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Removal of heavy metals from sewage sludge by low costing chemical method and recycling in agriculture

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Abstract—Experiments were carried out to study the removal of heavy metals from municipal sewage sludge by proper method for land application. The sequential extractions for metal fractionation showed that the non-digested sludge from Guangzhou contained Cu and Zn principally bound to carbonate and oxides and the metal sulfides were low. Among H_2SO_4, EDTA and NH_4HCO_3 extractant agents, H_2SO_4 was the most efficient and economic in removing the heavy metals, especially with the addition of the concentrated acid. Plant experiment in pots with Chinese cabbage (*Brassica Chinensis*) showed that the acidified sludges neutralized with alkaline amendments such as phosphate rock could increase significantly the plant yield and decreased the soil and plant contamination by heavy metals originated from sewage sludge.

Keywords: sewage sludge; heavy metal; chemical treatment; agricultural application.

1 Introduction

In 1984, about 6 million tons of dry sewage sludge was estimated to be produced annually in European Communities and an increase of 33% from 1984 to 1994 was predicted (Chang, 1994). A comparable amount may be found in the United States. In China, about 5.5% of municipal sewage was treated, sewage treatment plants are predicted to increase sharply in order to treat 20%—30% of municipal sewage in 2000 as planned by the government (Xiao, 1997). The sludges are costly to handle and there is no satisfactory solution for final disposal for the sludges with high content of heavy metals. Unfortunately, the sewage sludges produced in South China (ex: Shanghai, Guangzhou, Shenzhen, Hong Kong) generally contain high amount of Cu and Zn (1500—5000 mg/kg dry matter; Wu, 1992; 1996), and exceeds the national standards (GB4284-84) of sewage sludge for direct land applications.

The reduction of heavy metals in sewage sludge can be achieved either by source control or by removing metals from sludge. In source control, the major difficulty is identification of the source. Moreover, even with the complete elimination of toxic metals from all industrial discharges to sewers, the problem remains because of the metal content of domestic wastewater (Tyagi, 1988).

Metal extraction using EDTA showed high efficiencies of Cd, Pb and Cu (Jenkins, 1981), but the cost of the chemical is high. Hayes *et al*. (Hayes, 1980) developed an acid extraction process for sludge metals using aerobic autoheated thermophilic digestion (AATD). These authors also observed that, in general, various sludges acidified with HCl exhibited heavy metal solubilization efficiencies comparable to those produced by HNO_3 addition. Cheung (Cheung, 1988) investigated the effects of various common acids (HCl, HNO_3 and H_2SO_4) with and without the presence of H_2O_2 on the heavy metal content and dewaterbility of treated sludge. The results revealed the significant impact of H_2O_2 in various acid treatments and HCl had advantages concerning the lime treatability of the filtrate. The use of H_2SO_4 is advantageous because of its low cost and improved filterability of leach mixture (Scott, 1980; Jenkins, 1981; Tyagi, 1988). Solids concentration and pH are key factors in optimizing the removal process (Wozniak, 1982) and the extraction time needed to solubilize almost maximum metals is less than 3 hours in $pH<2$. However, no study was reported concerning the Chinese sewage sludges and the nature and source of sludge was shown to influence strongly metal removals (Tyagi, 1988).

The work was conducted to study the feasibility of removing heavy metals from non-digested sewage sludge from Guangzhou City of China, intending especially to find out the effective and economic treatment of sewage sludge for land application.

2 Materials and methods

2.1 Sewage sludge

Sludge samples were taken from Datansha Wastewater Treatment Plant of Guangzhou. The plant treats about 15×10^4 tons of wastewater every day and produces 50 to 60 tons of dewatered sludge (about 80% water). The end product is an activated sludge often disposed off in landfill. Three samples were taken in different periods and mixed up to carry out the experiment. Prior to analysis the samples were air-dried and ground to pass 2 mm, 1 mm and 0.125 mm sieves. The 2 mm size was used to carry out the chemical extraction and pot experiment, the other two to analyze the sludge properties. The main characteristics of the sludge is shown in Table 1. According to the Chinese National Standards of Sewage Sludge for Agricultural Application, the main contaminated metals are copper and zinc, other toxic metals were not severely exceeded the standards.

Table 1 Main characteristics of tested sewage sludge and soil

	Sewage sludge	Soil
Texture	–	Sandy loam
pH	6.7	5.2
Organic matter, g/kg	510	7.0
Total-N, g/kg	15.2	0.37
Total-P, g/kg	38.2	0.21
Total-K, g/kg	17.6	14.6
Available-N, mg/kg	210	22.3
Available-P, mg/kg	–	5.0
Available-K, mg/kg	–	85.6
Total Cu, mg/kg	3116	10.6
Total Zn, mg/kg	2290	66.4
Total Cr, mg/kg	1465	–
Total Cd, mg/kg	9.45	0.10

2.2 Soil

Soil sample was taken from the surface layer of lateritic red soil originated from granite in Guangzhou. The soil was analyzed for their physico-chemical properties and heavy metal content (Table 1).

2.3 Fractionation of heavy metals in sewage sludge

The sequential extractions similar to that for soil metal fractionation (Garcia-Miyaga, 1984) was applied to the sewage sludge to discriminate the bulk element concentration into different binding forms, which could help in determining what kind of sludge treatment to be adopted. Table 2 demonstrated the chemical extractant, the solid to solution ratios and extraction time used in this experiment.

Table 2 Fractionation by sequential extractions of heavy metals in sewage sludge

Fraction phase	Extractant	Solution /solid	Extraction time, h	Percent of total content, %	
				Cu	Zn
Water soluble	Deionized H_2O	10	1	0.1	0.1
Exchangeable	1 mol/L $CaCl_2$	10	5	1.4	0.5
Carbonate	2.5% CH_3COOH	10	6	20.0	22.7
Oxides	0.05 mol/L EDTA	10	1	41.2	22.2
Organic	1 mol/L Na_4PO_7	20	12	2.3	1.1
Sulfides	6 mol/L HNO_3	20	5	2.3	1.0
Residual	HF-HCl-$HClO_4^{\#}$	–	–	16.3	36.0

#: as in total metal analysis

2.4 Removal of heavy metals by chemical extractions

Three chemical extractants: H_2SO_4, EDTA and NH_4HCO_3 were tested in this study. The reagent concentration, extraction time and solid to solution ratio are shown in Table 3. H_2SO_4 was added with 0.05 mol/L diluted acid and the mixture was adjusted to pH 1. Another H_2SO_4 treatment was accomplished by direct addition of concentrated one using the same amount of the acid. NH_4HCO_3 was studied with 4 different mole concentrations. All solubilization tests were performed with 3 replications using plastic bottles and an electric shaker with constant speed. Solubilized metals were analyzed in the extract by atomic absorption spectrometry (Hitachi-180).

Table 3 Heavy metal removal with H_2SO_4, EDTA and NH_4HCO_3 extractions

Extractant	Extraction time, h	Solid/solution	Removed quantity, mg/kg	
			Cu	Zn
0.05 mol/L $H_2SO_4^{\#}$	0.5	1/5	1422	1400
0.05 mol/L $H_2SO_4^{\#\#}$	0.5	1/5	2070	1562
0.05 mol/L EDTA	5	1/10	1357	1201
0.5 mol/L NH_4HCO_3	3	1/10	630	11
1.0 mol/L NH_4HCO_3	3	1/10	780	36
2.0 mol/L NH_4HCO_3	3	1/10	1005	ND###
4.0 mol/L NH_4HCO_3	3	1/10	1355	ND

#: acid was diluted then added to sludge; ##: concentrated acid was added to sludge then diluted; ###: non-detectable with flame atomic absorption spectrometry

2.5 Precipitation of copper and zinc from the filtrate

To avoid environment pollution, heavy metals mobilized in the filtrate must be precipitated before discharge. Waste calcium carbonate from cane sugar industry was added to the filtrate to achieve a pH of 7.1.

2.6 Pot experiment

Plant experiment in pots was carried out to test the effect of the treated sludges on plant growth and heavy metal content in plant edible parts. Chinese cabbage (*Brassica chinensis*) was used as test-plant. Prior to the pot experiment, the acidified sludge was neutralized with 3 alkaline materials: waste $CaCO_3$ from cane sugar industry (pH 9.0), NH_4HCO_3 (pH 8.2) and phosphate rock (pH 8.7), with the acidified sludge to neutralizing agent ratio of 1:0.5, 1:1 and 1:1 respectively. The mixtures were incubated for 2 weeks. Each pot contained 2.5 kg dry soil. The soil treatments were: control (no fertilizer); raw sludge (10 g/kg soil); acidified sludge (10 g/kg soil); acidified sludge + waste $CaCO_3$ (10 g/kg soil); acidified sludge + NH_4HCO_3 (10 g/kg soil); acidified sludge + phosphate rock (10 g/kg soil); NH_4HCO_3 (0.15 N/kg soil) + P (Superphosphate; 0.10 gP/kg soil) + K (KCl, 0.15 g K/kg soil); Phosphate Rock (5 g/kg soil) + N ($CO(NH_2)_2$, 0.15 g N/kg soil) + K; NPK (Table 4). 5 replicates were applied for each treatment and 3 plants were grown on each pot. After the harvest of Chinese cabbage, the yield, Cu and Zn content of stem and leaves were measured; the pH, exchangeable Cu and Zn of soil were also determined.

Table 4 Effect of treated sludges on plant and soil (mg/kg dry matter)

Treatments	Chinese cabbage			Soil		
	Dry weight, g/plant	Metal content Cu	Metal content Zn	pH	Exchangeable metal Cu	Exchangeable metal Zn
Control (CK)	0.99a#	4.4	19.1	5.2	ND##	5.0
Sludge (S)	1.77cd	6.7	38.4	5.0	25.8	12.8
Acid. S. (AS)	1.86d	8.6	38.2	4.9	15.4	7.7
AS + $CaCO_3$	1.24abc	ND	17.3	6.2	11.7	7.5
AS + NH_4HCO_3	2.11de	ND	23.5	4.8	11.8	10.2
AS + Phos. Rock	1.88d	3.1	23.2	4.6	12.2	6.5
NH_4HCO_3 + PK###	2.26e	–	–	4.5	–	–
Phos. Rock + NK	1.51bc	–	–	4.6	–	–
NPK	2.32e	–	–	4.7	–	–

#: the means followed by the same letter were not significantly different according to LSD test ($r = 0.05$); ##: not detectable with flame atomic absorption spectrometry; ###: conventional chemical fertilizers: $CO(NH_2)_2$, superphosphate and KCl respectively

3 Results and discussion

3.1 Efficiency of chemical extractions

The fractionation of heavy metal in sludge showed that the Cu and Zn sorbed largely on carbonate and oxides for the tested sludge (Table 2). Only a small percent of Cu and Zn was observed in form of sulfides. It is reasonable for the studied non-digested sludge. These results suggested that the metals in the tested sludge might be less difficult to remove than that in others, especially the anaerobically digested ones which contained high amount of metal sulfides.

Under the conditions of this study, 0.05 mol/L H_2SO_4 extracted 45.6% of Cu and 61.10% of Zn (Table 3). It is found out that a better extraction was achieved where the acid was directly added to the sludge and then diluted, than where the acid was first diluted then added and adjusted the mixture to pH 1. An increase of 21% was observed for Cu while Zn had 7% increase. This increase in removed metals was probably due to the oxidation of organic matter.

The acid needed in this experiment was around 0.05 kg per kg of dried sludge which is much lower than the estimate of others which ranged from 0.4 to 0.5 kg per kg dried sludge (Scott, 1980; Tyagi, 1988). It might be due to low amount of metal sulfides and low pH (6.7) of the sludge tested, and low solution to solid ratio (5:1) and low pH (1.0) adopted in the removal procedure.

EDTA gave also rather high extraction rate. About 44% of Cu and 52% of Zn were removed (Table 3). But 0.05 mol/L EDTA was less efficient than 0.05 mol/L H_2SO_4.

Using NH_4HCO_3 in Cu removal from the sludge by formation of Cu-NH_3 complex could permit to recover the NH_3 in leachate by distillation and enrich the treated sludge in NH_4^+, and thus favorer the reuse of treated sludge as fertilizer. However, the removal efficiency is low for Cu even in high normality (Table 3), and Zn was almost not removed. It is unsuitable for the tested sludge if the treated sludge should reuse in agriculture.

3.2 Effect of treated sludges on plant and soil

The pot experiment with Chinese cabbage showed that the raw and treated sludges increased significantly the plant yield compared with the control (Table 4), and the application of conventional soluble NPK fertilizers resulted in the best harvest. The acidified sludges neutralized with phosphate rock and NH_4HCO_3 gave higher increase in plant yield than that neutralized with waste $CaCO_3$. Furthermore, the neutralized sludge with phosphate rock resulted in a significant higher yield than the application of phosphate rock. It could be explained by the fact that the soil studied in this experiment was deficient in available phosphorus (Table 1), the addition of soluble phosphorus with superphosphate favored the crop growth (Table 4), the acidified sludge and its mixture with phosphate rock could also increase the available phosphorus and the crop yield, but $CaCO_3$ treatment resulted in a negative effect on soluble phosphorus.

Concerning the heavy metal content in plants, the acidified sludge did not decrease the Cu and Zn content in edible parts of the vegetable (Table 4), thought it contained less amount of Cu and Zn than the raw sludge. The acidification could increase the metal mobility and thus the plant uptake. However, the neutralized sludges decreased significantly the Cu and Zn contents in plants.

The measurements of exchangeable metals in soil after the pot experiment showed that all the treated sludges decreased the residual available Cu and Zn in soil than the raw sludge (Table 4), and could ameliorate the environmental quality of sludge amended soils.

3.3 Discussion

As discussed in the first section, the removal of heavy metals from sewage sludge has been studied by many scientists. In spite of good metal extraction achieved in the acid treatment method, the factors such as cost (especially HCl and HNO_3), large acid requirement (0.4—0.9g H_2SO_4 per g dry weight of sludge) and lime consumption for neutralize the leachate made practical application of these methods unattractive. However, the present study demonstrates that, with the most of non-digested sludge in China which contains less difficult solubilized metal sulfides, the acid extraction could process with relatively low pH (pH = 1) and low solution/solid ratio (5—10:1), the sulfuric acid requirement was low and economically acceptable (< 1 RMB Yuan /kg H_2SO_4 in Guangzhou). Moreover, the direct addition of concentrate H_2SO_4 was more efficient than the diluted one using the same amount of acid, and could kill somewhat harmful micro-organisms (no measurement made) and substitute the anaerobic digestion. Furthermore, the removal of heavy metals from sewage sludge with H_2SO_4 could coupled with the production of a new kind of organic-phosphate fertilizer which is well known to be more available to plants than the inorganic one (Peng, 1980; Lu, 1992), and accordingly make it economically more attractive. However, the present results were obtained with dry ground sludge samples, the wet sludge might need more acid. But the preliminary test of acid leaching of wet sludge showed that 10 ml concentrated acid per kg wet sludge (about 40L H_2SO_4 per ton dry sludge) could removed about 1000 mg/kg of Cu or Zn at the solution to solid ratio of 5, it remained economically feasible.

Another alternative method for removing the heavy metals in sludges is bacterial leaching (Schonborn, 1978; Tyagi, 1988; 1993). The presence of sulfur-oxidizing bacteria (*Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans*) is the basis of the microbial metal leaching explored (Blais, 1992). The leaching tests conducted with metal sulfides as substrate showed that metals solubilization from sulfides occurred by an indirect mechanism (due to the action of the acid produced). No evidence of direct oxidation of metal sulfides was observed (Tyagi, 1993). It means that the bioleaching is also via H_2SO_4 attract and if cheap H_2SO_4 is locally available, the bioleaching is not surely more economic, because it needs more installations and time consuming, additional cost factors have to be included in the final cost estimation, though the cost of bioleaching in terms of chemicals was found to be decreased by 80% (Tyagi, 1988).

4 Conclusion

The present experiment compared the efficiency of 3 types of extractant in removing heavy metals from sewage sludge originated from Guangzhou of China, the direct addition of concentrated H_2SO_4 resulted in a higher efficiency and lower cost than EDTA and NH_4HCO_3. The acid needed is low and economically acceptable, probably due to low amount of metal sulfides in the studied non-digested sludge and low solution to solid ratio, low pH adopted in the removal procedure. The acid treated sludge showed the similar or higher fertilizer value than the untreated sludge and decreased soil heavy metal contamination, but the acidified sludge had to neutralized in order to reduce significantly the plant uptake. The alkaline wastes or fertilizers such as phosphate rock could be used for limiting the lime consuming and recycle in agriculture. The removal of heavy metals from sewage sludge with H_2SO_4 coupled with the organic-phosphate fertilizer production for agricultural application might be a favored final disposal method for heavy metal contaminated sewage sludges. However, the removal or recovery of heavy metals in leachate and the process economically treating wet sludges need further studies.

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