fe) were measured during extraction. The results revealed that both citric and oxalic acid had increased heavy metal extraction (70% and 60%, respectively, for Cu; 90% and 70%, respectively, for Zn) at a mildly acidic pH of 3–4 as compared to HNO_3 (38% and 65%, respectively, for Cu and Zn) at pH of 1.5–2. The extraction efficiencies for the two metals were high enough to remove metals from sewage sludge originating from agro-industries to levels below the Dutch legal standards of 75 mg/kg DM and 300 mg/kg DM, respectively. Citric acid, being tri-carboxylic, was found to be better than oxalic acid, which is di-carboxylic, because oxalic acid is removed from solution by precipitation as calcium oxalate. Moreover, oxalic acid is a strong reducing agent that might become oxidized in an organic matter matrix. This causes the decrease of oxalate ions available for leaching, resulting to a lower extraction for the metals compared to citric acid.

The metal partitioning in the ASPSS samples as determined by sequential chemical extraction is shown in Fig. 1a. Regarding ASPSS samples, almost all of the chromium and copper were bound to the organic and residual fractions with less than 2% being removed during the ion exchangeable and carbonate fractions. A significant amount of chromium was found in the reducible frac-



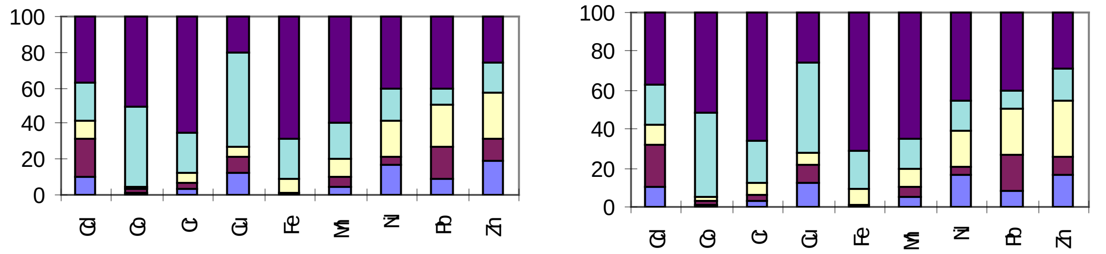
a : in ASPSS

b: in treated sample with 5% v/v HNO_3 and 30 min contact time



c: in treated sample with 10% v/v HNO_3 and 30 min contact time

d: in treated sample with 15% v/v HNO_3 and 30 min contact time



e: in treated sample with 20% v/v HNO_3 and 30 min contact time

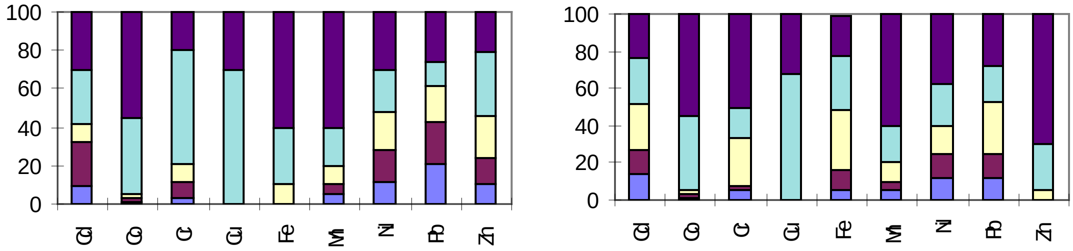
f: in treated sample with 30% v/v HNO_3 and 30 min contact time

Fig. 1. Metals partitioning in ASPSS and in the treated sample with HNO_3.

tion. In the case of cadmium and manganese, they were bound to the reducible fraction (60%). Iron, cobalt and lead were found to be bound in reducible and residual fractions (about 95% for the iron and 83% for the lead). Only nickel and zinc had substantial proportion of metal in all phases.

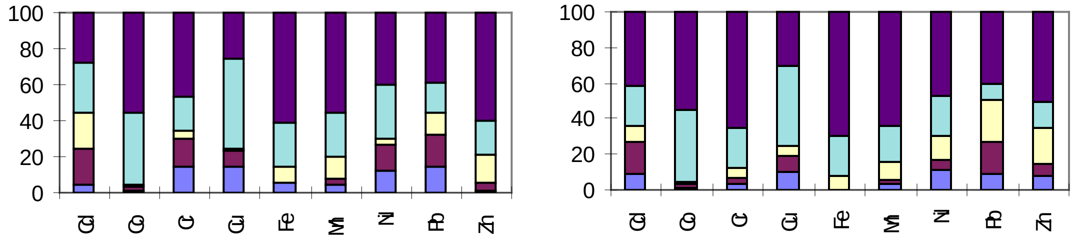
Figs. 1b–1f show the partitioning of the metals after nitric acid treatment. It is observed that the amount of metal that does not extract from the nitric acid which is bound (most of it) in residual fraction, except for the Cu and Co that is bound in organic fraction. Similar behaviours are observed in Figs. 2a–2e (samples treated with hydrochloric acid) and in Figs. 3a–3e (samples treated with acetic acid). This fact suggests that in the case of the sludge (after acid treatment) disposal in agriculture or in landfills no problem is expected as far as the extraction of metals in groundwater is concerned. Chemical specifications studies [14] show a wide variation in the forms of metals present in sewage sludge, although the following forms of metals seem to predominate: Cd, Cr, Cu, Pb and Ni in carbonate, organic and residual forms; while Mn is mostly in an organically bound form. It was also found that each individual metal had a characteristic fraction profile depending on the type of sludge. Moreover, metals in the exchangeable and organically bound fractions are likely to be comparatively mobile once disposed to land [14].

The sequential chemical extraction (SCE) methods are widely used for the chemical speciation of heavy metals in sludge. They include utilization of a series of chemical extractants in a sequence of reagents of increasing strength. For each extraction step, a particular chemical form of the metal is expected to dissolve [35]. The different forms of metals which may occur in sludges as defined by several researchers have been vague with the definition of one often overlapping that of another. Oake et al. [36] found that each individual metal had a characteristic fractionation profile independent of the type of sludge, with metals in the exchangeable, adsorbed and organically-bound fractions likely to be comparatively mobile once disposed to land. Moreover, mobilization of metals could result from dissolution of the carbonate fractions of Cd, Pb, and Ni or oxidation of the sulfide fraction of Cu. Furthermore, as organic matter decays to



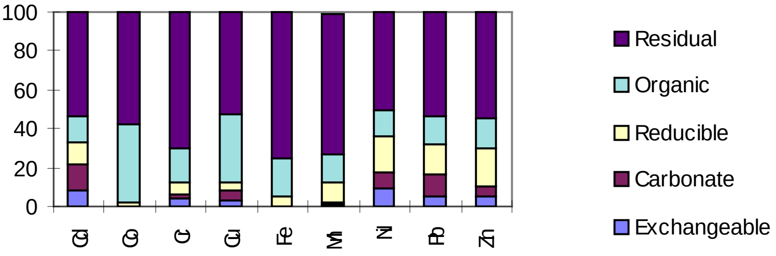
a: in treated sample with 5% v/v HCl and 30 min contact time

b: in treated sample with 10% v/v HCl and 30 min contact time



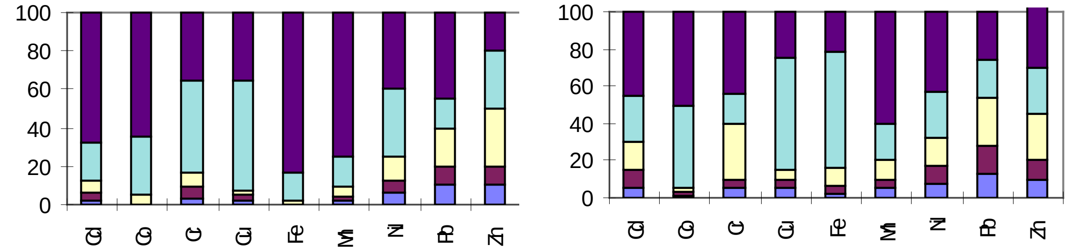
c: in treated sample with 15% v/v HCl and 30 min contact time

d: in treated sample with 20% v/v HCl and 30 min contact time



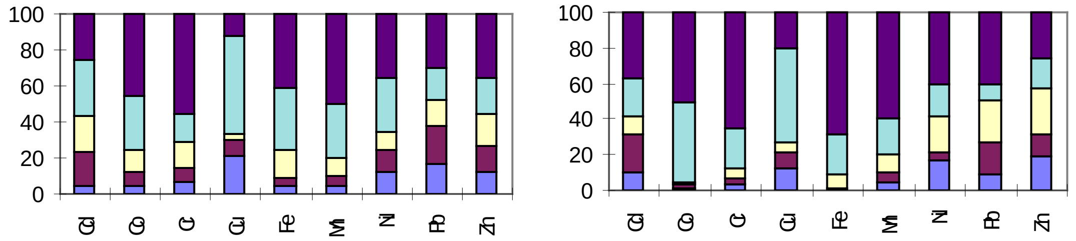
e: in treated sample with 30% v/v HCl and 30 min contact time

Fig. 2. Metals partitioning in the treated sample with HCl.



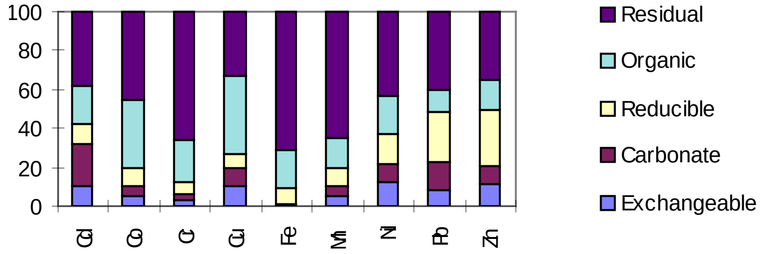
a: in treated sample with 5% v/v CH_3COOH and 30 min contact time

b: in treated sample with 10% v/v CH_3COOH and 30 min contact time



c: in treated sample with 15% v/v CH_3COOH and 30 min contact time.

d: in treated sample with 20% v/v CH_3COOH and 30 min contact time



e: in treated sample with 30% v/v CH_3COOH and 30 min contact time.

Fig. 3. Metals partitioning in the treated sample with CH_3COOH

low levels, the nature of the major inorganic constituents in sludge (Fe, Al, Ca, or P), as well as the properties of the soil receiving the sludge, will ultimately affect the mobility of heavy metals disposed to land [37]. Ali [38] found that residual, organic and carbonate fractions contained more than 95% of metals studied, whereas metals in exchangeable and adsorbed forms were negligible (less than 5%). Marchioretto et al. [34] compared the heavy metals behavior in all of the fractions among the three SCE schemes used, and found that the distribution in each fraction is almost the same for both Veeken, and Sims and Kline schemes, although it was difficult to distinguish between what is bound to organic and what is bound to inorganic matter in the Veeken scheme. On the other hand, the Tessier and Veeken schemes were different in several aspects. In general, the forms of heavy metals present in sewage sludges vary widely according to the nature of the individual metal, characteristics of the wastewater treated and the sludge treatment employed [33,39]. The disadvantages of the SCE scheme as cited by some researchers include its lack of specificity; absence of selectivity; read sorption; and dependence on many factors such as type of sample, size of particulates, pH, temperature, contact time, concentration of extractant, and solid–liquid ratio.

4. Conclusions

It is obvious that the ASPSS contains high amounts of organic constituents, due to the fact that the main loads of the treated wastes were municipal. By increasing the concentration of acid and the contact time, the leachability of heavy metals increases as well. Also the final result indicates that a sufficient metal amount, about 60% is removed by the application of HNO_3 (using 20% v/v HNO_3), 50% is removed by the application of HCl (using 20 v/v HCl) and 30% is removed by the application of CH_3COOH (using 20 % v/v CH_3COOH). By using the sequential chemical extraction procedure most of the metals were found to be bound in stable fractions. And finally after the acid treatment most of the metals are bound to the residual form as indicated by the sequential extraction. This fact suggests that in the case of the sludges (after acid treatment) disposal in agricultural or in landfills no problem is expected as far as the extraction of metals in groundwater is concerned.

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