



FRACTIONATION AND LEACHABILITY OF Cu IN LIME-TREATED SEWAGE SLUDGE

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Abstract—Lime-treated sewage sludge was produced using a bench process to study the leachability and fractionation of Cu, which has a great affinity for organics in sewage sludges. The amount of Cu fractionated to the organically-bound form in sewage sludge was 73.7% by weight, while the lime treatment resulted in a decrease to 55.6%. The addition of lime to lime-treated sludge mainly led to an increased shift in Cu from the organically-bound fraction to exchangeable and acid-soluble fractions, indicating that the lime treatment caused Cu in sewage sludge to become unstable. The instability resulted from the affinity of Cu for organics, which irreversibly dissolve with Cu at very high pH during processing and natural drying of sludge. Semi-dynamic extraction revealed that the lime treatment also increased percent cumulative leaching of Cu from sewage sludge after the extraction period of 12 days.
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Key words—copper, lime, sequential extraction, sewage sludge

INTRODUCTION

Lime treatment of sewage sludges is an alkaline treatment process (Sloan and Basta, 1995) which has been used for centuries to reduce the odor generation and pathogen levels of biological matter. It is a simple and effective method of sludge processing that requires little specialized equipment (Outwater, 1994). While literature contains little data on the characteristics of heavy metals in lime-treated sludge, guidelines have been designed to limit the application of sewage sludge to agricultural land (Lake *et al.*, 1984) because sewage sludge may contain high levels of heavy metals that are harmful to the environment. Of the heavy metals which commonly occur in sewage sludges, Cu has a relatively high affinity for organic ligands (McLaren and Crawford, 1973; Kerndorff and Schnitzer, 1980; Emmerich *et al.*, 1982) and in some reports it reached the concentrations of 2,080 mg/L (Spiegel *et al.*, 1985) and 10,440 mg/L (Sommer, 1977), thus interesting us to study the effects of lime treatment on its characteristics in sewage sludges. For this objective, lime was used in this study to treat the sewage sludge cake (13.61% solids) from the Min-Sheng Wastewater Treatment Plant in Taipei City, using a bench process to produce the lime-treated sludge samples for our experiments.

Analytical limitations imposed by interference, selectivity, and sensitivity do not allow a complete

differentiation of metals between physicochemical forms in the sludge matrix. However, a number of schemes have been proposed to fractionate metals on the basis of extractability in various chemical reagents either discretely or sequentially (Lake *et al.*, 1984; Tack and Verloo, 1995). Metal forms have been investigated by many authors using selective chemical extraction techniques to obtain fractions corresponding to soluble, exchangeable, organic, adsorbed, and precipitated forms (Bloomfield and Pruden, 1975; Stover *et al.*, 1976; Rudd *et al.*, 1986). Of these methods, the sequential extraction presented by Tessier *et al.* (1979) has been widely used in soil and calcareous soil samples. Soon and Bates (1982) stated that metals present in soluble, exchangeable, and organically-bound fractions are the most available to plants. Therefore, the harmful effects of sewage sludge can be determined by extractions. To study the effect of lime treatment on Cu in sewage sludge, sequential and semi-dynamic extractions were used to extract the samples, including lime-treated (treatment) and untreated (control) sewage sludges. Extraction of samples at various pH was also conducted to obtain more information on Cu leachability.

EXPERIMENTAL

Preparation of treated and untreated sludges

The materials used in this study were lime [reagent grade Ca(OH)₂] and aerobically digested sewage sludge cake (13.61% solids) sampled from the filter press outlet of the Min-Sheng Wastewater Treatment Plant in Taipei

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Table 1. Sample types and compositions

Samples	Compositions	
	Sewage sludge cake (g) ^a	Lime (g) ^b
Lime-treated sludge	200	20, 0 ~ 40 ^c
Untreated sludge	200	0

^aAerobically digested sewage sludge cake (13.61% solids).

^bReagent grade Ca(OH)₂.

^cSamples for sequential extraction

City. According to Outwater (1994), directly mixing lime with sludge cake is a commonly used lime treatment procedure of sewage sludges. Therefore, lime-treated sludge in this study was prepared by mixing sewage sludge cake with lime followed by natural drying. Untreated sludge was prepared by heat drying (60°C) of sewage sludge cake. Both final products were ground and sieved (80-mesh), and stored in PVC bottles. The sample compositions are listed in Table 1.

X-ray diffractometry

X-ray diffractometry was performed with powdered samples (80-mesh). XRD patterns were obtained with a X-ray diffractometer (SHIMADZU, XD-5) using CuK α radiation. The operation conditions for the X-ray examinations were the following: 45 KeV accelerating voltage, 35 mA current, 10 ~ 60 2 θ scanning range, 0.02° step-width, and 4 /min scanning speed.

Extraction tests

Three extraction tests of ground samples (80-mesh) were conducted. Semi-dynamic extraction was conducted to examine the dynamic leaching behavior of Cu. The extractants used were 0.01 M HCl and 0.1 M NaOH. Extraction was performed in 50-mL centrifuge tubes, which were shaken in a reciprocal shaker bath (Yihder, BT350R) at 125 rpm, 25°C. Each tube contained 40 ml of extractant and 2 g of sample. Each extraction run included 12 batches, each batch lasting for 24 h. At the end of each extraction batch, the extract was separated in a high-speed centrifuge (Kubota, 6800) at 10,000 rpm (12,000 g) for 10 minutes. The supernatant was removed and analyzed with an AA (Perkin Elmer, 4000) for heavy metals concentrations and the residue was subjected to the next extraction batch by repeating the same procedure.

To fractionate Cu and analyze the total amounts of heavy metals, Tessier's method of sequential extraction was followed (Tessier *et al.*, 1979). Extraction was performed in 50-mL centrifuge tubes as before. Cu in the sample was fractionated according to exchangeable, acid-soluble, oxide-bound, organically-bound and residual forms.

Extraction at various pH was also conducted. 125-mL flasks were used and placed in the same bath as in semi-dynamic extraction and shaken at 125 rpm, 25°C. Each flask contained 1 g of sample (80 mesh) diluted to 40 ml. Fixed amounts of 1 M NaOH or 1 M HCl were used to adjust the pH to range from 1 ~ 13 prior to full dilution. Each extraction run lasted for 24 h. Separation was conducted as in semi-dynamic extraction. The supernatant was removed and analyzed with an AA (Perkin Elmer, 4000) and a TOC analyzer (O-I CORPORATION, 700) for concentrations of heavy metals and organics (dissolved organic carbon, DOC), and then the residue was discarded.

RESULTS AND DISCUSSION

The content of heavy metals in lime-treated sludge was reduced (Table 2) because lime added

Table 2. Characteristics of lime-treated and untreated sludges (by average)

Parameters	Sample types	
	Lime-treated sludge	Untreated sludge
pH ^a	12.05	7.65
Water (%)	6.99	0 ^c
VS ^b (%)	33.2	62.2
Cr (mg/Kg)	52.16	89.89
Pb (mg/Kg)	97.12	138.43
Zn (mg/Kg)	621.6	1089
Cu (mg/Kg)	119.4	202.0

^aDetermined in a 1:10 sample:0.01 M CaCl₂ solution.

^bDetermined by dry combustion in a muffle furnace at 550°C.

^cDetected after oven-dried

[reagent grade Ca(OH)₂, which did not contain any heavy metals] composed about one-half the total weight of lime-treated sludge after natural drying, thus diluting the concentration of heavy metals in the sludge. Because the combined water in lime-treated sludge varied after natural drying, we did not calculate the mass balance of the treatment. Lime-treated sludge was very alkaline (pH = 12.05); the effect of pH on leachabilities of Cu and organics was significant and will be discussed in the later sections. The other basic characteristics of lime-treated and untreated sludges are shown in Table 2.

Fractionation of Cu

Fractionation of Cu in untreated sludge to the exchangeable fraction was 4.99%; acid-soluble fraction, 3.14%; oxide-bound fraction, 1.23%; organically-bound fraction, 73.65%; and residual fraction, 17.0% (Fig. 1). Fractionation to the organically-bound form occurred the most often. This was consistent with the known affinity of Cu for organic ligands (McLaren and Crawford, 1973; Kerndorff and Schnitzer, 1980; Emmercih *et al.*, 1982). An increase in lime addition in lime-treated sludge led to an increase in the shift of Cu from the organically-bound fraction to the exchangeable and oxide

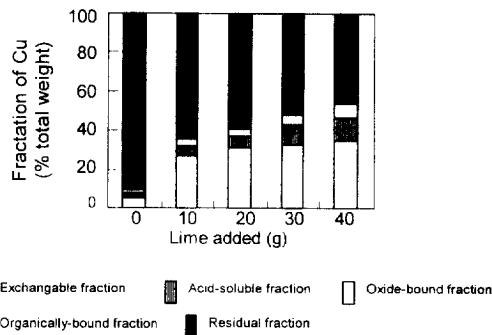


Fig. 1. Effects of lime addition on fractionation of Cu in sludges. *Compositions of samples, corresponding to the samples special for sequential extraction in Table 1, were: sewage sludge cake = 200 g (wet base); lime = 0 ~ 40 g. Tessier's method of sequential extraction was followed (Tessier, 1979).

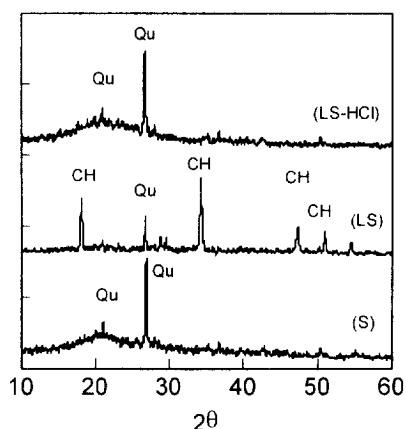


Fig. 2. XRD patterns of untreated sewage sludge (S), lime-treated sewage sludge (LS), and lime-treated sewage sludge after extraction by 0.01 M HCl (LS-HCl). *CH: calcium hydroxide; CC: calcium carbonate; and Qu: Quartz (SiO₂).

fractions (Fig. 1). Therefore, Cu in the treated sludge with a high level of lime leached more easily since the exchangeable Cu was the most labile. In other words, the lime treatment caused the Cu contained in sewage sludge to become unstable. This was attributed to the irreversible dissolution of organics with organically-bound Cu at very high pH during processing and natural drying of sludge. Conner (1990) stated that the cement-based organic immobilization process, which is also a kind of alkaline treatment, of organic wastes can increase heavy metal leaching if the pH of the process exceeds the normal range. The data of Sims (1991) also showed an increase in plant uptake of Cu due to increasing liming rate in the soils amended with composted sewage sludge. Some other authors have reported that liming increased heavy metal extractabilities (Bloomfield and Pruden, 1975; Kelling *et al.*, 1977).

The XRD patterns indicated that quartz (26.90°2θ) was the main mineral component in untreated sludge (Fig. 2). The lime treatment

reduced the peak intensity of quartz (26.90°2θ), which resulted from the reduced amount of inert matter in lime-treated sludge. Strong Ca(OH)₂ peaks and a weak CaCO₃ peak appeared for lime-treated sludge (Fig. 2), indicating that much of lime added was not exhausted by carbonation. The Ca(OH)₂ and CaCO₃ peaks of lime-treated sludge all disappeared after extraction by 0.01 M HCl for 12 batches in semi-dynamic extraction, indicating that CaCO₃ and Ca(OH)₂ were acid-soluble (Fig. 2). The XRD patterns of lime-treated sludge also indicated that concentrated OH⁻ was in the sludge during processing. A portion of Cu was thus assumed to have shifted from the organically-bound fraction to form hydroxides in lime-treated sludge. From the results of sequential extraction, Cu hydroxides possibly corresponded to the exchangeable and acid-soluble forms.

Extraction at various pH

The effects of both pH and organics on Cu in lime-treated and untreated sludges were significant. Cu leached more easily than its hydroxides at pH > 5 and less at pH < 5 using the calculated solubility of Cu hydroxides for comparison (not presented schematically). The leaching of Cu from lime-treated sludge was much higher than that from untreated sludge at almost all pH (Fig. 3a), and the trends of Cu leaching from lime-treated and untreated sludges (Fig. 3a) were similar to those of organic leaching (DOC) (Fig. 3b) except for very low pH. The association of Cu leaching to organics was obvious. The organic content of lime-treated sludge evaluated by muffled combustion was about one-half that of untreated sludge but its organic leaching (DOC) was many times that of untreated sludge at pH < 10 (Fig. 3b). The enhanced leaching of Cu and organics from lime-treated sludge was attributed to the irreversible dissolution of organically-bound Cu with organics at very high pH during processing and natural drying of sludge. After processing and natural drying of sludge, the

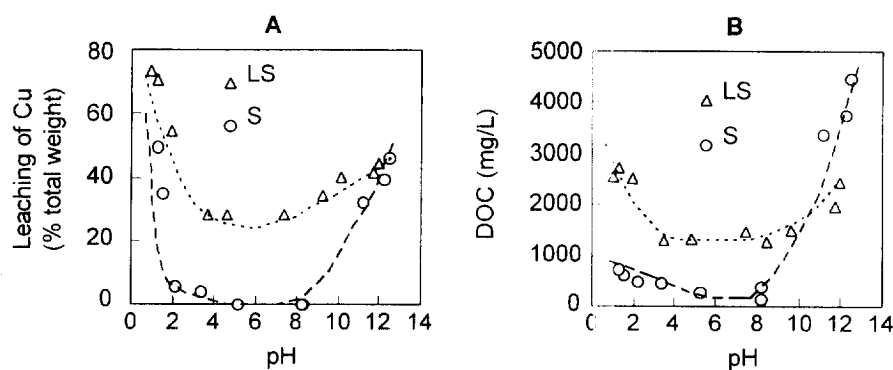


Fig. 3. Results of extraction at various pH. (a) Leaching of Cu from untreated and lime-treated sludges. (b) Leaching of organics (DOC) from untreated and lime-treated sludges. *pH was adjusted with 1 M HCl and 1 M NaOH. S: untreated sludge; LS: lime-treated sludge.

derived precipitants (due to drying of sludges) of organics and organically-bound metals from dissolution were acid-soluble and exchangeable, leading to the enhanced leaching of metals when extracted with a more acidic solution or an ion-exchangeable media. Organic matter was usually alkali-extractable. Thus, many other authors, such as Stover *et al.*, (1976) and Sposito *et al.*, (1982), extract organically-bound heavy metals from sewage sludge with NaOH as an extractant. The processing and natural drying of lime-treated sludge would lead to dissolution of organically-bound Cu with organics, which was due to the high pH associated with lime addition. Leita and Nobili (1991) mentioned that higher solubility of heavy metals at alkaline pH was attributed to enhanced formation of organic matter-metal complexes. The processing conditions of lime-treated sludge were similar to the extraction conditions of untreated sludge at very high pH, leading to strong leaching of organics and organically-bound Cu (Fig. 3a and 3b). Figure 3(a) and 3(b) also show that the leaching of Cu from lime-treated

sludge was less dependent on pH than was untreated sludge. This result was the same as those published by Bloomfield and Pruden (1975), who reported that raising the pH by the addition of lime did not decrease the extractability of heavy metals and that the extractable Cu appeared to be independent of pH.

As for extraction at acidic pH, a leaching break-point of Cu for untreated sludge at about pH = 2 reveals that the leaching of Cu (Fig. 3a) was unassociated with organics at very low pH since the leaching of organics (DOC) (Fig. 3b) from untreated sludge was still relatively low at that pH. Competition of protons for Cu binding sites was obvious. At about pH < 1, the percent leaching of Cu from untreated sludge was nearly the same as that from lime-treated sludge (Fig. 3a), but the leaching of organics from untreated sludge was much lower than that from lime-treated sludge (Fig. 3b), suggesting that Cu leaching was independent of organic leaching (DOC) at very low pH. Thus, proton competition controlled the leaching of Cu at very low pH.

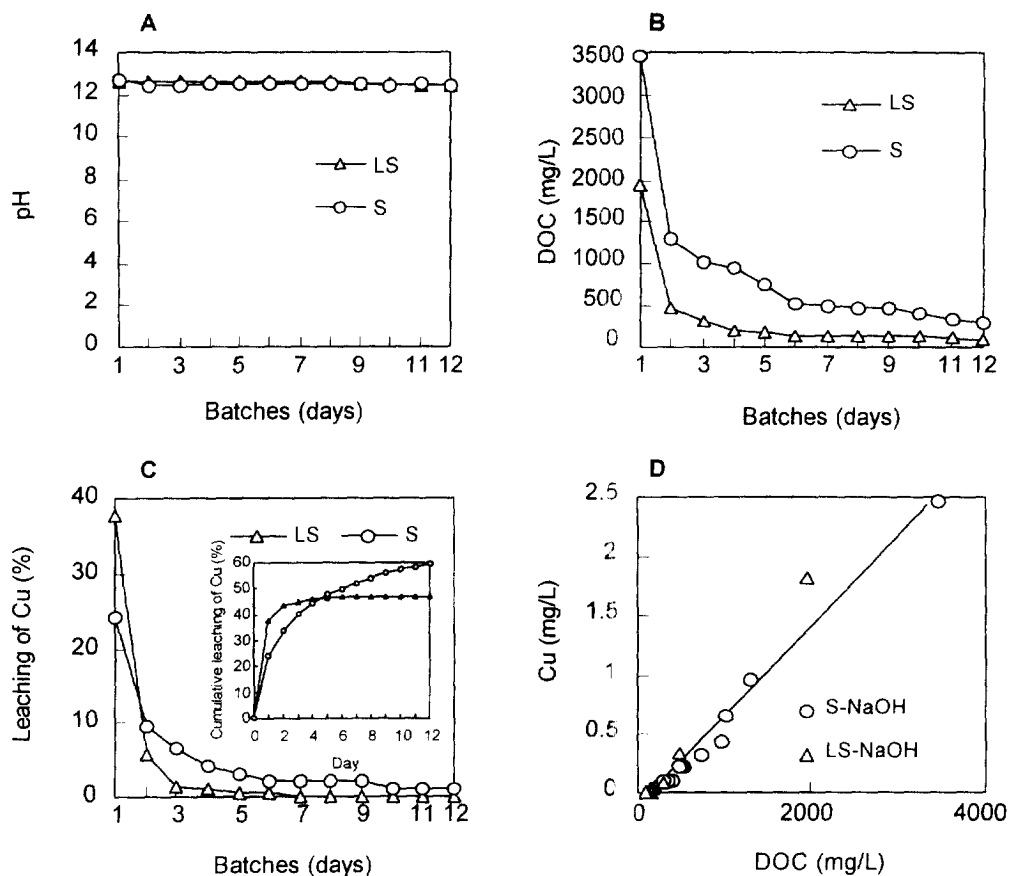


Fig. 4. Results of semi-dynamic extraction by 0.1 M NaOH. (a) Variations in pH; (b) variations in leaching concentration of organics (DOC); (c) variations of percent leaching of Cu; and (d) relationship between Cu concentration and dissolved organic carbon concentration (DOC) in the supernatant, of which the pH corresponds to (a). *LS: lime-treated sludge; S: untreated sludge.

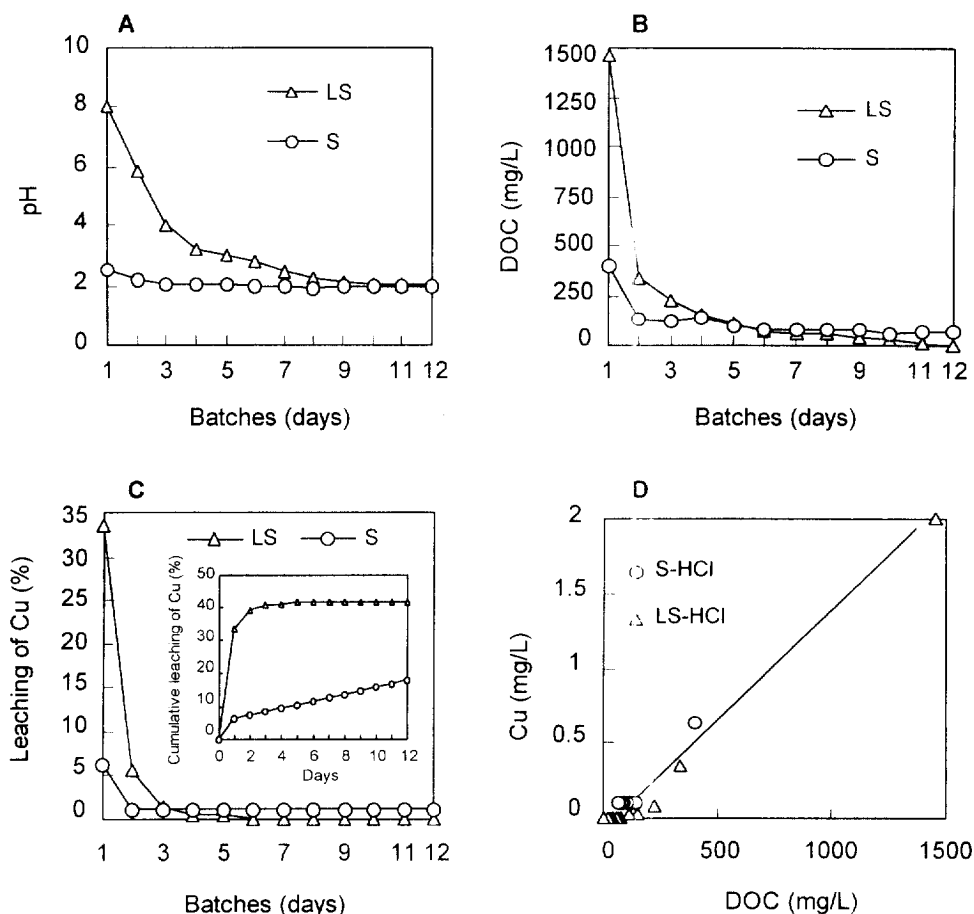


Fig. 5. Results of semi-dynamic extraction by 0.1 M HCl. (a) Variations in pH; (b) variations in leaching concentration of organics (DOC); (c) variations of percent leaching of Cu; and (d) relationship between Cu concentration and dissolved organic carbon concentration (DOC) in the supernatant, of which the pH corresponds to (a). *LS: lime-treated sludge; S: untreated sludge.

Semi-dynamic leaching of Cu

A major portion of Cu in lime-treated sludge leached before the third batch (day) when extracted with 0.1 M NaOH (Fig. 4c). The percent leaching of Cu from lime-treated sludge (38%) was higher than that from untreated sludge (24%) for the first batch (day) (Fig. 4c) and then was exceeded by untreated sludge after the second batch (day). This means that the percent leaching of Cu from lime-treated sludge was more rapid but that from untreated sludge lasted for more time, which are illustrated by the percent cumulative leaching of Cu in the inset diagram of Fig. 4(c). The curves depicting the leaching behavior of Cu (Fig. 4c) and organics (DOC) (Fig. 4b) were very similar in shape. Thus, the plot of Cu concentration (mg/L) versus organic carbon concentration (DOC) (mg/L) in the supernatant, of which the pH corresponds to Fig. 4(a) and ranges from 12 ~ 13, shows a linear relationship, indicating that the leaching of Cu depended on the leaching of organics (Fig. 4 d). Leaching of Cu was thought to be due to complexa-

tion of Cu with alkali-soluble organics in the extracts because both Cu carbonates and Cu hydroxides are of low solubility at such alkaline pH when extracted by 0.1 M NaOH.

When extracted with 0.01 M HCl, the curves depicting the leaching behavior of Cu (Fig. 5c) and organics (DOC) (Fig. 5b) were also very similar in shape. Thus, the plot of Cu concentration (mg/L) versus organic carbon concentration (mg/L) in the supernatant of which the pH corresponds to Fig. 5(a) and ranges from 2 to 8, also shows a linear relationship, suggesting the association of Cu leaching with organics (Fig. 5 d). Hence, the leaching of Cu from lime-treated and untreated sludges was assumed to be caused also by complexation of Cu with organics in the extracts (at about pH > 2) when extracted by 0.01 M HCl. However, at about pH < 2, proton competition for Cu binding sites would lead to strong leaching of Cu as discussed in the above section (Fig. 3a).

On the other hand, the percent leaching of Cu from lime-treated sludge was much higher than that from untreated sludge for the first batch (day)

(Fig. 5c), resulting in a great difference of percent cumulative leaching of Cu between untreated sludge and lime-treated sludge. By redrawing Fig. 5(c) cumulatively (See the insert diagram in Fig. 5c), we can see that the percent cumulative leaching of Cu from lime-treated sludge (41%, 12th day) was much higher than that from untreated sludge (18%, 12th day). This is consistent with the assumption in the previous section that the enhanced leaching of Cu from lime-treated sludge was attributed to the irreversible dissolution of organically-bound Cu at very high pH during processing and natural drying of sludge. The processing condition of lime-treated sludge and the extraction condition of untreated sludge at very high pH was very similar, leading to the strong leaching of organics and organically-bound Cu (Fig. 3a). As a consequence, the lime treatment of sewage sludge increased not only the percent leaching of Cu after one day of extraction, but also the percent cumulative leaching of Cu after 12 days of extraction when extracted with dilute acid (0.01 M HCl).

CONCLUSIONS

Of the five forms in untreated sludge, the organically-bound form (73.7% by weight) was the form most favored by Cu after fractionation. The lime treatment, on the other hand, resulted in a decrease of organically-bound Cu. Increasing lime addition in lime-treated sludge mainly caused a shift of Cu from the organically-bound to the exchangeable and acid-soluble fractions, meaning that lime treatment caused Cu to become unstable. Extractions performed at various pH also indicated that leaching of Cu from lime-treated sludge was much higher than that from untreated sludge at most pH. The leaching trend was consistent with that of organics (DOC), suggesting that the enhanced leaching of Cu resulted from an irreversible dissolution of organically-bound Cu at highly alkaline pH during processing and natural drying of sludge. Considering that the instability of Cu in sewage sludge after lime treatment resulted from its known affinity for organics, the affinity of other heavy metals for organics in sewage sludges would be also an interesting factor for their stability when treated with lime or other alkaline additives.

REFERENCES

- Bloomfield C. and Pruden G. (1975) The effects of aerobic and anaerobic incubation on the extractabilities of heavy metals in digested sewage sludge. *Environ. Pollut.* **8**, 217-232.
- Conner J. R. (1990) *Chemical Fixation and Solidification of Hazardous Wastes*. Reinhold, New York. 376-406.
- Emmerich W. E., Lund L. J., Page A. L. and Chang A. C. (1982) Predicted solution phase forms of heavy metals in sewage sludge-treated soils. *J. Environ. Qual.* **11**, 178-182.
- Kelling K. A., Keeney D. R., Walsh L. M. and Ryan J. A. (1977) A field study of the agricultural use of sewage sludge: III. Effect on uptake and extractability of sludge-borne metals. *J. Environ. Qual.* **6**, 352-358.
- Lake D. L., Kirk P. W. and Lester J. N. (1984) Fractionation, characterization, and speciation of heavy metals in sewage sludge and sludge-amended soil: A review. *J. Environ. Qual.* **13**, 175-183.
- Leita L. and Nobili M. D. (1991) Water-soluble fractions of heavy metals during composting of municipal solid waste. *J. Environ. Qual.* **20**, 73-78.
- Lo K. S. L. and Chen Y. H. (1990) Extracting heavy metals from municipal and industrial sludges. *The Science of the Total Environment* **90**, 99-116.
- McLaren R. G. and Cuawford D. V. (1973) The fractionation of copper in soils. *Journal of Soil Science* **24**, 172-181.
- Outwater A. B. (1994) *Reuse of Sludge and Minor Wastewater Residuals*. CRC press, Florida. 101-111.
- Ruce T., Campbell J. A. and Lester J. N. (1986) Characterization of metal forms in sewage sludge by chemical extraction. *Chemicals in the Environment*. Lester J. M., Perry R. and Sterritt R. M. (Eds).
- Sims J. T. (1991) Chemical fractionation and plant uptake of heavy metals in soils amended with co-composted sewage sludge. *J. Environ. Qual.* **20**, 387-395.
- Sloan J. J. and Basta N. T. (1995) Remediation of acid soils by using alkaline biosolids. *J. Environ. Qual.* **24**, 1097-1103.
- Soon Y. K. and Bates T. E. (1982) Chemical pools of cadmium, nickel, and zinc in polluted soils and some preliminary indications of their availability to plants. *J. Soil Sci.* **33**, 477-488.
- Sommer L. E. (1977) Chemical composition of sewage sludges and analysis of their potential use as fertilizers. *J. Env. Qual.* **6**, 255.
- Spiegel S. J., Farmer J. K. and Garver S. R. (1985) Heavy metal concentrations in municipal wastewater treatment plant sludge. *Bull. Env. Contam. Tox.* **35**, 18.
- Stover R. C., Sommers L. E. and Silvera D. J. (1976) Evaluation of metals in wastewater sludge. *J. Water Pollut. Control Fed* **48**, 2165-2175.
- Stumm W. and Morgan J. J. (1981) *Aquatic Chemistry*. 2nd ed. John Wiley & Sons, New York.
- Tack F. M. G. and Verloo M. G. (1995) Chemical speciation and fractionation in soil and sediment heavy metal analysis: A review. *Intern. J. Environ. Anal. Chem.* **59**, 225-238.
- Tessier A., Campbell P. G. C. and Bisson N. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* **51**, 844-851.