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Extraction of copper from sewage sludge using biodegradable chelant EDDS

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Abstract

[*S*,*S*]-Ethylenediaminedisuccinic acid (EDDS), a biodegradable chelant, was used to separate the heavy metals from the sewage sludge based on chemical extraction technology. Under various conditions, the extraction experiments were carried out for the sewage sludge from Shanghai Taopu Municipal Wastewater Plant, China. The influences of pH and the concentration of EDDS on the extraction efficiency for copper (Cu) were discussed. The results showed that EDDS had higher extraction efficiency for Cu from the sewage sludge than other heavy metals. The system pH and the concentration of EDDS had a significant effect on the extraction efficiency. The extraction efficiency of Cu increased gradually with the increase of system pH and reached a higher efficiency within pH range of 3–10. The extraction efficiency maintained at approximately 70% when the pH $\geqslant$ 4.5 and the molar ratio of EDDS to total heavy metals was 10:1. From the fractional analysis of the heavy metals in sewage sludge before and after the extraction, it was found that the extracted Cu mainly came from the following four fractions, i.e. water soluble, acid-soluble, reducible, and oxidizable fractions.

Key words: copper; EDDS; extraction; sewage sludge; biodegradable

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Introduction

Heavy metal pollution of soil, sediment, and sewage sludge is widespread across the globe (Shiro and Tahei, 2000; Philippe *et al*., 2001; Sun *et al*., 2001; Susan *et al*., 2004; Pueyo and Ruret, 2004; Wang *et al*., 2006), and the decontamination of heavy metal remains a difficult task. Sewage sludge is recognized as a valuable resource that can be reused as fertilizer and soil improvement material for land. This is because sewage sludge consists largely of organic substances and nitrogen and phosphorus, which are the main nutritional elements for plants. However, sewage sludge consists of not only valuable components such as nutrients but also heavy metals. Heavy metals are nonbiodegradable and accumulate in the environment. The retained heavy metals in sewage sludge, thus, pose a risk to human health and phytotoxicity from land application which restricts significantly the reuse of sewage sludge (Veeken *et al*., 1999; Shiro and Tahei, 2000). Therefore, methods to remove the heavy metals from sewage sludge has attracted a lot of attention in recent years (Philippe *et al*., 2001; Sun *et al*., 2001; Susan *et al*., 2004; Pueyo and Ruret, 2004; Wang *et al*., 2006). Copper (Cu), being an environmental priority pollutant, has been given more attention for its transportation, decontamination, and biological enrichment (Philippe *et al*., 2001; Zeng *et al*., 2003; Susan *et al*., 2004; Pueyo and Ruret, 2004; Zhu *et al*., 2006).

Various methods for heavy metal removal from sewage sludge have been investigated to minimize the prospective health risks due to sludge during land application. Despite many efforts, sufficient removal of heavy metals from sewage sludge remains unachievable (Shiro and Tahei, 2000). One possible remedial technique is *ex-situ* washing using a chelating agent that has a high potential extraction efficiency and specificity for heavy metals (Van Benschoten *et al*., 1997; Sun *et al*., 2001; Theodoratos *et al*., 2000; Barona *et al*., 200l; Zeng *et al*., 2006; Lei *et al*., 2005). Till date, ethylenediaminetetraacetic acid (EDTA), a very effective chelating agent, is used widely for heavy metal decontamination (Theodoratos *et al*., 2000; Barona *et al*., 2001; Zeng *et al*., 2003; Zeng *et al*., 2006). However, the possibility of secondary pollution of the chelating agent itself also must be considered because a part of the chelating agent will remain in the sewage sludge after the extraction. Thus, it is important to consider the degradability of chelating agents (Paul and David, 2001; Philippe *et al*., 2001; Susan *et al*., 2006; Qian *et al*., 2006). EDTA is very effective in mobilizing metals, but unfortunately, EDTA has the disadvantage of being quite persistent in the environment due to its low biodegradability. Recently, the easily biodegradable chelating agent

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[*S,S*]-ethylenediaminedisuccinic acid (EDDS) has been proposed as a safe and environmentally benign replacement for EDTA in soil washing (Philippe *et al*., 2001; Paul and David, 2001; Susan *et al*., 2004; Lukas *et al*., 2005). In addition, it is also used for chelant enhanced phytoremediation (Susan *et al*., 2006; Qian *et al*., 2006). EDDS has shown good ability of chelating with various metal ions (Philippe *et al*., 2001; Paul and David, 2001; Susan *et al*., 2004; Lukas *et al*., 2005) and has shown ready biodegradability (Susan *et al*., 2006; Philippe *et al*., 2001). Researchers also investigated the possibility for using EDDS to decontaminate heavy metals from sewage sludge and harbor sediments. However, previous work in relation to EDDS has mostly concentrated on soil remediation field (Susan *et al*., 2004, 2006; Qian *et al*., 2006).

This investigation is focused on the removal of Cu retained in sewage sludge using EDDS as an environmental benign extractant. Hopefully, the study will be helpful in the formation of green remediation technology of soils and sewage sludge contaminated with heavy metals.

1 Materials and methods

1.1 Sewage sludge

The sewage sludge used in this study was obtained from Shanghai Taopu Municipal Wastewater Plant, China. The sewage sludge samples were air dried naturally, ground, and sieved to a size less than 2 mm. The sludge is solid with 27.97% total organic carbon (TOC) and 8.23% water. The tested sludge contains heavy metals including Zn, Cu, Cr, Ni, Pb, and Cd. The sum of the heavy metals Zn, Cu, Cr, Ni, Pb, and Cd in sewage sludge was found to be 255.4 mmol/kg. The content of Cu was found to be 4,260 mg/kg (Table 1), which exceeded the "third level" limited value of Environmental Quality Standard for Soils in China and the limited level of Sludge Agricultural Utilization Standard for Soil in China. Cu, thus, must be removed from sewage sludge before the agricultural use of the sludge.

1.2 Chelating agent

EDDS was obtained from Sigma-Aldrich Company (USA). EDDS is readily biodegradable and its structure is shown in Fig.1. The molecular weight of trisodium salt of EDDS ($C_{10}H_{13}N_2Na_3$) is 358.19, solid content is 30%, and density is 1.274 g/cm^3 at 20°C. The other reagents are all analytical grades and obtained from the National Chemical Reagent Company Limited in Shanghai, China.

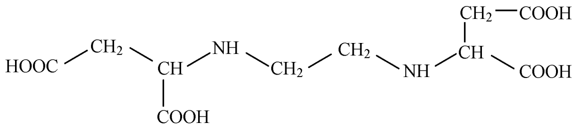

Fig. 1 Structure of [*S,S*]-ethylenediaminedisuccinic acid (EDDS).

1.3 Extraction experiments

The extraction experiments were carried out in centrifugal tubes in an aqueous suspension. Chelating agents were applied in two concentrations, and the molar ratio between chelant and the sum of the total metals of Zn, Cu, Cr, Ni, Pb, and Cd in sewage sludge was 1:1 and 10:1, respectively.

For each batch test, 0.5 g of sewage sludge was suspended in 25 ml of the solution and the extraction time was fixed at 24 h. Metal extractions were carried out in batch experiments at a solid: solution ratio of 1:50. The pH was adjusted with HNO_3 or NaOH at 2 d before the addition of the chelating agent. The system pH was measured in suspension and readjusted, if necessary. The suspensions were shaken at 200 r/min for 24 h at room temperature. All suspensions were centrifuged at 4,000 r/min for 20 min and passed through 0.45 μm membrane filters before the metal analysis.

To determine the total content of heavy metals in tested sewage sludge, sludge samples were digested with HF-HCl-HNO_3 with ETHOS E Microwave Extraction/Digestion System (Mile Stone s.r.l., Italy). For determining the fractional distribution of heavy metals in sewage sludge, samples of 0.5 g of sewage sludge were analyzed by modified BCR sequential extraction method (Quevauviller *et al*., 1997; Davidson *et al*., 1998) before and after the extraction with EDDS.

1.4 Analytical methods

The TOC of the sewage sludge was determined by SSM-5000A Total Organic Carbon Analyzer (SHIMADZU, Japan). The concentration of dissolved heavy metals in the digestion solutions and extraction solutions were measured with Optima 2100 DV Inductively Coupled Plasma Optical Emission Spectrometry (PerkinElmer, USA). The extraction solution pH was measured with PP-15 Professional pH meter (Sartorius, Germany).

The work conditions of plasma were listed as follows: plasma gas flow 15 L/min, auxiliary gas flow 0.2 L/min, nebulizer gas flow 0.80 L/min, RF power 1,300 W, sample flow rate 1.50 ml/min, and the determination temperature 20°C.

Triplicate extractions were performed, and the data from the three parallel experiments were averaged.

2 Results and discussion

2.1 Extraction of Cu from sewage sludge with EDDS

The influence of solution pH on the extraction efficiency

Table 1 Content of Cu in tested sewage sludge (unit: mg/kg)

Heavy metal	Content	The sludge agriculture utilization standard[a]		Environment quality standard for soils (the third level)[b]
		Acid soil (pH < 6.5)	Alkali soil (pH ⩾ 6.5)	
Cu	4,260	800	1,500	400

[a] National Standard GB 18918-2002, China. [b] National Standard GB 15618-1995, China.

of Cu from the sewage sludge was examined with a series of pH from 1 to 10. The extraction efficiency of Cu from sewage sludge with EDDS is shown in Fig.2. This showed that the pH of extraction system affected significantly the extraction efficiency of Cu. The results indicated that without chelant the extraction efficiency decreased rapidly with increase in pH and was below 5% when the solution pH > 3.5. As it contained EDDS as the extractant, the extraction efficiency was improved obviously within a wide pH range from 3 to 10. The extraction efficiency of Cu maintained approximately 70% under conditions of the molar ratio of EDDS to total heavy metals being 10:1 and system pH ⩾ 4.5. The extraction efficiency of Cu still maintained above 50% when the molar ratio was 1:1 and system pH ⩾ 3.5. For the EDDS extraction experiments, the Cu extraction efficiency also decreased with increasing pH within the pH range 1–3. The possible reason is the solubility reduction of EDDS in water. It was found that the EDDS would deposite in the water solution when the system pH < 3. Thus, the extraction efficiency of Cu mainly contributed to the acidity of the solution when pH < 3 even when EDDS was used as the extractant.

The molar ratio of chelating agent to heavy metals is another important factor affecting the extraction efficiency. Some studies have found that a ratio more than 1 between chelant and toxic metal is required to give good toxic metal extraction (Susan *et al.*, 2004). One reason for an excess of chelating agent is that major cations in the sewage sludge, such as Ca and Fe along with toxic metals existing in smaller amounts, compete with the metals being studied for the chelating agent and were extracted too. The extraction efficiency of Cu reached approximately 70% when the molar ratio of EDDS to heavy metals was 10:1, whereas the extraction efficiency was only approximately 50% when the ratio was 1:1.

2.2 Relationship between extraction efficiency and distribution of copper in sewage sludge

The factors which affect the extraction efficiency of Cu from sewage sludge include not only the system pH and EDDS concentrations, but also the content and fractional distribution of the heavy metals in the sewage sludge. Total concentration of heavy metals provide little indication of environmental impact because they do not provide detailed information on potential environmental mobility or bioavailability. The sequential extractions could give the information needed to explain different extraction efficiencies for different heavy metals (Susan *et al.*, 2004). Among various sequential extraction techniques, Tessier sequential extraction (Tessier *et al.*, 1979) and BCR sequential extraction (Quevauviller *et al.*, 1997; Davidson *et al.*, 1998) are two usual techniques to determine the fractional distribution of heavy metals in soil, deposition, and sewage sludge. BCR method has better reproducibility, precision, and comparable performance (Quevauviller *et al.*, 1997). In BCR sequential extraction method, the metal elements are divided into acid-soluble, reducible, and oxidizable fractions. In modified BCR sequential extraction method, two fractions including water soluble and residual fractions are added.

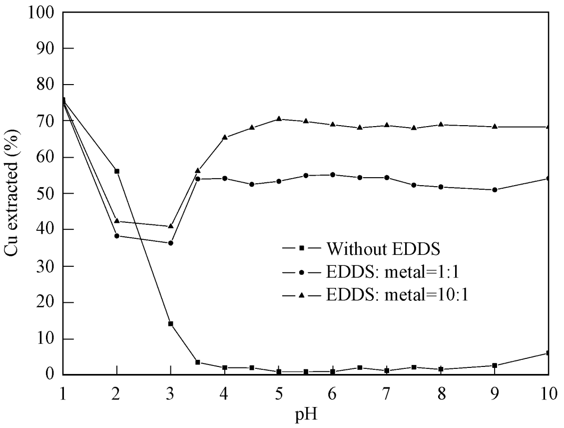

Fig. 2 Extraction of Cu from sewage sludge with EDDS.

The distribution of heavy metal fractions in tested sewage sludge before and after the extraction with EDDS were examined using the modified BCR sequential extraction method. The experiments were carried out under the condition of pH 8 and the molar ratio between the chelant and the sum of the total metals in sewage sludge was 10:1. As shown in Fig.3, Cu in tested sludge before extraction existed mainly in oxidizable fraction, the content was approximately 75%. Whereas the residual fraction, reducible fraction, and acid-soluble fraction were found with the content approximately at 15%, 5%, and 4%, respectively, and water soluble fraction was approximately at 1%. After the extraction with EDDS, the fractional distribution of Cu had changed. It was found that Cu existed mainly in residual fraction and oxidizable fraction, whereas other fractions including oxidizable fraction reduced remarkably in the solid state of sewage sludge after the extraction with EDDS. This indicated that the extracted Cu from the tested sewage sludge with EDDS came mainly from the following fractions, the water soluble, acid-soluble, reducible, and oxidizable fractions. The highest extraction efficiency of Cu reached approximately 70% under the experimental conditions. The results of the extraction efficiency and the change of distribution of heavy metals before and after the extraction with EDDS were in consistent.

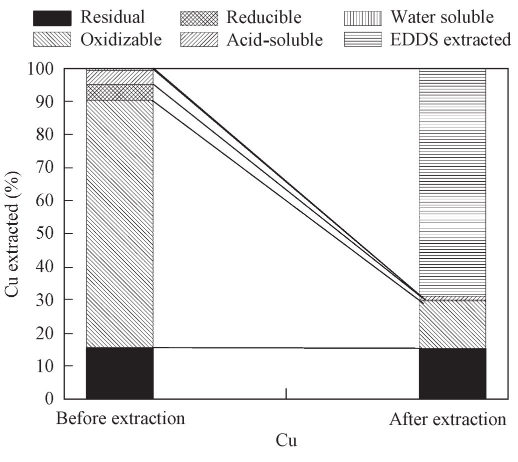

Fig. 3 Distribution of Cu fractions in sewage sludge before and after extraction with EDDS (extraction conditions: pH 8, ratio of EDDS and sum of heavy metals 10:1).

Table 2 Comparison of Cu extraction efficiency obtained in this study with other published data at pH 7 and contacting time 24 h

Chelant	Medium	Chelant : Metal	Extraction efficiency (%)	Reference
EDTA	Soil	1:1	36	Susan *et al*., 2004
EDTA	Soil	1:1	50	Philippe *et al*., 2001
EDTA	Soil	10:1	84	Susan *et al*., 2004
EDTA	Sewage sludge	10:1	72	This study
EDDS	Soil	1:1	53	Susan *et al*., 2004
EDDS	Soil	10:1	67	Susan *et al*., 2004
EDDS	Sewage sludge	1:1	55	This study
EDDS	Sewage sludge	10:1	70	This study

2.3 Comparison with other chelants

To compare the Cu extraction efficiency between EDDS and EDTA, the extraction of Cu from the sewage sludge with EDTA was conducted simultaneously under the same conditions with ratio of 10:1. As shown in Fig.4, within the pH range 4–10, both EDDS and EDTA had a good and similar efficiency for the Cu extraction from the sewage sludge. This can be explained by the stability of Cu complexes with EDDS and EDTA because EDDS-Cu and EDTA-Cu have a similar stability constant with the logβ of 18.4 (Martell *et al*., 2001) and 18.78, respectively. While the system pH was lower than 4, EDDS showed a special phenomena (Fig.2). This may be mainly attributed to the solubility reduction of EDDS in water. When pH was lower than 4, the extraction efficiency of Cu under the experimental conditions mainly depended on the acidity of the solution for EDDS.

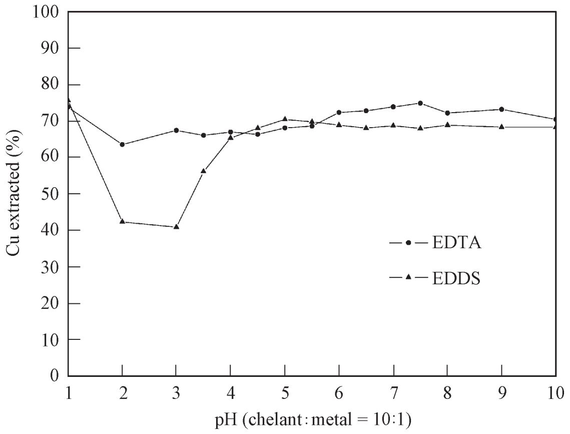

Fig. 4 Comparison of Cu extraction with EDDS and EDTA.

The extraction results in this study and some previous reports are listed together in Table 2. The extraction efficiency of Cu covers a range from 36% to 84% (Table 2). The result obtained with EDDS and EDTA in this study is comparative with the reports in other literature. Compared with the difficult biodegradable EDTA, EDDS can be considered as a promising biodegradable chelating agent for extraction of heavy metals such as Cu from sewage sludge.

3 Conclusions

EDDS had a good efficiency for the extraction of Cu from the sewage sludge. The extracted Cu came mainly from the four fractions including the water soluble, acid-soluble, reducible, and oxidizable fractions. The extraction efficiency for Cu reached approximately 70% under the condition of pH $\geqslant$ 4.5 and the molar ratio of EDDS to the total heavy metals in sewage sludge was 10:1. Compared with the difficult biodegradable EDTA, EDDS can be considered as a promising biodegradable chelating agent for extraction of heavy metals such as Cu from sewage sludge.

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