Extractability and fractionation of heavy metals in chemically treated sewage sludges

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Abstract Four chemically treated sludges, lime-treated (LS), lime/sodium silicate-treated (LSS), cement-treated (CS), and cement/sodium silicate-treated (CSS) were produced from the chemical treatment of aerobic digested sewage sludge cake, using lime, cement, and sodium silicate as additives. Extractability and fractionation of the heavy metals (Cu, Pb, Cr, and Zn) in these products and untreated sludge (S) were investigated using sequential extraction, single extraction, and 13C cross-polarization magic angle spinning nuclear magnetic resonance analysis (13C-NMR). These approaches revealed that chemical treatment of sewage sludge makes sludge Cu, Pb, and Cr more extractable. It was attributed to the irreversible dissolution of a portion of organics at very high pH during chemical treatment of sludge. The enhanced extraction of some metals having higher affinity to organics, e.g., Cu and Pb, from the chemically treated sludges was due to their complexation with the above soluble organics.

Keywords Chemical treatment, heavy metals, sequential extraction, single extraction, sewage sludge, optical microscopy

Introduction

Chemical treatment of sewage sludge has been used for many years (Reimers, 1991); the products of it have relatively high CaCO3 equivalent (CEE) and can be utilized as liming amendment (Little et al., 1991). Because the heavy metals in sewage sludge are more concentrated than in plants and soils (Baker and Senft, 1995), it is necessary to characterize their extractabilities and fractionation in chemically treated sludges. While much research indicated that heavy metals in soil can be stabilized by adding liming additive (Chaney et al., 1987; Woodbury, 1992), some data in the studies by Sims and Kline (1991) and Little et al. (1991) indicated that the plants grown in soils with liming additives and sewage sludge increased their intake of Cu. Stehouwer et al. (1995) also indicated that adding the by-product from FGD and sewage sludge into soils increased its leachability of Cu, but decreased that of Zn. Because there is still only limited data about this issue, in this research we introduce four chemically treated sewage sludges and characterize the heavy metals in them in order to consider their reuse value and harmful potential to the environment.

Methods

The materials used in this study were sodium silicate (Merck; Na2O = 7.5–8.5%; SiO2 = 25.5–28.5%; density = 1.296–1.396 g m/L; water consent = 62%), sewage sludge cake (aerobically digested sludge sampled from the Ming-Shan Municipal Water Treatment Plant; water content = 86.4%), lime (reagent grade Ca(OH)2) and Portland cement (type I). Four chemically treated sludges were prepared: the lime treated, lime/sodium silicate treated, cement treated, and cement/sodium silicate treated. The lime/sodium silicate treated and cement/sodium silicate treated were prepared in three steps: manual mixing of the sludge with sodium silicate, further mixing (also manual) with added lime or cement and curing by air drying. The lime treated and cement treated were prepared by manual mixing of sludge with lime and cement, respectively, followed by air drying. Untreated sludge was prepared by oven drying (60°C) of sewage sludge cake. Final products form the above treatment were stored in PVC bottles.
The single extraction test was performed with the distilled water adjusted to various pH (1–13) and carried out in 50 ml centrifuge tubes shaken in a reciprocal shaker bath (Yihder BT350R) at 1250 rpm, 25°C. Each tube contained 1g of sieved sample (80 mesh) diluted to 40 ml with extraction solution. Each extraction lasted for 24 h, after which the supernatant from the configuration (Kubota 6800) at 1200 g for 10 min was decanted, then analyzed with an atomic absorption spectrometer (Perkin Elmer 4000) and a total organic carbon analyzer (O • I Corporation 700) for concentrations of heavy metals and dissolved organic carbon (DOC). The residues from the centrifugation were discarded.

To fractionate heavy metals in treated sludges, Tessier’s method of sequential extraction was performed. Heavy metals in each sample were fractionated into exchangeable, carbonate, oxide-bound, organically bound and residual forms (Tessier et al., 1979).

The optional characteristics of organic matter was detected with 13C cross-polarization magic angle spinning nuclear magnetic resonance analysis (Bruker CP 100, Cross Polarization Magic Angle Spinning, 25.1 MHz).

Results and discussion
While the treated sludges had less organic matter than untreated sludge, the DOC in their extracts at pH 2–10 was much higher (Figure 1). It reveals that a portion of organic matter in treated sludge was transferred to soluble forms, possibly due to high pH during treatment.

The concentrations of Cu in S and LSS extracts were both increased with pH value, and the extraction pattern of Cu in untreated sludge at alkaline pH (Figure 2) and that of DOC (Figure 1) are similar, indicating that Cu was closely related to organic matter. Zn showed much different results. The concentration of it decreased obviously with pH (Figure 3) and seems to be independent of DOC. Sequential extraction indicated that 4.99% of Cu fractionated to exchangeable form, 3.14% to carbonate form, 1.23% to oxide-bound form, organically bound form, and 17.0% to residual form (Figure 4). That Cu fractionated most to the organically bound form is consistent with the reports of its high affinity to organic matter (McLaren and Crawford, 1973; Kernadoff and Schnitzer, 1980; Emmerich et al. (1982). Chemical treatment of sewage sludge made Cu transferred from organically bound form to exchangeable form (Figure 4). In other words, Cu in treated sludges is more unstable than in untreated sludge. This result is consistent with some data of Sims and Kline (1991), Little et al. (1991) and Stehouwer et al. (1995), which showed increased plant intake of Cu after treatment.

The extraction results for Zn were very different from those of Cu. Chemical treatment was of most advantage to stabilization of Zn. Sequential extraction indicated that untreated sludge consisted of 10.0% exchangeable Zn, which was all transferred to other relatively
stable forms (Figure 5). Zn had only 21.4% fractionated to organically bound form in untreated sludge. The rate was the least compared to other metals in this study, indicating its least affinity to organic matter. Therefore, it was not like Cu which was unstabilized during chemical treatment due to complexation with soluble organic matter.

The percentages of Pb and Cr fractionated to organically bound form were in between those of Cu and An. The order was Cu > Pb > Cr > Zn. This is similar to the results by Tessier et al. (1979), Baham et al. (1978), Saar and Weber (1982), and Tack and Verloo (1993). Sequential and single extractions both indicated that chemical treatment did not make Pb and Cr stabilize. The extent was in between that of Cu and Zn, but close to Cu.

Figure 6 indicates the effects of lime treatment on organic matter in sludge via $^{13}$C-NMR analysis. After treatment, aliphatic-C in sludge changed $-9.9\%$, O-alkyl-C changed $-12.1\%$, aromatic-C changed $+6.4\%$, carboxyl-C changed $+1.5\%$, carbonyl-C changed $+91.4\%$, indicating that oxidation and hydrolysis of the organic matter took place in sludge after treatment. Carboxyl-C and carbonyl-C are relatively acid soluble. Their increase indicates chemical treatment made organic matter more soluble, consistent with the previous observations.

**Conclusions**

Chemical treatment was most adverse to Cu with regard to stabilization. In untreated sludge, 4.99% of Cu fractionated to exchangeable form, 3.14% to carbonate form, 1.23% to oxide-bound form, organically bound form, and 17.0% to residual form, indicating its affinity to organic matter. The adverse effect on heavy metal is due to complexation to soluble organic matter during chemical treatment. The extraction pattern of Zn was quite different from that of Cu. Chemical treatment was advantageous to Zn stabilization, due to its least affinity to organic matter. The effects of chemical treatment on Pb and Cr were in
between those on Cu and Zn. These results derived from the extraction experiment were also consistent with $^{13}$C-NMR analysis.

References


