

Effect of acid treatment on the removal of heavy metals from sewage sludge

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Abstract

In this paper, sludge samples that were collected from the municipal wastewater treatment plant in Psittalia (Athens, Greece) were subjected to acid treatment using sulphuric acid. Furthermore, a sequential extraction scheme was applied in order to determine the chemical forms of Ni, Cu, total Cr, Pb and Zn in sewage sludge. The optimum combination was achieved through a variety of tests by applying a ratio of 1:5 of sludge quantity (g) per volume of acid (mL). The concentration of the acid used was in the range of 10–20% at two different temperatures (25–80°C) and the contact times ranged from 1 to 60 min. The optimum combination was achieved when the sludge samples were in contact with H₂SO₄ (20%) for 30 min at 80°C, as these experimental conditions resulted in the highest heavy metal removal efficiency. In addition, the metal distribution in the residue was investigated and the heavy metal partitioning was found to be different after acid treatment.

Keywords: Heavy metals; Acid treatment; Sludge; Sequential extraction

1. Introduction

Wastewater treatment leads to the generation of large quantities of sludge that must be disposed off [1]. There is a great interest in spreading sludge on agricultural land due to the potential of recycling valuable components: organic matter,

N, P and other plant nutrients [2]. However, due to the physical–chemical processes involved in activated sludge wastewater treatment, heavy metals that are existent in the wastewater tend to accumulate in the generated sludge. As a result, heavy metal levels are generally higher in the sludge than in the soil, where these elements can be retained indefinitely in cultivated soil layers. Therefore, repeated applications of sludge

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gradually increase the trace element content of the soil [3,4]. In order to retain the use of agricultural land as a disposal route of sewage sludge, it is necessary to minimize the amount of heavy metals in sludge [4]. Sludge management methods include composting, thermal and acid treatment, etc. Several studies have dealt with acid treatment methods [1,4–6] for the removal and/or stabilization of heavy metal content.

Zinc, copper, nickel, lead and chromium are the principal elements limiting sludge recycling to agricultural land. Their potential 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 of 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 [3]. According to Tessier et al. [7], heavy metals are associated with the following fractions: the exchangeable fraction, which is likely to be affected by changes in water ionic composition as well as sorption–desorption processes; the carbonate fraction, that is susceptible to changes in pH; the reducible fraction, that consists of iron and manganese oxides which are unstable under anoxic conditions; the organic fraction, that can be degraded leading to a release of soluble metals under oxidizing conditions and the residual fraction, that contains mainly primary and secondary minerals, which may hold metals within their structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature.

During recent decades a great variety of extraction schemes, both simple and sequential, have been developed and, although some methods have been widely used [7,8], none has been unreservedly accepted by the scientific community.

Indeed, given the wide range of procedures employed, the results obtained are rarely comparable, since they present important variations that depend on the extraction method used [9–17]. For this reason, the Community Bureau of Reference (BCR) in 1987 began a programme to harmonise the methodology used in the sequential extraction schemes used for determining metals [2,3,18–20].

The present paper studies the removal of heavy metals by acidification in different concentrations and temperatures using sulphuric acid, since this acid had been previously found to be more effective in comparison with nitric, hydrochloric and phosphoric acid [1]. In addition, the chemical forms of the metals remaining in the residue after the treatment were investigated using the sequential extraction procedure developed by Bodog et al. [16], Hlavay et al. [15] and Rauret [20].

2. Materials and methods

2.1. Sample collection and preparation

Sludge samples were collected from the municipal wastewater treatment plant in Psittalia (Athens, Greece) and stored at 4°C. The sludge was air-dried in thin layers and continuously moved and mixed in order to avoid fungal development. The material was passed through a 2-mm sieve discarding the fraction exceeding 2 mm. The final material was stored in desiccators at room temperature until the time of analysis.

2.2. Analysis of sludge

Three replicates of each dried sample (<2 mm) were analyzed for several known chemical variables related to the intake of heavy metals by the sludge: sludge pH was measured in deionised water using 1:2 (w/v) sludge/solution ratio (30 min), water content (105°C), organic matter (O.M.) was determined by weight loss on ignition at 430°C for 24 h and by Walkley-Black Wet Combustion

Method (%C_{org}) [%OM = %C_{org}*(100/58)] [21,22], total N-NH₄ and P-PO₄ (UV-VIS) [22,23]. Metals concentrations were determined after digestion in concentrated H₂SO₄ and 33% H₂O₂ at 440°C (Digesdahl digestion apparatus of Hach). The concentrations of metal ions were measured by atomic absorption spectroscopy (AAS), using a Perkin Elmer Model 2380 spectrophotometer (Table 1).

The sludge samples were subjected to the sequential leaching procedure developed by Bodog et al. [16], Hlavay et al. [15] and Rauret [20]. Analytical reagent-grade solutions were used and a total of four fractions were obtained: Step 1. Exchangeable and bound to carbonate cations extracted with 0.11 M CH₃COOH at pH 2.8 under stirring for 16 h at room temperature. Step 2. Cations bound to Fe/Mn oxide, extracted overnight (16 h) with 40 mL of 0.5 M NH₂OH.HCl (pH 2 with conc. HNO₃) under stirring at room temperature. Step 3. Cations bound to organic matter and sulfide, treated by careful addition of 10 mL of 8.8 M H₂O₂ (pH 2–3 with HNO₃), digestion was continued by heating the tube at 85°C in a water bath for 1 h, a second 10-mL aliquot of hydrogen peroxide was added and the

tube was again covered and heated at 85°C for 1 h. Afterwards, the cover was removed and the volume was reduced as mentioned previously. About 50 mL of ammonium acetate (1 M, adjusted to pH 2 with nitric acid) was added to the cool, moist residue. Step 4. Acid soluble (total residual cations). A solution containing 7.5 mL concentrated HNO₃ and 5 mL HClO₄ was added to the residue from step 3. The digestion was accomplished in 2 h at 100°C in a water bath. After cooling, 1.5 mL concentrated HNO₃ and double distilled water was added to the mixture and the solution was filtered and made up to 50 mL.

The solutions were stored at 4°C prior to analysis. In all cases, three replicate samples were extracted and measured. With each batch of extractions, blank samples (vessel/solutions with no sludge) were carried out through the complete procedure. Before extraction, all glassware and plastic vessels were treated in a solution of 10% HNO₃ for 24 h and washed with double-distilled water.

2.3. Acid treatment of sludge

The sludge samples were acidified using sulphuric acid (H₂SO₄). The tests were performed under two different acid concentrations (10 and 20% v/v), different contact times (1, 5, 20, 30, 45, 60 min) and two different temperatures (25 and 80°C) in order to determine the optimum combination in terms of metal removal efficiency and environmental impacts. The ratio of sludge quantity (g) per volume of acid (mL) was 1:5 (4 g/20 mL).

After acidification, the samples were centrifuged at 3000 rpm for 20 min and the liquid was separated from the sludge solid. Both liquid and sludge cake were analyzed in respect to the heavy metal content. Additionally, the solid residue was subjected to sequential extraction procedure (for samples of 30-min acidification), in order to determine the removal efficiency of the acid in each fraction.

Table 1
Characteristics of sludge

Parameters	Unit	Value
Water content	%	76.5
pH		8.2
Organic matter	%F.W.	14.3–38.6
C _{org}	%D.W.	22.4
P-PO ₄	mg/kg D.W.	5113.34
N-NH ₄	mg/kg D.W.	569
Ni	mg/kg D.W.	63
Cu	mg/kg D.W.	259
Total Cr	mg/kg D.W.	550
Pb	mg/kg D.W.	300
Zn	mg/kg D.W.	1298

F.W., Fresh weight; D.W., dry weight (105°C, 12 h).

The samples were analyzed for heavy metals by atomic absorption spectrometry (Perkin Elmer model 2380 spectrophotometer).

3. Results and discussion

3.1. Characterization of sludge

The sludge characteristics are presented in Table 1. The water content of sludge was found to be 76.5%. High levels of P-PO₄, %C_{org}, and N-NH₄ were found due to the fact that sludge was produced by primary treatment of urban wastewater. The concentrations of heavy metals were found to be below the limits set by E.U. concerning the safe disposal of sludge. However, their removal is strongly recommended, since the accumulation of the metal load at a disposal site constitutes a serious threat to the environment.

The metal partitioning of sludge, as determined by the sequential chemical extraction, is shown in Table 2. It can be observed that most of the content of Cu, Cr and Pb are bound to organic matter and sulfide fraction, but Ni and Zn are bound to Exchangeable + Carbonate and organic matter and sulfide fraction, and more specifically:

Ni: Exchangeable + Carbonate ≥ Organic + sulfide > Residual > Reducible

Cu: Organic + sulfide > Exchangeable + Carbonate = Residual > Reducible

Total Cr: Organic + sulfide > Residual > Exchangeable + Carbonate ~ Reducible

Pb: Organic + sulfide > Residual > Exchangeable + Carbonate ~ Reducible

Zn: Exchangeable + Carbonate > Organic + sulfide > Reducible > Residual

The metal content for the different fractions was found to be

Exchangeable + Carbonate: Ni > Zn > Pb > Cu > total Cr

Reducible: Zn > Ni > Pb > total Cr > Cu

Organic: Cu > total Cr > Pb > Ni > Zn

Residual: Pb > Ni > total Cr > Cu > Zn

It can be observed that the exchangeable fraction represents the dominant part for both Ni and Zn. This fraction is very unstable and sensitive to the environmental conditions. On the contrary, Pb mobilizes much harder than the other metals, because Pb is found in the residual fraction in a relatively high proportion. Cu and total Cr are mainly associated with organic matter and the greatest extraction percentage is obtained in the oxidizable fraction. This fact indicates that the undesirable solubilization and the release of these trace metals in the ecosystem can be avoided under appropriate conditions.

3.2. Acid treatment of sludge

It is well known that, if acid is added to sludge, the heavy metals present in the sludge can be

Table 2
Heavy metal partitioning in the raw sludge (% percentage)

Metal fraction	Metal				
	Ni	Cu	Total Cr	Pb	Zn
Exchangeable and bound to carbonate	40.5	5.1	3.0	6.3	39.5
Bound to Fe/Mn oxide	6.3	0.4	1.4	5.1	21.4
Bound to organic matter and sulfide	39.1	89.3	85.1	61.2	36.9
Acid soluble (total residual metal)	14.1	5.2	10.5	27.4	2.2

dissolved and then exist in solution. The process is brought about by the exchange of protons (from the acid) through the solubilization of heavy metals in sludge as shown in Eq. (1).



After extraction, heavy metals are removed from the extracting solution to recover the extracting agent and prevent environmental impact associated with the discharge of extracting fluid. Removal of the solubilized heavy metals from the extracting solution can be accomplished by precipitation process followed by a separation step [28].

In our study, comparisons of the percentages of heavy metals removed using different acid concentrations and temperatures versus the contact time are shown in Fig. 1. The percentage of extraction increased as the acid concentration, temperature and the contact time increased. This can be explained by the fact that an increase of the acid concentration and contact time results in a corresponding increase of the offered energy for the breakdown of the chemical bonds of the metals in the sludge [1].

After 30 min treatment, no further removal of metals was observed. The optimum combination of contact time, acid concentration and temperature for maximum removal was considered to be 30 min, 20% v/v H₂SO₄ and 80°C, respectively. This combination led to an efficient percentage of heavy metal removal and more particularly 74% for Ni, 86% for Cu, 99% for total Cr, 11% for Pb and 72% for Zn. The extracted percentage follow the sequence total Cr > Cu > Ni > Zn > Pb.

In Table 3, for comparison reasons, the % metal removal of different studies, found in literature, are reported. It is obvious that removal efficiency of sulphuric acid depends on various parameters, such as the initial concentration of sludge, the acid concentration, the agitation time and finally the temperature. This is why the results cannot be directly compared. For example,

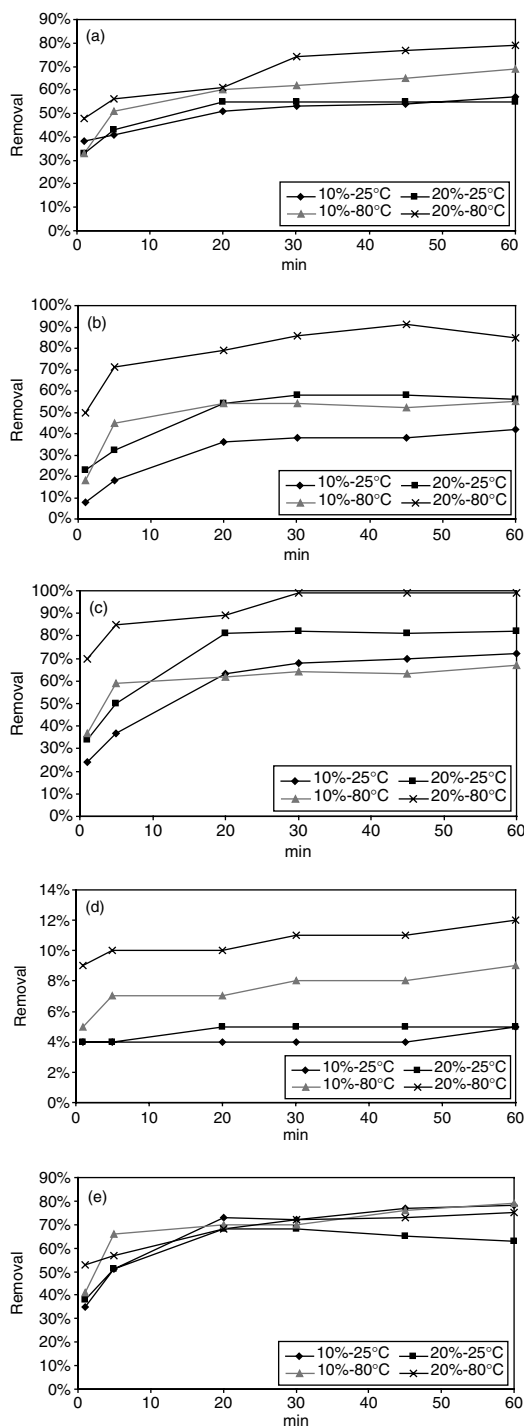


Fig. 1. % Removal of (a) Ni, (b) Cu, (c) Total Cr, (d) Pb and (e) Zn from the sludge.

Table 3
Comparison of metal removal (%) from sludge by sulphuric acid extraction

Test type	Metal removal (%)					Literature
	Ni	Cu	Total Cr	Pb	Zn	
20% H ₂ SO ₄ , T = 80°C, 1:5 S/L, 30 min	74	86	99	11	72	Present study
10% H ₂ SO ₄ , T = 80°C, 1:5 S/L, 30 min	62	54	64	8	70	Present study
20% H ₂ SO ₄ , T = 25°C, 1:5 S/L, 30 min	55	58	82	5	68	Present study
10% H ₂ SO ₄ , T = 25°C, 1:5 S/L, 30 min	53	38	68	4	72	Present study
20% H ₂ SO ₄ , T = 25°C, 1:5 S/L, 60 min	80	50	97.5	50	70	[1]
100 g/L H ₂ SO ₄ , T = 25°C, 1:5 S/L, 24 h	98	88.6	98.2	5.6	99.2	[6]
200 g/L H ₂ SO ₄ , T = 25°C, 1:5 S/L, 24 h	95.4	77.6	99.2	4.9	89.8	[6]
1 N H ₂ SO ₄ , T = 25°C, 1 h	72	20	29	37	78	[24]
1N H ₂ SO ₄ , T = 25°C, 1 h	94	98	–	–	–	[25]
H ₂ SO ₄ , T = 25°C, 48 h	–	76	–	–	–	[26]
H ₂ SO ₄ , T = 25°C, 0.5 g/250 mL, 12 h	75	57.8	20.3	27.6	82.3	[27]
H ₂ SO ₄ , T = 25°C, 0.5 g/250 mL, 12 h	69	47.1	32.4	42.9	88.9	[27]
H ₂ SO ₄ , T = 25°C, 0.5 g/250 mL, 12 h	66.7	35.7	34.8	22.5	84.4	[27]
H ₂ SO ₄ , T = 25°C, 0.5 g/250 mL, 12 h	47.7	33.7	9.8	21.5	93.6	[27]
1N H ₂ SO ₄ , T = 25°C, 24 h	74	1	76	13	72	[28]
H ₂ SO ₄ , T = 21°C, 24 h	68	41	27	22	66	[28]
H ₂ SO ₄ , 4 h	70	10	69	66	100	[28]

S/L, solid to liquid ratio.

Mingot et al. [27] reported that acid extracted amounts vary for each cation under examination and for each type of sludge. Furthermore it was reported that Cu, Ni and Pb were best extracted from those sludges which had received aerobic treatment. In another study Babel et al. [28] dosed with 1 N sulfuric acid to effect metal solubilization of sludges. The results revealed that the most difficult metal to solubilize 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 sludge exists as an organic complex and that the organic-metal bond strength is greater than Cd and Pb.

As seen in Table 3, there is a considerable scatter among the obtained results. Nevertheless, the obtained results are generally within the limits found in the other studies. The most apparent difference is the removal of Pb, which is 4–11% in our study while it can reach 66% [28]. On the

other hand the results for Ni and Zn are very close to those presented in the other studies. Furthermore, another general conclusion is that the removal of Ni and Zn is higher than that of other three metals.

3.3. Heavy metal partitioning after acid treatment

Speciation of each cation in acid extraction residues was studied in order to establish the fraction from which the cations were extracted under the conditions given and how they remained in these residues.

On the basis of Fig. 2, it can be observed that acid treatment leads to changes in the metal partitioning in the sludge content. The percentage of metal in the organic matter-sulfide fraction decreased, but an increase for exchangeable-carbonate fraction was observed for all metals

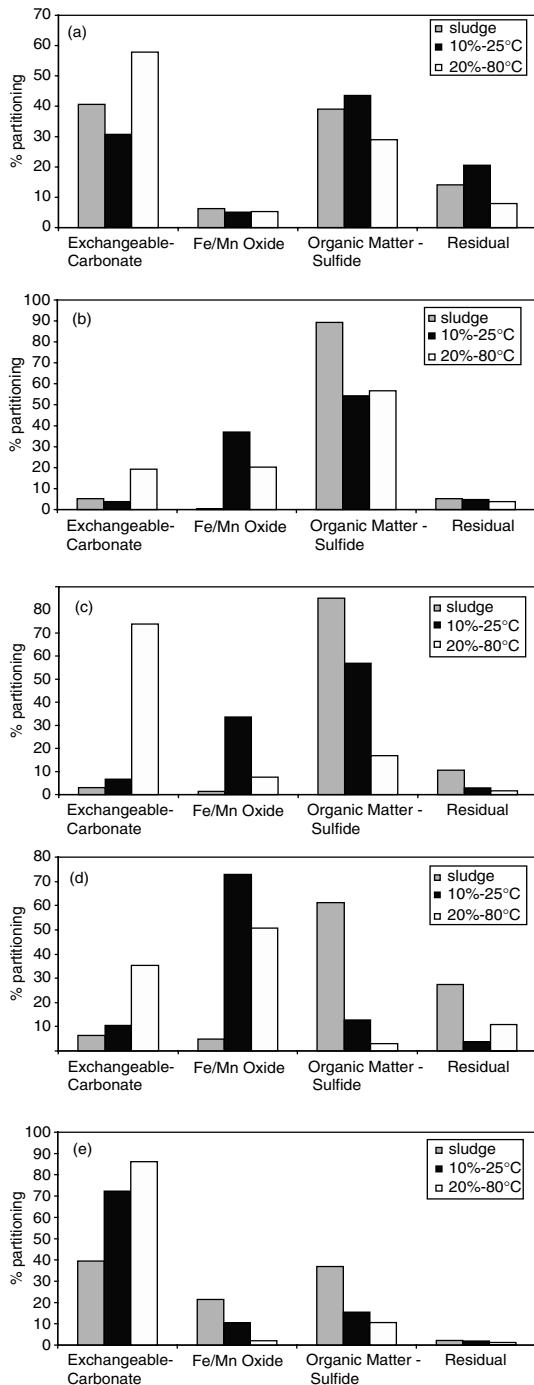


Fig. 2. Changes of (a) Ni, (b) Cu, (c) Total Cr, (d) Pb and (e) Zn partitioning in sludge, after acidification with H_2SO_4 .

and especially for 20%-80°C treatment. However, in the case of Cu, total Cr and especially Pb, an increase can be seen in the proportion of the Fe/Mn oxide fraction, possibly at the expense of the fraction that cations associated to organic matter, which are generally found in the greatest proportion. Such behaviour could be justified by the destruction of organic matter due to acid treatment giving rise to a Pb fixing, which does not occur in the initial sample due to the high stability of Pb complexes with organic matter and particularly with humic and fulvic acids [27].

It can also be seen that the residual fraction is extracted in percentages which are high in many cases. Moreover, an increase in the exchangeable-carbonate fraction can be seen. This is very important bearing in mind that the sum of the amounts present in this fraction is usually considered as the maximum amount which may be mobilized within the soil-plant system and therefore, liable to pollute the agricultural environment [27]. However, metals bound in this fraction can be easily removed by an ion exchange system (e.g. addition of zeolite [29,30]) so that the end product can be safely disposed off.

Comparing our results with previous studies we refer that, Naoum et al. [1] reported that acid treatment leads to the stabilization of sludge as most of the heavy metals were found to be in the more stable fractions. Particularly, for Cr and Cu, a slight augmentation was observed concerning the metals proportion in the exchangeable and carbonates fraction as well as an increase of the metals proportion in the residual one. In the case of Ni, there was a significant increase in the proportion in the residual fraction, and in the cases of Pb and Zn, the metals percentage in the residual phase increased, while none of the metals was found to be bound to the exchangeable phase. Mingot et al. [27] reported that sludge speciation after acid treatment shows cation mobilization initially associated with the residual fraction.

4. Conclusions

The removal of heavy metals by acidifying sludge was investigated. The optimum condition was achieved through variations of concentration, temperature and contact time. The optimum condition was achieved when the sludge samples were in contact with H₂SO₄ 20% for 30 min at 80°C, as these experimental conditions resulted in the highest heavy metal removal efficiency, and more specifically 74% for Ni, 86% for Cu, 99% for total Cr, 11% for Pb and 72% for Zn. Furthermore, by testing the metal distribution in the residue, it can be observed that acid treatment leads to changes in the sludge metal partitioning.

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