Speciation of heavy metals in sewage sludge co-composted with sodium sulfide and lime

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Abstract: A batch composting study was performed to evaluate the feasibility of co-composting sewage sludge with sodium sulfide and lime mixture (SSL) (Na$_2$S/CaO=1:1), aiming at reducing the availability of heavy metals in the sludge compost. Sewage sludge with sawdust as bulking agent was amended with SSL at 3% (w/w dried weight), and composted for 15 days 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 ≤3 (w/w dried weight) is recommended to co-compost with sewage sludge.

Keywords: Sewage sludge; Co-composting; Heavy metals; Sequential extraction

INTRODUCTION

Municipal wastewater in China is usually mixed with industrial wastewater before treatment and this results in much higher metal concentrations than in rural sludges. Generally, Chinese sewage sludge contains higher concentrations of Cu, Zn and Ni than of 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 bioavailable fractions of heavy metals that would expect to correlate with 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; Carmalin Sophia and Swaminathan, 2005). To our best knowledge, no previous work describing co-composting sewage sludge with sodium sulfide has been reported to date. In this experiment, the mixture of sodium sulfide and lime (SSL) was used for the stabilization and solidification of sewage sludge. The effect of SSL mixture amendment on the availability of heavy metals was investigated aiming at evaluating the feasibility of co-composting sewage sludge with SSL.
**Materials and methods**

**Preparation of composting mass**

Dewatered aerobic sewage sludge was collected from the Quyang sewage treatment plant in Shanghai. The sawdust was selected as the bulking agent since it is readily available and has a good moisture absorption capacity. Selected physicochemical properties of the experimental materials are given in Table 1. The dewatered sewage sludge was mixed with sawdust at about 4:1 (w/w fresh weight) to obtain a C/N ratio of 30. The sewage sludge-sawdust mixture was then mixed thoroughly with solidification agent, sodium sulfide and lime (SSL) mixture (Na2S/CaO = 1:1) at 3% (w/w dried weight). For each treatment 100 kg of the mixture was prepared and composted for 15 days 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 was taken from each treatment for analysis.

**Table 1. Physicochemical properties of sewage sludge and saw dust**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sewage sludge</th>
<th>Saw dust</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.5-7.0</td>
<td>5.5-6.0</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>80 (±4)</td>
<td>13 (±2)</td>
</tr>
<tr>
<td>Total organic matter (g.kg-1 dried weight)</td>
<td>500 (±50)</td>
<td>850 (±50)</td>
</tr>
<tr>
<td>Total N (g.kg-1 dried weight)</td>
<td>27 (±3)</td>
<td>---</td>
</tr>
<tr>
<td>Total heavy metals (mg.kg-1 dried weight)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cu</td>
<td>159 (±5)</td>
<td>---</td>
</tr>
<tr>
<td>Zn</td>
<td>1653 (±15)</td>
<td>---</td>
</tr>
<tr>
<td>Ni</td>
<td>42 (±3)</td>
<td>---</td>
</tr>
</tbody>
</table>

**Chemical analysis**

The toxicity characteristic leaching procedure (TCLP, US EPA Method 1311) 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 requisite amount of deionised water using a mixer. TCLP leaching of raw and solidified sludge were carried out by extracting at a liquid to solid ration of 20:1 using glacial HAC solution (pH 2.8) as medium. The raw and solidified samples after crushing to size <9 um 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 of samples was extracted with 25 ml of 1.0 M MgCl2 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 M 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 M NH4OH.HCl in 25% acetic acid (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% H2O2 at pH 2.0 and shaken for 1 h at 90 °C. (5) Residual: Residue from (4) was digested in 6 ml concentrated HNO3.
and 70% HClO₄ (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 mm membrane filter and diluted to volume. The residue was washed with 10 ml of Mill-Q water by shaking and centrifugation without loss of solids. Total metal content from a separate sample was analysed to evaluate the performance of sequential extraction by digesting it with HF and HClO₄ (5:1). Heavy metal concentrations of all extracts were determined by flame atomic absorption spectrophotometry (FAAS). All extractions were performed in triplicates and the mean values are presented with standard deviation.

Seed germination assay
Sludge extracts were obtained by shaking 10 g of dried sludge with 100 ml of distiller 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).

Results and discussion
TCLP extractable metals in SSL solidified sewage sludge
The TCLP extractable metal contents in the raw and solidified sewage sludge are presented in Fig. 1. It can be seen from Fig. 1 that SSL amendment at 3% (w/w dried weight) significantly reduces the TCLP extractable metals, which is comparable with that at 5% (w/w dried weight) of SSL amendment. As a compromise between the solidification rate and SSL cost, 3% (w/w dried weight) was chosen as amendment rate for the co-composting experiments.

Fig. 1. Concentrations of TCLP extractable metals in SSL-solidified sewage sludge (mg/L); At SSL amendment rates (w/w dried weight) of: A, 0%; B, 1%; C, 3%; D, 5%.

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 Fig. 2 and Fig. 3, respectively.

Copper
Fig. 2 and Fig. 3a showed 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 and Smeyers, et al. (2006). In sewage sludge, the percentage distribution of different species of Cu followed 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 to a value of 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 was transformed mainly into residual fraction during composting. The other fractions, carbonate bound and exchangeable are still less important.

![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.](image)

![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 dried weight) SSL amendment.](image)

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 SSL amendment compost. This report is in contrast with Levy et al. (1992), who reported that alkaline lime could neutralize the organic acids released during composting, and thus reduced the formation of metal-organic matter complexes during lime-sludge co-composting. The increase in organic matter and sulfide fraction is mainly due to the conversion of heavy metals to sulfides. When Na2S is added to sewage sludge, S2- ions are consumed by the following reactions.

\[
\text{Me}^{2+} + \text{S}^{2-} = \text{MeS} \quad (1)
\]

\[
\text{S}^{2-} + 2\text{O}_2 = \text{SO}_4^{2-} \quad (2)
\]
Heavy metals are converted to metal sulfides by sulfidation reaction expressed in Eq. (1). Eq. (2) describes the oxidation of $S^2-$, which becomes significant when $O_2$ is present in water. In SSL amendment compost, the exchangeable, carbonate bound and Fe-Mn oxide bound fractions increased slightly after composting and the addition of SSL reduced this transformation.

**Zinc**

In sludge, the order for different fractions of Zn was: CAR (27.5%) > OMS (25.2%) > RES (24.4%) > Fe-Mn (12.9%) > EXC (10.0%) (Fig. 2). It can be found that the exchangeable and carbonate bound fractions are very high for Zn in the sewage sludge. Taking into consideration 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 due to the potentially hazardous effect of Zn on the terrestrial environment. Initially, the carbonate bound fractions of Zn dominated in the sewage sludge, but after composting, the residual fractions of Zn dominated in the compost. The order 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 dried weight), organic matter and sulfide fraction is higher than the residual fraction, which is mainly due to the conversion of Zn$^{2+}$ to ZnS by sulfidation reaction expressed in Eq. (1). This report is in contrast with Wong and Selvam (2006), who reported that the residual fraction of Zn was the dominant fraction in the lime treated compost at 1% and 1.63%. 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 can 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%) comparing with that in the control, which might be also mainly due to the formation of NiS by sulfidation reaction expressed in Eq. (1). In the SSL amendment compost, both exchangeable and carbonate bound fractions contributed about 2.7% of the total Ni content. The significant increase in residual fraction and decrease in exchangeable, carbonate bound fractions suggests that the addition of SSL could effectively prevent the mobility of Ni.

**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 residual fraction, which agreed with the report of Su and Woog (2004). After composting, the residual fraction was still the domination 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 can 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%) comparing with that in the control, which might be also mainly due to the formation of NiS by sulfidation reaction expressed in Eq. (1). In the SSL amendment compost, both exchangeable and carbonate bound fractions contributed about 2.7% of the total Ni content. The significant increase in residual fraction and decrease in exchangeable, carbonate bound fractions suggests that the addition of SSL could effectively prevent the mobility of Ni.

**Germination test**

This simple bioassay was included since 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 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 dried weight). Most phytotoxic substances, including ammonia and low molecular weight organic acids, were contained and produced during the thermophilic phase. These compounds may have suppressed cabbage seed germination. Once these substances disappeared, plant growth was markedly enhanced. After a decrease in the first 6 days, GI increased significantly and reached 60% at around 15 days, the compost could be classified as non-phytotoxic (Wong, 1985). Therefore, all treatment reached maturation after 15 days of composting. SSL amendment did not prolong the length of the maturation period.
Fig. 4. Germination index (GI) during co-composting of sewage sludge with SSL. Control, sludge only; SSL-amendment rate at 3% (w/w dried weight).

CONCLUSION
The results of our study showed that the SSL amendment could be used as a co-compost material for sewage sludge composting. Addition of 3% (w/w dried weight) SSL amendment was significant in reducing the exchangeable and carbon bound Cu, Zn and Ni of SSL-sludge compost, thus reduced 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 dried weight), and the final composting product was mature after 15 days of composting. SSL amendment did not prolong the length of the maturation period.

REFERENCES

