嘉南藥理科技大學專題研究計畫成果報告

以生物淋溶法去除大型綜合污水處理廠污泥中重金屬之研究

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中文摘要

本研究目的乃在探討以生物淋溶法去除大型污水處理廠三種污泥中重金屬銅、鋅之可能性。結果顯示，經生物淋溶後，硫氧化菌對濃縮池及消化槽污泥之氧化活性較大。濃縮池及消化槽污泥之 pH, ORP 及硫酸鹽之變化及銅、鋅之去除率皆顯著比曬乾床污泥大。在經 16 天淋溶後，銅、鋅在濃縮池及消化槽污泥之主要鍵結態由與有機物鍵結態轉為與碳酸鹽鍵結態。

Abstract To investigate the effect of bioleaching on the removal of Cu and Zn from varying kinds of sludge from large wastewater treatment plant for evaluate the possibility of treatment, three kinds of sludge (thickener, digester and drying-bed) were tested. Results indicate that oxidizing activity of sulfur-oxidizing bacteria to the sludge was greatest in the sludge of both thickener and digester. The changes of pH, ORP and sulfates in the sludge of both thickener and digester were faster than that in drying-bed sludge whereas the removal efficiencies of the total extractable Cu and Zn in the sludge of both thickener and digester were also significantly higher than that in drying-bed sludge. The mainly partitioning pool of Cu and Zn in both thickener and digester sludge after 16 days of bioleaching were switched to carbonates fraction.

Keywords Bioleaching; heavy metal; sludge; sulfur-oxidizing bacteria

Introduction

Wastewater treatment plants generate large amount of residual sludge, which maybe contain some toxic substances, such as heavy metals and chlorinated organics. The application of sludge on agricultural land might result in the pollution of soil. Several chemical and microbial methods have been reported for the treatment of sludge (Seidel, 1997;Ito, 2000;Tyagi, 1993;Blais, 1992a, b, c;Couillard, 1991; Kitada, 2000). Although mineral acids and chelating agents have commonly been used to mobilize heavy metals, such chemical methods are more costly than microbial ones. Tyagi *et al.* (1993) found a microbial method of metal leaching to be 80% cheaper than an acid-requiring chemical one due to a lesser requirement for acid and lime. Operational difficulties in using acids, including the need for acid-resistant apparatus and safe storage and transportation facilities for the acid, also make such chemical methods unattractive. In the past decade, the ability of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* to remove trace metals from sewage sludge and from sediments has been studied. Operational conditions studied include sediment characteristics, initial pH of sediment, percentage of inoculum, retention time, total solid content, percentage of substrate added, temperature, and nutrition.

In the above studies, heavy metal derived from bioleaching was termed ‘total metal content.’ In addition to the total metal content, the distribution of metals among various fractions in the sediment is a useful measure as it determines the behavior of the metal in the environment. Chartier *et al.* (2001) describe the partitioning of trace metals into different fractions before and after their biological removal from sediments. Partitioning information would allow an investigation of which metals, bound to which fractions, are removed during bioleaching.

The An-Ping industrial wastewater treatment plant, located in southern Taiwan, has the average treatment capacity of about 7000CMD. The influent of this plant discharging from varying industries contains different kinds of pollutants, including heavy metals. The treatment process of this plant mainly consists of the activated sludge system and chemical coagulation units. Therefore, a large amount of biological and chemical sludge containing heavy metals are produced.

The aim of this study is (1) to investigate the effect of bioleaching on the removal of Cu and Zn from varying kinds of sludge (thickener, digester and drying bed) for evaluate the possibility of treatment, and (2) to explore the changes in metal binding characteristics that occur during bioleaching.

Materials and Methods

Sampling

Three sludge samples were taken from

thickener, anaerobic digester and drying bed of the An-Ping industrial wastewater treatment plant.

Chemical analysis

The gravimetric method was used for the measurements of total solids and volatile solids in sludge. Heavy metals (Cu and Zn) partitioning in five different fractions (exchangeable, bound to carbonates, bound to Mn-oxides, bound to Fe-oxides, and bound to organic matters) were analyzed using the modified sequential extraction procedure (SEP) (Nelson, 1982; Tessier, 1979) to determine in which fraction they were held, and in what amounts. After the first extraction, the sludge was washed by shaking with de-ionized water for 1 minute, and centrifuged, prior to each subsequent extraction.

The amount of Cu and Zn in each fraction was determined using an atomic absorption spectrophotometer (GBC AA960, Australia). The total extractable amount of any specific heavy metal (TEHM) is defined as the sum of the amounts of that metal found in the five fractions.

Enrichment and bioleaching

Sulfur-oxidizing bacteria were enriched by adding bacteria-containing sludge from the An-Ping industrial wastewater treatment plant to a culture medium (1.29g/L sulfur [prepared from $Na_2S_2O_3 \cdot 5H_2O$], 1g/L NH_4Cl, 1g/L KH_2PO_4, and 0.5g/L $MgCl_2 \cdot H_2O$), at 2% (v/v). The medium provided nutrition, a sulfur substrate, and buffer capacity, for the growth of sulfur oxidizing bacteria in the sludge. This solution was shaken in a flask at either 25℃ until the pH of the sludge solution had steadied at <2.0.

Batch experiments were performed in 500mL Erlenmeyer flasks at three controlled temperatures (25 ℃) and 120rpm. A concentration of 6.4 g/L (dry wt) sludge was prepared in the Erlenmeyer flasks containing 250mL of the same culture medium used in enrichment. Each of the flasks was inoculated with 2% (v/v) of bacteria-enriched solution. Duplicate flasks were used at each temperature for both enrichment and bioleaching.

Results and Discussion

Characteristics of sludge

The thickener sludge consisted of 97.68 % water and 2.32 % solids. 73.15% of the thickener solids were volatile solids (VS) (see Table 1). The digester sludge consisted of 97.14 % water and 2.86 % solids. 57.58 % of the digester solids were VS. The drying-bed sludge consisted of 8.73 % water and 91.27 % solids. 59.60% of the drying-bed solids were VS.

Copper and Zn provided TEHM figures in thickener sludge, at 448.38 mg/kg and 325.83 mg/kg respectively (see Table 2). Distribution of heavy metals in each fraction is also shown in Table 3. Of total extractable Cu, 92.2% was bound to organic matters, showed a high affinity for binding organics. Of total extractable Zn, 40.56% was bound to Fe-oxides and 40.86% was bound to organic matters.

TEHM of Cu and Zn in digester sludge were 449.63 mg/kg and 2699.86 mg/kg respectively (see Table 2). Distribution of heavy metals in each fraction is also shown in Table 3. Of total extractable Cu, 96.89% was bound to organic matters, showed a high affinity for binding organics. Of total extractable Zn, 23.36% was bound to carbonates, 23.67 % was bound to Fe-oxides and 25.11 % was bound to organic matters.

Copper and Zn provided high TEHM in drying-bed sludge, at 1255.66 mg/kg and 3307.61 mg/kg respectively (see Table 2). Distribution of heavy metals in each fraction is also shown in Table 3. Of total extractable Cu, 89.00 % was bound to organic matters, showed a high affinity for binding organics. Of total extractable Zn, 20.57 % was bound to carbonates, 20.12 % was bound to Fe-oxides and 28.87 % was bound to organic matters.

Changes of pH, ORP, and sulfates in sludge after bioleaching

In bioleaching, because removal of heavy metals from sludge occurs via bio-oxidation and acidification, changes in sediment pH over time can be used to represent the degree of bioleaching. Sludge pH decreased from 6.67 (initial pH) to 1.53 after 10 days in thickener sludge, and from 6.66 (initial pH) to 1.74 after 12 days in digester sludge. This result indicates that the bioleaching rate of both sludge are fast.

However, sludge pH increased from 7.18 (initial pH) to 8.80 in drying-bed sludge and then decreased to pH 2.02 after 27 days (Fig. 1). In drying-bed sludge there was an initial rise in pH, perhaps caused by the buffer or by the release of alkaline from sediment during the initial stage of bioleaching. In accordance with this result and analysis, Sreekrishnan *et al.* (1996) indicated that an initial rise in pH in their investigation of bioleaching in sludge could be due to the release of alkaline, as did Seidel *et al.* (2001) in their study of bioleaching in coal fly ash.

Changes in oxidation-reduction potential (ORP) also indicate the level of activity of sulfur oxidizing bacteria. The ORP in both sludge of thickener and digester increased more rapidly than it did in drying-bed (Fig. 2). This indicates that there was more oxygen input and uptake to satisfy sulfur-oxidation by sulfur oxidizing bacteria as well as the formation of oxidized substances highly increased in the sludge of both thickener and digester.

A third indicator of bioleaching efficiency is sulfate concentration. The amount of sulfides oxidized to sulfates in the sludge of both thickener and digester was markedly higher than that in drying-bed sludge (Fig. 3).

TEHM changes after bioleaching

In the sludge of thickener, the removal efficiencies of total extractable Cu and Zn after 16 days were 89.2 % and 71.8 %, respectively (Table 3). Removal efficiencies of Cu and Zn in the sludge of digester after 16 days were 65.6 % and 90.4 %, respectively. However, the removal efficiencies of Cu and Zn in the sludge of drying-bed sludge after 16 days were only 22.3 % and 15.7 %, respectively. This result indicate that the removal of Cu and Zn from drying-bed sludge by bioleaching is not effective than that from both sludge of thickener and digester.

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Table 1 Characteristics of raw sludge

Items	Thickener	Digester	Drying bed
Raw sludge			
Water content, %	97.68	97.14	8.73
Total solids, %	2.32	2.86	91.27
Volatile solids, %	73.15	57.58	59.60
Fixed solids, %	26.85	42.42	40.40

Table 2 Binding fractions of heavy metals in raw sludge

Metals	Exchange-able (%)	Bound to carbonates (%)	Bound to Mn-oxides (%)	Bound to Fe-oxides (%)	Bound to organic matters (%)	TEHM (mg/Kg)
Thickener						
Cu	6.2	1.3	0.0	0.3	92.2	448.38
Zn	3.4	10.5	15.2	40.6	40.7	325.83
Digester						
Cu	2.3	0.6	0.0	0.2	96.9	449.63
Zn	10.4	23.4	17.4	23.7	25.1	2699.86
Drying-bed						
Cu	6.3	4.3	0.0	0.4	89.0	1255.66
Zn	15.2	20.6	15.3	20.1	28.8	3307.61

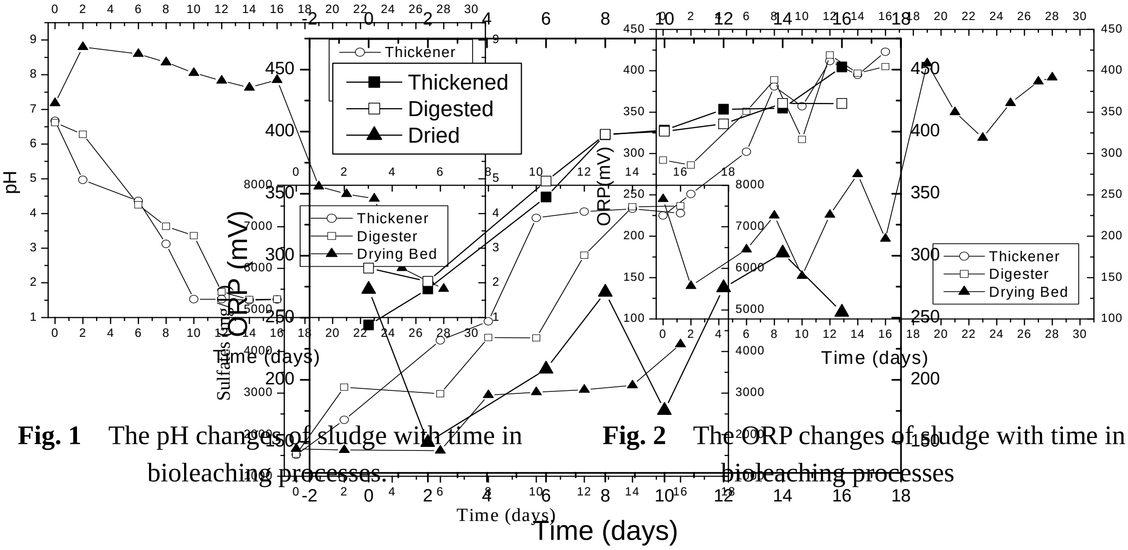

Fig. 1 The pH changes of sludge with time in bioleaching processes.

Fig. 2 The ORP changes of sludge with time in bioleaching processes

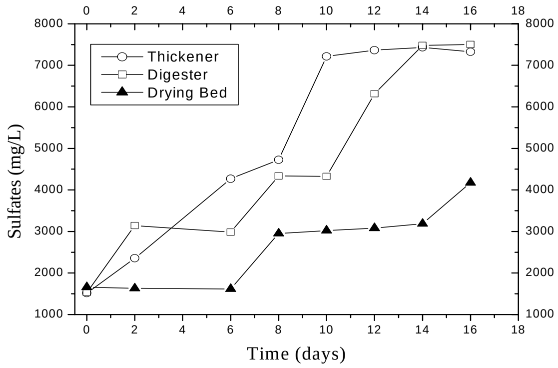

Fig. 3 The sulfates changes of sludge with time in bioleaching processes.

Table 3 Changes in TEHMs of sludge after bioleaching

	TEHM-Cu (mg/Kg)		TEHM-Zn (mg/Kg)	
	Raw	After bioleaching[a]	Raw	After bioleaching
Thickener sludge	448.38	48.44 (89.2%)[b]	325.83	92.04 (71.8%)
Digester sludge	449.63	154.61 (65.6%)	2699.86	260.29 (90.4%)
Drying-bed sludge	1255.66	975.32 (22.3 %)	3307.61	2786.32 (15.7 %)

[a]: after 16 days of bioleaching
[b]: removal efficiency

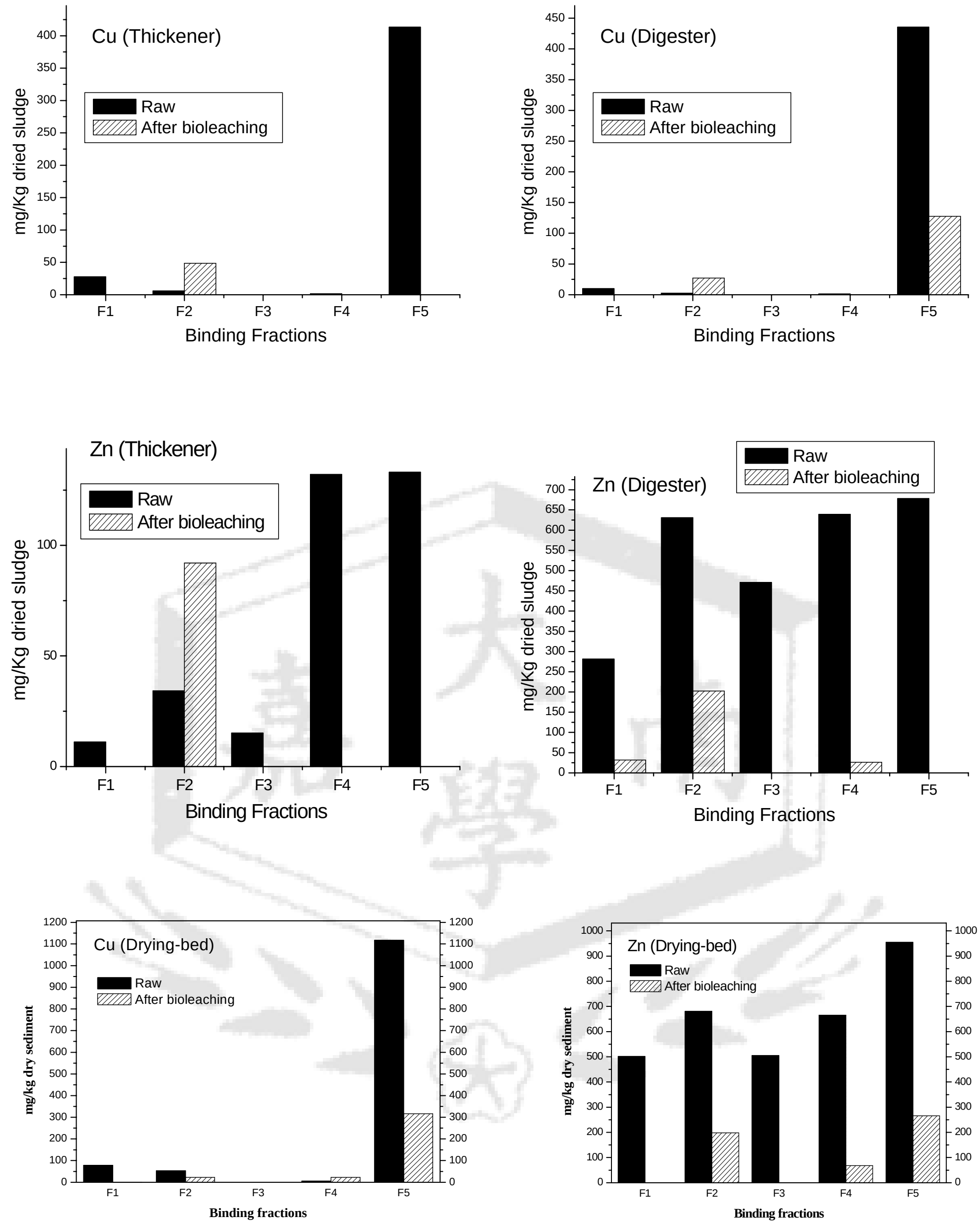

Fig. 4 Binding fractions of Cu and Zn in sludge before and after bioleaching. (F1: exchangeable; F2: bound to carbonates; F3: bound to Mn-oxides; F4: bound to Fe-oxides; F5: bound to organics)