



## Changes of Cu, Zn, and Ni chemical speciation in sewage sludge co-composted with sodium sulfide and lime

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Received 13 April 2007, revised 5 July 2007, accepted 16 July 2007

### Abstract

A batch composting study was performed to evaluate the feasibility of co-composting sewage sludge with sodium sulfide and lime (SSL) mixture ( $\text{Na}_2\text{S}/\text{CaO}=1:1$ ), aiming at reducing the availability of heavy metals in the sludge compost. Sewage sludge with sawdust as a bulking agent was amended with SSL at 3% (w/w, dw), and composted for 15 d in laboratory batch reactors. The four stages of the Tessier sequential extraction method was employed to investigate changes in heavy metal fractions of Cu, Zn, and Ni in sewage sludge composted with SSL. For all the three metals, the mobile fractions, such as, exchangeable and carbonate bound were mainly transformed into low availability fractions (organic matter and sulfide, Fe-Mn oxides bound and residual forms), and the addition of SSL enhanced this transformation. Therefore, SSL is a suitable material to co-compost with sewage sludge to reduce the availability of heavy metals. According to the cabbage seed germination test, a SSL amendment of  $\leq 3\%$  (w/w, dw) is recommended to co-compost with sewage sludge.

**Key words:** sewage sludge; co-composting; heavy metals; sequential extraction

### Introduction

Wastewater treatment plants usually generate millions of tons of residual sludges worldwide every year. Sewage sludge from municipal wastewater treatment plants contain organic compounds, macronutrients, micronutrients, nonessential trace elements, organisms, and eggs of parasitic organisms (Alloway and Jackson, 1991). 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. Although such applications may be beneficial to soil, concern about possible environmental pollution hazards, for example, odor, water pollution, veterinary hazards, and contamination by heavy metals have to be considered (Alloway and Jackson, 1991; Baveye *et al.*, 1999). Therefore, sewage sludge composting is often required before its land application, to reduce many phytotoxic substances related to the biodegradation of organic matter and pathogenic microorganisms. However, the major drawback of sewage sludge composting is the high heavy metal content in the end-product, especially for sewage sludge derived from industrial activities (Fang and Wong, 1999).

Municipal wastewater in China is usually mixed with industrial wastewater before treatment, and this results in much higher metal concentrations in municipal sludges than in rural sludges. Generally, Chinese sewage sludge

contains higher concentrations of Cu, Zn, and Ni than other metals (Chen *et al.*, 2003). They are often the elements that exceed national standards for land application of sewage sludge. Various approaches have been adopted to reduce the bioavailable fractions of heavy metals that would expect to correlate with the phytotoxicity in sludge amended soils.

Previous studies showed that co-composting sewage sludge with alkaline materials, such as, coal fly ash, lime, and alkaline bauxite residue was feasible in reducing the soluble and exchangeable fractions of heavy metals in sludge compost (Chaudhuri *et al.*, 2003; Fang and Wong, 1999; Zorpas *et al.*, 2000; Veeresh *et al.*, 2003; Sophia and Swaminathan, 2005). Recently, Dalibor *et al.* (2006) reported the conversion of heavy metals involved in incineration fly ashes to heavy metal sulfide resources by sulfidation treatment with sodium sulfide, which was considered to be a suitable technique for the immobilization and recovery of heavy metals from various types of wastes. To the best of the authors' knowledge, to date, no previous study describing co-composting sewage sludge with sodium sulfide has been reported. In this experiment, the mixture of sodium sulfide and lime (SSL) was used for the stabilization and solidification of sewage sludge. The effect of the SSL mixture amendment on the availability of heavy metals was investigated, aiming at evaluating the feasibility of co-composting sewage sludge with SSL.

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## 1 Materials and methods

### 1.1 Preparation of composting mass

Dewatered aerobic sewage sludge was collected from the Quyang Sewage Treatment Plant in Shanghai. The dewatered sludge may lack sufficient porosity for adequate aeration. Bulking agents are needed to provide structural support when the composting materials are too wet to maintain air spaces within the composting pile, and to reduce moisture content or change the C/N ratio. Sawdust is selected as the bulking agent, as it is readily available and has good moisture absorption capacity. Selected physico-chemical properties of the experimental materials are given in Table 1.

**Table 1** Physicochemical properties of sewage sludge and sawdust

Parameter	Sewage sludge	Sawdust
pH	6.5–7.0	5.5–6.0
Moisture content (%)	80 (±4)	13 (±2)
Total organic matter (g/kg dw)	500 (±50)	850 (±50)
Total N (g/kg dw)	27 (±3)	—
Total heavy metals (mg/kg dw)		
Cu	159 (±5)	—
Zn	1653 (±15)	—
Ni	42 (±3)	—

The dewatered sewage sludge was mixed with sawdust at about 4:1 (w/w, fw) to obtain a C/N ratio of 30. The sewage sludge-sawdust mixture was then mixed thoroughly with the solidification agent, SSL mixture (Na<sub>2</sub>S/CaO = 1:1), at 3% (w/w, dw). For each treatment, 100 kg of the mixture was prepared and composted for 15 d in a bench-scale composting system. Air was supplied to the composting mass, and the moisture content was maintained between 60% and 70% throughout the composting phase. About 100 g of subsamples were taken from each treatment for analysis.

### 1.2 Chemical analysis

The toxicity characteristic leaching procedure (TCLP) (USEPA, 1993) was designed to simulate the leaching of metals from the sludge samples and their solidifications. Solidification of sewage sludge was carried out by making mortar samples with air-dried sludge and SSL. The dried sewage sludge and SSL was mixed thoroughly with the requisite amount of deionized water using a mixer. TCLP leaching of raw and solidified sludge were carried out by extracting a liquid-to-solid ratio of 20:1, using glacial HAc solution (pH 2.8), as a medium. The raw and solidified samples, after crushing to size smaller than 9 μm, along with leaching fluid were placed in a rotatory shaker, shaken at 120 r/min for 20 h. The samples were filtered and analyzed for metals.

The method of sequential extraction used in this study followed that of Tessier *et al.* (1979). The heavy metals were partitioned into five operationally defined fractions: exchangeable, carbonate bound, Fe-Mn oxides bound, organic matter and sulfides, and residual fraction. The extraction was carried out in polypropylene centrifuge

tubes of 50 ml capacity with an initial mass of 2.5 g oven dried (105°C) fine fraction (<1 mm) of the samples. Each of these chemical fractions is as follows: (1) exchangeable: 2.5 g samples were extracted with 25 ml of 1.0 mol/L MgCl<sub>2</sub> at pH 7.0 with agitation at 200 r/min for 1 h at 20°C; (2) carbonate: residue from (1) was extracted with 25 ml of 1 mol/L NaOAc at pH 5.0 with agitation for 5 h at 20°C; (3) Fe-Mn oxides: residue from (2) was extracted with 25 ml of 0.1 mol/L NH<sub>2</sub>OH·HCl in 25% HAc (v/v, pH 4.0) for 6 h at 90°C, in a water bath, with agitation; (4) organic matter and sulfide: residue from (3) was extracted with 25 ml of 30% H<sub>2</sub>O<sub>2</sub> at pH 2.0 and shaken for 1 h at 90°C; (5) residual: residue from (4) was digested in 6 ml concentrated HNO<sub>3</sub> and 70% HClO<sub>4</sub> (v/v). After each successive extraction, the supernatant was collected after centrifugation at 8000 r/min for 15 min and filtered through a 0.45-μm membrane filter and diluted to the required volume. The residue was washed with 10 ml Mill-Q water by shaking and centrifugation without loss of solids. The total metal content from a separate sample was analyzed, to evaluate the performance of sequential extraction, by digesting it with HF and HClO<sub>4</sub> (5:1).

Heavy metal concentrations of all extracts were determined by flame atomic absorption spectrophotometry (FAAS) (Analytick Jena A G, Germany). All extractions were performed in triplicate and the mean values were presented with standard deviation.

### 1.3 Seed germination assay

Sludge extracts were obtained by shaking 10 g dried sludge with 100 ml distilled water for 2 h at room temperature, in the dark. The flasks were then centrifuged at 5000 r/min for 20 min and the supernatant filtrated through Whatman No. 1 filter paper. Fifty seeds of cabbage were placed in culture dishes containing 5 ml of each extract, and then placed in an incubator at constant temperature and humidity, suitable for germination. Seed germination and the length of the longest root produced by the seeds were measured at 48 h. A visible root was used as the operational definition of seed germination. The germination index (GI) after sewage extract exposure were calculated as follows (Hoekstra *et al.*, 2002).

$$GI = \frac{G_s \% \times L_s}{G_c \% \times L_c} \times 100\% \quad (1)$$

where,  $G_s$  is seed germination in sludge extract;  $L_s$  is root length in sludge extract;  $G_c$  is seed germination in control;  $L_c$  is root length in control.

## 2 Results and discussion

### 2.1 TCLP extractable metals in SSL solidified sewage sludge

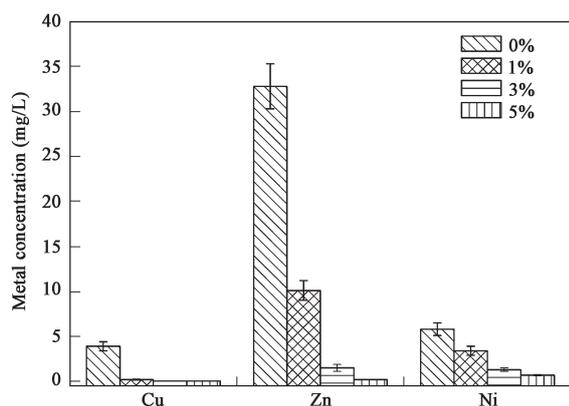
The measurement of the total metal content of sewage sludge using the analytical method is well established. However, even as total concentrations of metals indicate the extent of contamination, they provide less information with regard to the forms in which the metals are present in the sludge. Hence, a detailed knowledge of the speciation

of metals in the sludge itself and the changes in speciation that will probably occur following disposal, is very important, to estimate their mobility, bioavailability, and related ecotoxicity.

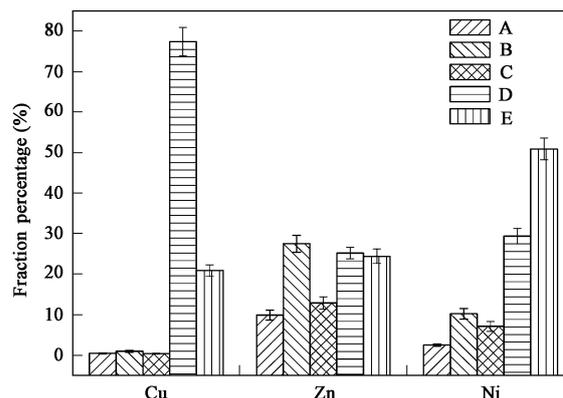
The TCLP extractable metal contents in the raw and solidified sewage sludge are presented in Fig.1. It can be seen that the extractable contents of Cu, Zn, and Ni decreased with an increase in SSL amendment rate. It is probable that the TCLP extractable heavy metals can form less soluble metal sulfides and hydroxides with SSL and thereby reduce its availability. SSL amendment at 3% (w/w, dw) significantly reduces the TCLP extractable metals, which is comparable with that at 5% (w/w, dw) of SSL amendment. As a compromise between the solidification rate and SSL cost, 3% (w/w, dw) was chosen as the amendment rate for the co-composting experiments.

## 2.2 Metal speciation

The percent contribution of exchangeable (EXC), carbonate bound (CAR), Fe-Mn oxides bound (Fe-Mn), organic matter and sulfide (OMS), and residual fractions (RES) of Cu, Zn, and Ni, in their total metal contents of sewage sludge and its composts are presented in Figs.2 and 3, respectively.



**Fig. 1** Concentrations of TCLP extractable metals in SSL-solidified sewage sludge at different SSL amendment rates (w/w, dw).

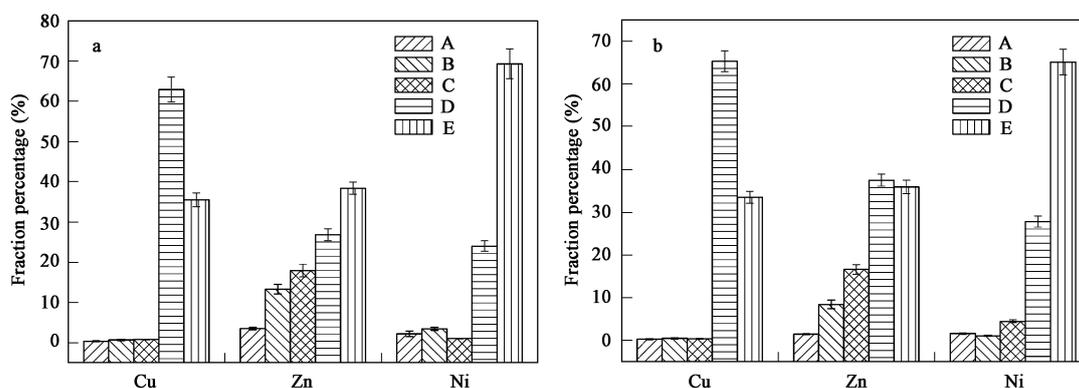


**Fig. 2** Percentage of exchangeable (A), carbonate bound (B), Fe-Mn oxide bound (C), organic matter and sulfides (D), and residual fractions (E) of Cu, Zn, and Ni in their total contents in sewage sludge.

### 2.2.1 Copper

Figures 2 and 3a show no significant difference in Cu speciation between the beginning and end of the composting. At the beginning of the composting, copper was predominantly in its organic matter and sulfides (77.7%) (Fig.2). This result is in agreement with the fact that copper has a high affinity for organic ligands, as proposed by Su and Wong (2004) and Aarab *et al.* (2006). In the sewage sludge, the percentage distribution of different species of Cu follows the order: OMS (77.7%) > RES (20.9%) > CAE (0.6%) > EXC (0.4%) > Fe-Mn (0.4%) (Fig.2). After composting, the amount of Cu in the organic matter and sulfide fraction is reduced from 77.7% to 62.9%, and residual Cu increases from 20.9% to 35.5% (Fig.3a). It can be concluded that the organic matter and sulfide bound Cu is transformed mainly into a residual fraction during composting. The other fractions, carbonate bound and exchangeable are still less important.

The addition of SSL did not cause marked changes in the form of Cu during composting (Fig.3b). However, the organic matter and sulfide bound Cu increased from 62.9% in control compost to 65.3% in the SSL amendment compost. This report is in contrast with Levy *et al.* (1992), who reported that alkaline lime could neutralize the or-



**Fig. 3** Percentage of exchangeable (A), carbonate bound (B), Fe-Mn oxide bound (C), organic matter and sulfides (D), and residual fractions (E) in their total contents of Cu, Zn, and Ni in sewage sludge compost (a) without and with (b) 3% (w/w, dw) SSL amendment.

ganic acids released during composting, and thus reduce the formation of metal-organic matter complexes during lime-sludge co-composting. The increase of organic matter and sulfide fraction is mainly because of the conversion of heavy metals to sulfides. When  $\text{Na}_2\text{S}$  is added to sewage sludge, the heavy metals are converted to metal sulfides by the sulfidation reaction expressed in Eq. (2).



The exchangeable, carbonate bound, and Fe-Mn oxide bound fractions of Cu increased slightly after composting without SSL and the addition of SSL reduced this transformation.

### 2.2.2 Zinc

In sludge, the order for different fractions of Zn is: CAR (27.5%) > OMS (25.2%) > RES (24.4%) > Fe-Mn (12.9%) > EXC (10.0%) (Fig.2). For Zn, it can be found that the exchangeable and carbonate bound fractions are very high in the sewage sludge. Taking into consideration of the high mobility and potential bioavailability of heavy metals in these fractions, it can be concluded that the sewage sludge cannot be used directly in agriculture, because of the potentially hazardous effect of Zn on the terrestrial environment. Initially, the carbonate bound fractions of Zn dominated the sewage sludge, but after composting, the residual fractions of Zn dominated in the compost. The order of Zn speciation in the compost was: RES (38.4%) > OMS (26.8%) > Fe-Mn (17.9%) > CAR (13.3%) > EXC (3.51%). In SSL treated compost at 3% (w/w, dw), the organic matter and sulfide fraction are higher than the residual fraction, which is mainly because of the conversion of  $\text{Zn}^{2+}$  to ZnS by the sulfidation reaction expressed in Eq. (2). This report is in contrast with Wong and Selvam (2006), who have reported that the residual fraction of Zn is the dominant fraction in the lime-treated compost at 1% and 1.63%. The exchangeable and carbonate bound fractions decrease from 10.0% and 27.5% in sewage sludge to 1.5% and 8.5% in SSL amendment compost, respectively. From these studies, it can be concluded that the SSL amendment is significant in reducing the mobile and easily available fractions (exchangeable and carbonate bound Zn) of the co-compost.

### 2.2.3 Nickel

In sewage sludge, the order for different fractions of Ni was: RES (50.9%) > OMS (29.4%) > CAR (10.2%) > Fe-Mn (7.1%) > EXC (2.5%). Ni occurred predominately in the residual fraction, which agreed with the report of Su and Wong (2004). After composting, the residual fraction was still the dominate fraction, and the order of different fractions in the compost was: RES (69.3%) > OMS (24.0%) > CAR (3.4%) > EXC (2.2%) > Fe-Mn (1.0%). The exchangeable, carbonate bound, Fe-Mn oxide bound and organic matter, and sulfide fractions decreased after composting. A similar observation was also reported during lime amendment composting of sewage sludge by Wong and Selvam (2006). It could be concluded that the carbonate bound, Fe-Mn oxide bound and organic matter,

and sulfide Ni were transformed mainly into residual forms of Ni during composting (Fig.3). The addition of SSL caused an increase in organic matter and sulfide fraction (27.8%) compared to that in the control, which might also be mainly because of the formation of NiS, by the sulfidation reaction expressed in Eq. (2). In the SSL amendment compost, both exchangeable and carbonate-bound fractions contributed to about 2.7% of the total Ni content. The significant increase in the residual fraction and decrease in exchangeable, carbonate-bound fractions suggested that the addition of SSL could effectively prevent the mobility of Ni.

### 2.3 Germination test

This simple bioassay was included as it was used to determine the maturity and phytotoxicity of composts and other biowaste materials (Roe *et al.*, 1997). From Fig.4, it can be seen that the GI values of all sludge mixtures at the beginning of the composting process were below 15%, indicating that amending the soil with fresh sludge mixture would cause plant toxicity. The SSL addition caused a slight reduction of GI at the amendment rate of 3% (w/w, dw). Most phytotoxic substances, including ammonia and low molecular weight organic acids, were contained and produced during the thermophilic phase. These compounds might have suppressed cabbage seed germination. Once these substances disappeared, plant growth was markedly enhanced. After a decrease in the first 6 d, GI increased significantly and reached 60% at around 15 d. The compost could be classified as nonphytotoxic (Wong, 1985). The pathogenic bacteria, such as *E. coli* and roundworm eggs were also measured according to USEPA (1993).

As is known, if the thermophilic duration is long enough, pathogens and parasites are killed or partly killed. In this study, after 7 d of composting, the value of *E. coli* met the standard and all the roundworm eggs were destroyed after 15 d of composting. Therefore, all treatment reached maturation after 15 d of composting and SSL amendment did not prolong the length of the maturation period.

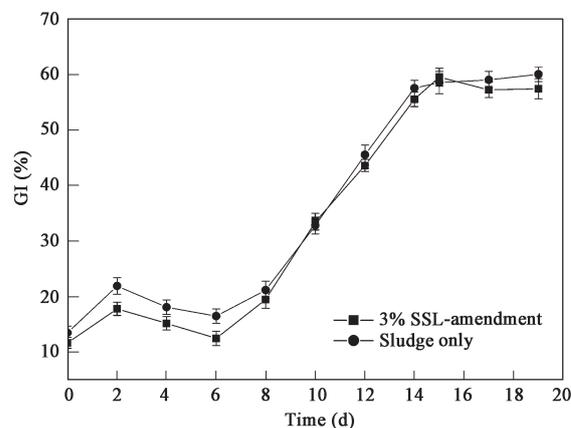


Fig. 4 Germination index (GI) during co-composting of sewage sludge with SSL.

### 3 Conclusions

The results of this study showed that the SSL amendment could be used as a co-compost material for sewage sludge composting. Addition of 3% (w/w, dw) SSL amendment was significant in reducing the exchangeable and carbon bound Cu, Zn, and Ni of the SSL-sludge compost, thus reducing the availability of heavy metals. The GI test showed that the cabbage germination was not markedly inhibited by the SSL amendment at 3% (w/w, dw), and the final composting product was mature after 15 d of composting. SSL amendment did not prolong the length of the maturation period.

### Acknowledgements

This work was supported by the National New Century Scholarship of China (No. NCET-05-0387); the Specialized Research Fund for the Doctoral Program of Higher Education (No. 20050247016) and the Guangda Environment Protection Innovative Funds.

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