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Extraction of certain heavy metals from sewage sludge using different types of acids

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ABSTRACT: The removal of heavy metal from sludge before disposal or application to farmland is a necessary step to achieve a more safe sludge usage or disposal. Chemical extraction using inorganic acids (nitric, hydrochloric) and organic acids (citric, oxalic) were tested for extraction of chromium, copper, nickel, lead and zinc from contaminated sewage sludge at different pH and reaction time. Results revealed that solubilization of metals using inorganic acids achieved its maximum extraction efficiency (Cr-88%, Cu-82%, Ni-86%, Pb-94%, Zn-89%) at pH value lower than 2 and acid contact times of 1hour. while in case of organic acids oxalic acid does not show good results comparing to citric acid that at pH 2.43 citric acid seemed to be highly effective in extracting Cu (86%), Zn(88%), mostly after 1 day of extraction time, Cr (90%), Ni (96%) at 5 days leaching time, while Pb(85%) removal at the same pH was at a longer leaching time 10 days. At pH 3, citric acid seemed to be also highly effective in extracting Cr (66%), Cu(48%), Pb (66%), Zn(69%) at 1 day, while higher removal was also attained for Ni(68%) at only 4 h leaching time. Finally the extraction efficiencies of citric acid for Cr, Cu, Ni, Pb, Zn, are high enough to reduce the heavy metal content in sludge to levels below the legal standards.

Keywords: Acid leaching; Heavy metals; Metal precipitation; Sewage sludge.

Introduction

Sewage sludge from municipal wastewater treatment plants contains organic compounds, macronutrients, micronutrients and non-essential trace elements, organic micro pollutants, microorganisms and eggs of parasitic organisms (Alloway and Jackson, 1991). Disposal alternatives for such waste material are application to agricultural land or to land not precluding use for agriculture, land filling, incineration or composting. The high content of organic matter and substantial N and P concentrations suggest its use preferentially as a fertilizer in agriculture or as a regenerator for soil (Janez *et al*, 2000). Many wastewater treatment plants receive discharges not only from residential area but also from industry. Sludge generated at these plants contains heavy metals at relatively high concentrations, which may vary considerably with time and mostly depend on industrial activities (Baveye, *et al*., 1999).

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However the high level of heavy metals in sludge frequently prevents the reuse of sludge in agriculture. The removal of heavy metal from sludge before disposal or application to farmland therefore is a necessary step to achieve a more safe sludge usage or disposal. The application of chemical extraction as a part of the treatment is a feasible option, especially when it is applied as a pre-treatment aiming at heavy metals removal. Once they are soluble, heavy metals can be precipitated again and further be removed by a physical separation, e.g. flotation (Veeken, and Hamelers, 1999). One of the most influential parameters controlling the solubility of metals is pH. In the single extraction process of heavy metals from sludge, the inorganic acids such as nitric, hydrochloric and sulfuric and organic acids such as citric and oxalic have been widely used (Wong and Henry, 1998; Marchioretto, *et al*., 2002; Dacera and Babel, 2006).

In this work the chemical leaching process was applied to assess the mobilization of Zn, Cu, Cr, Ni, Pb in the sludge and the possibility of using chemical leaching as an applicable part of the treatment aiming at these heavy metals removal from sewage sludge. In this way, inorganic acids (Nitric, Hydrochloric), organic acids (citric and oxalic) were tested at different conditions of pH and reaction time.

Materials and Methods

Sample collection and pretreatment

All the studied sewage sludge were taken from oxidation ponds in El-Sadat City, an industrial city in Egypt, in which About 15000 m^3 of wastewater (domestic 5000 m^3 and industrial 10000 m^3) are received per day. Freshly deposited sludge was collected in polyethylene bags and brought to the laboratory, air dried and grinding with crusher to pass through a 2 mm sieve.

Sludge characterization

The sludge sample was analyzed in terms of its physical and chemical characteristics, including heavy metals content using the Standard Methods for the Examination of Water and Wastewater, 20th Edition (1999). Heavy metals were analyzed using Inductively Coupled Plasma with mass Spectroscopy (ICP-MS) Perkin-Elmer model ELAN 9000 after microwave digestion.

Chemical leaching of heavy metals

Leaching of heavy metals from sewage sludge by organic and inorganic acids was performed, four acids were attempted separately Nitric, hydrochloric, oxalic and citric. Samples of 7 g sludge were prepared with 150 ml distilled water in 500 ml Erlenmeyer flask different dosage of acids were added to sludge solution to adjust pH from 1 to 4 ±0.1 for Nitric and hydrochloric, and from 2 to 5 ±0.1 oxalic and citric (The lower pH value for citric acid achieved was 2.43, since the required dosage of citric acid to achieve pH= 2 was too high) Mixtures were stirred continuously at 125 rpm at room temperature and pH was monitored. Samples of 10 ml were collected at certain times intervals (1h, 4h, 1day, 5 day, 7 day and 10 day) and centrifuged at 4000 rpm for 30 minutes. The supernatant was filtered through 0.45 um membrane filter and analyzed for heavy metals using (ICP-MS). The experiments were accomplished in triplicate.

Heavy metals removal from the leachate

The liquid containing the solubilized metals is separated from the suspended solids fraction by a physical separation step, e.g., centrifugation. The soluble metallic ions can be ideally converted to insoluble metallic forms by chemical precipitation. The precipitate formed is subsequently removed from the liquid by a physical separation process, e.g. sedimentation, flotation, or membrane filtration.

The precipitation experiments were carried out using hydroxide precipitation with NaOH and sulfide precipitation with Na_2S. NaOH was applied in such doses to increase the original pH value of the liquid from 1 till 5, 7, 9 and11. Secondly Na_2S was applied at the same pH values used in hydroxide precipitation. After each experiment the liquid was filtered by filter paper (12-25 μm) and two samples were collected and analyzed for their heavy metals (Cr, Cu, Pb, Ni and Zn) content. All the experiments were performed in triplicate.

Result and Discussion

Physicochemical characteristics of sludge

The main physico-chemical properties of the raw sludge are presented in Table 1. The pH values ranged from 7.1 to 8.21 which indicate that the sludge is slightly alkaline. The tested samples of sewage sludge have a high percentage of organic matter and nitrogen which may be present in the ammonium, nitrate and organic forms.

Table 1: Physico-chemical properties of sewage sludge

Sample	1	2	3	4	5	6	7	8	9	10	11	12
pH	7.19	7.82	7.86	7.71	7.1	7.63	8.21	8.17	7.59	7.57	7.46	7.45
TOC g/kg	249	175	342	428	265	388	200	177	382	275	283	351
TKN g/kg	14	10.1	27.5	28.9	17.4	25.3	13.6	10.5	20.3	14.3	17.8	18.65
Ca g/kg	52.7	40.6	32.5	26.6	33.7	39.4	29	43.5	45.3	30.5	48.6	28.45
K g/kg	5.25	3.6	2.5	2.3	3.4	3.3	2.8	4.3	5.12	3.15	6.5	4.2
Mg g/kg	7.55	6.4	7.4	5.6	6.8	5.8	5.4	5.66	7.8	5.7	8.45	6.23
Na g/kg	4.24	2.2	1.45	1.8	2.4	1.7	1.8	3.6	3.2	2.11	4.6	3.71

As regarded cationic macroelments, calcium is the most abundant, followed by magnesium, potassium and sodium in all the sludge tested samples. All the parameters closely reflect those found by the bibliography of sludges of similar characteristics, some of which have been used for soil amendment (Mercedes, *et al*., 2004; Hernandez *et al*., 1991). Total metal concentrations of Zn, Cu, Cr, Ni and Pb in sewage sludge are presented in Table 2. Concentrations are expressed on a dry mass basis. Table 2 also includes comparisons with sludge legal standard established by U.S.EPA-40 (2000) and standard by EU Commission (1986).

According to Table 2, the total metal concentrations ranged from 555 to 1026 mg/kg for Zn, 256-802 mg/kg for Cu, 125-510 mg/kg for Cr, 170-385 mg/kg for Ni and 100-215 mg/kg for Pb. the sludge contain a high concentration of Al (3210 - 8570 mg/kg), Fe (2114 - 5650 mg/kg) and Mn (50-241 mg/kg). These data show a wide variation of the concentration ranges of heavy metals that may be due to irregular input from the industrial waste water. Also sludges are exceeding the allowed limits of the EU Commission standard, (with exception of Zn). In contrast, according to U.S.EPA-40, the sludge could be disposed to agricultural land. It is also noted that EU Commission, U.S.EPA-40 standards does not contain the legal values of all metals like (Al, Fe, Mn).

Chemical leaching of heavy metals from sewage sludge

Effect of leaching agent.
The effect of the pH on the heavy metals extraction with Nitric (HNO_3), Hydrochloric (HCl), Citric ($C_6H_8O_7$), and Oxalic ($C_2H_2O_4$) acids are shown in figure 1. As shown, there was a wide variation of removal efficiencies for all metals at different pH at the same acid contact times of 1hour.

Table 2: Total metal content (dry Mass basis) in sewage sludge samples and comparisons with sludge legal standard

Metal	Concentration ranges In Sludge samples (mg/kg DM)	U.S.EPA CRF 503.13 (mg/kg DM)	EU Commission (mg/kg DM)
Al	3 210 - 8 570	Not available	Not available
Cr	125 - 510	3000	Not available
Cu	256 - 802	1500	600
Fe	2 114 - 5 650	Not available	Not available
Mn	50 - 241	Not available	Not available
Ni	170 - 385	420	100
Pb	100 - 215	300	200
Zn	555 -1026	2800	1500

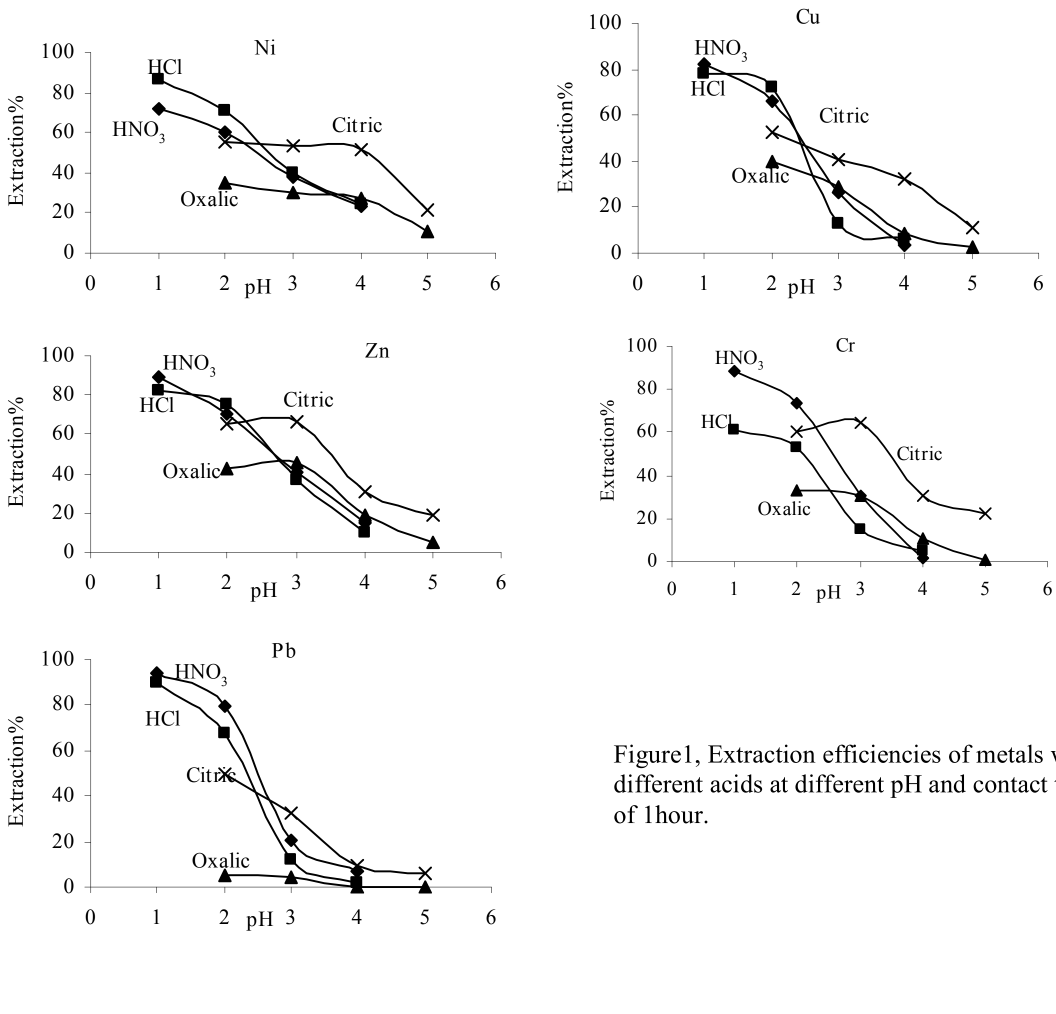

Figure1, Extraction efficiencies of metals with different acids at different pH and contact time of 1hour.

Solubilization of metals using inorganic acids (HNO_3, HCl) started at pH values around 2, achieved its maximum extraction efficiency (Cr-88%, Cu-82%, Ni-71%, Pb-94%, Zn-89%) at pH value around 1. when a complexing agent like citric acid, oxalic acid are applied, metals start solubilization at a higher pH value (3-5) than when a strong acid such as HNO_3 and HCl are applied at the same pH as shown in figure 1.

Both oxalic acid and citric acid have increased heavy metal extraction at mildly acidic pH but citric acid has better prospects because oxalic acid is removed from solution by precipitation as calcium oxalate. The calcium oxalate precipitates causes that oxalate become less available for heavy metals leading to a lower extraction for metals compared to citric acid (Veeken and Hamelers, 1999). The organic acids efficiency in metal solubilization was not so high; the maximum extraction efficiency achieved was 66% for Zn using citric acid at pH 3. This might be due to the low pH value required for the metals to solubilize and or to the short acidification time applied in these experiments.

Effect of time on leaching with citric acid.

The effect of leaching time and pH on the efficiency of citric acid in extracting heavy metals from sewage sludge are shown in Figure 2. As shown, the removal efficiencies of heavy metals are completely changed as the extraction time increased from 1 hour to 10 days.

For Cr, maximum removal (90%) achieved at pH 2 after 5 day of contact with citric acid while at pH around 3 maximum removal of Cr (66%) attained at one day of contact. For Cu, one day of extraction duration is the optimum condition that achieve higher removal efficiency at pH 2 (86%) and at pH 3 (48%). For Ni, as shown previously in figure 1 change in the pH value (2-4) has no significant effect on the extraction efficiency of nickel but as the time passing the situation is different, that at pH 2 an increase in Ni extraction efficiency starts after one day duration to achieve higher removal efficiency (96%) after 5 day of extraction as shown in figure 2. For Pb, maximum removal efficiency (85%) achieved after 10 days contact with citric acid at pH around 2, while at pH 3 maximum efficiency of lead removal (66%) attained after 1 day of extraction. For Zn, optimum extraction time is one day duration it gives maximum efficiency (88%) at pH around 2 followed by pH 3 (68%).

Removal of heavy metals from the leachate

The heavy metals concentrations were measured in both the filtered leachate (used in the heavy metals precipitation experiments) and in the original sludge, the results are compared to each other in Table 3.

Table 3: Heavy metals content of the original sludge and the leachate applied in the precipitation experiments

	Metal content in mg/l [%OS]							
	pH	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Al**	**Fe**
Original Sludge (OS)	8.32	90	275	77	121	445	1250	920
Leachate	1.1	83 [92.2]	245 [89]	65 [84.4]	108 [89.2]	365 [82]	1070 [85.6]	780 [84.8]

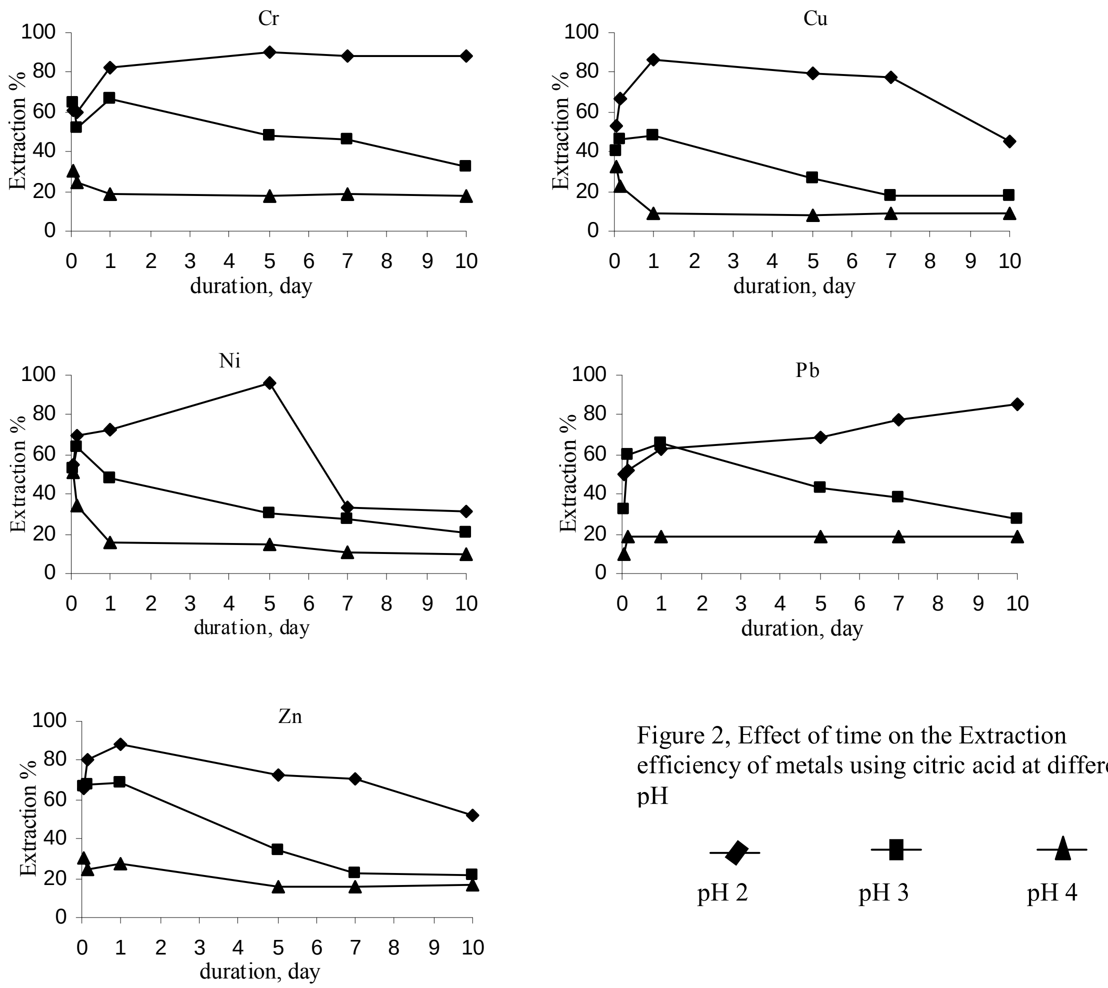

Figure 2, Effect of time on the Extraction efficiency of metals using citric acid at different pH

Hydroxide precipitation.

Figure 3 shows that when NaOH was applied, more than 95 % of Cr, Ni and Pb were already removed at pH value of 5. When the pH value was higher than 5, Zn started to be removed and at the pH value of 9 Zn achieved its best removal efficiency more than 99%. Cu removal was low, independently on the range of the investigated pH.

As exposed in Table 3 Fe and Al are abundant in the sludge and in the acidified liquid, comparing to the other metals. The removals of Cr, Pb, Ni and Zn depend on the precipitation of Fe and Al, which act as sorbents and coprecipitants (Lee, *et al*., 2002). $Cu(OH)_2$ has lower solubility than other studied metals This contradicts the extremely low removal achieved for Cu (Veeken, *et al*., 2003).

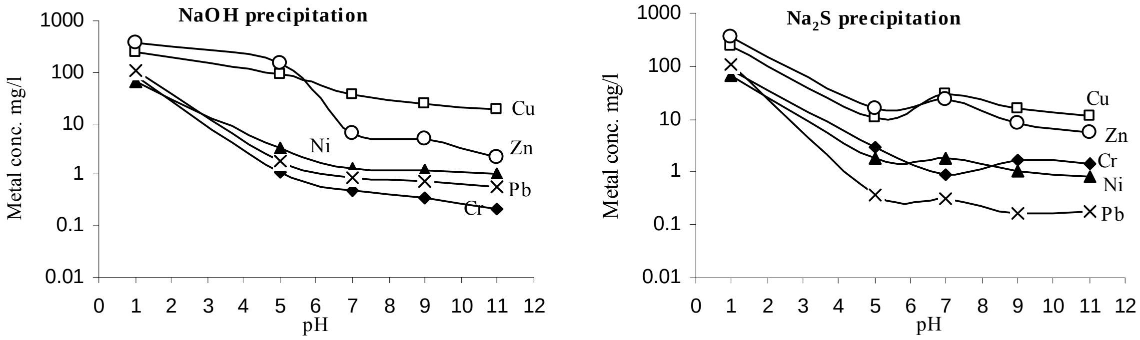

Figure 3, Heavy metals content in the remaining liquid after hydroxide and sulfide precipitation

Sulfide precipitation.

When Na_2S was applied at a pH value of 5, all metals were removed at a level higher than 92 %, (see figure 3). Lead showed the highest removal efficiency of all the metals. It suggests that, at a pH value below 5, PbS was already almost totally removed (>99%). Zinc sulfide removal was less efficient at a pH value of 7 than at a pH value of 5. Perhaps the threshold for increasing the solubility of ZnS is at this pH range.

It is observed in figure 3, Despite the relatively high range of removal of CuS it is lower than the other metal sulfides, A possible explanation is the fact that CuS has a low solubility comparing with other metal sulfides. The low solubility product favors the decrease in the particle sizes (Mersmann, 1999). Moreover, the slight decrease in CuS removal at a pH value 7, as shown in figure 3, could be due to the change in the solubility of CuS at this pH.

When Na_2S was applied, it seems that Cr was still being removed by adsorption and coprecipitation with $Fe(OH)_3$ and $Al(OH)_3$ that might be present in the liquid as long as the pH value increases. Comparing both graphs of NaOH and Na_2S in figure 3, Cr removal was better when NaOH was applied, since $Fe(OH)_3$ and $Al(OH)_3$ might be formed in larger extend than when Na_2S is used. In general, sulfide precipitation was more effective in removing all the metals together even at pH value of 5.

Conclusion

The extraction of heavy metals from the sludge before composting is a necessary step to achieve a more sustainable sludge treatment. Organic acids are attractive extracting agents because extraction can be performed at mildly acidic conditions and they are biologically degradable. Results of the acid leaching study revealed that at pH 2.43 citric acid seemed to be highly effective in extracting Cu, Zn, mostly after 1 day of extraction time, Cr, Ni at 5 days leaching time, while Pb removal at the same pH was also high but at a longer leaching time 10 days. At pH 3, citric acid seemed to be also highly effective in extracting Cr, Cu, Pb, Zn at 1 day leaching time, although a relatively higher removal was also attained for Ni at only 4 h leaching time.

Finally, it can be concluded that citric acid is a promising extractant for the removal of heavy metals from sewage sludge. The extraction efficiencies for Cr, Cu, Ni, Pb, Zn, are high enough to reduce the heavy metal content in sludge to levels below the legal standards.

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