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RESEARCH ARTICLE

Bio-immobilization of Cu and Zn in recirculated bioreactor landfill

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Abstract
Purpose To protect the environmental quality of soil, groundwater, and surface water near the landfill site, it is necessary to make an accurate assessment of the heavy metal mobility. This study aims to present the bio-immobilization behavior of heavy metals in landfill and provide some reference suggestion for the manipulation of heavy metal pollution control after closure.
Materials and methods Two simulated bioreactor landfill system loaded with real municipal solid waste (MSW), namely, conventional bioreactor landfill (CL) and leachate recirculated bioreactor landfill (RL), were operated. Cu and Zn, the two conventional heavy metals with the highest contents in MSW, were chosen to track the heavy metal bio-immobilization behavior in landfill.
Results The MSW in landfill is a great threat to environment because much of the heavy metal is "hidden" in different components. The weight ratio of Cu and Zn in landfill amounts to 0.00427% and 0.00437%, respectively. The accumulated effluent masses of Cu and Zn in CL increased all along, while they still kept at a stable level after day 105 in RL.
Conclusions The microbes like sulfate-reducing bacteria mediate the behavior of Cu and Zn in bioreactor landfill system. Cu and Zn can be bio-immobilized in bioreactor landfill system with leachate recirculation like RL.

Keywords Bio-immobilization · Heavy metal · Bioreactor landfill · Leachate

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1 Introduction

Heavy metals are the most toxic contaminants in both landfill site and landfill leachate (Abu-Rukah and Abu-Aljarayesh 2002). They migrate in landfill leachate when the pH of the environment reduces to acid values (pH<7; Christensen et al. 1994; Yanful et al. 1988). However, this migration can be decreased by physical processes (such as adsorption, sedimentation, and filtration) or chemical barriers (such as complexation and precipitation; Baun and Christensen 2004; Christensen et al. 1999; Förstner 1995; Ward et al. 2005; Weng et al. 2002; Wu and Li 1998). Investigations indicated that the migration of heavy metals was very low during the first decades after deposition compared to the accumulated amount (Finnveden et al. 1995). Christensen et al. (1994) proposed that the leaching of heavy metals from municipal solid waste (MSW) in landfill sites did not constitute a frequent groundwater pollution problem because they were subjected to strong attenuation by sorption and precipitation mechanisms. Chemical stabilization of waste offers the potential to

reduce the leachability of heavy metals. The principal objective is to form new mineral phases with low solubility and increased geochemical stability in a leaching environment (Eighmy et al. 1997).

However, the diversity of heavy metal attenuation processes in leachate has probably not yet been full understood (Christensen et al. 2001). The microbial processes dominate the stabilization of the waste in landfill (Christensen and Kjeldsen 1989). Heavy metals, a kind of biologically mediated substance (Flyhammar 1997), can be bio-accumulated by organisms (Abu-Rukah and Abu-Aljarayesh 2002; Anand et al. 2006; Gardea-Torresdey et al. 2004; Ortiz and Alcañiz 2006; Peverly et al. 1995; Sahoo et al. 1992). They may experience release or immobilization along with the MSW decomposition during the stabilization of the landfill. In a well-constructed landfill with a top layer, there will be no oxygen available below the top layer, and this will promote the growth of anaerobic bacteria. The growth of anaerobic bacteria will, in general, lead to a reducing environment. Among the microbiological processes happening in landfill, sulfate-reducing bacteria (SRB) can reduce available sulfate (for instance from decomposed amino acids at acid environment) to sulfides (Øygard et al. 2004). Therefore, heavy metals in landfill can be immobilized as metallic disulfide, a metallic compound with the lowest solubility. Moreover, heavy metals can also complex with some organic or inorganic macrocomponents such as NH_4^+ and volatile fatty acid (VFA), a key metabolite of microbe in landfill, and attenuate their migration. Therefore, bio-immobilization might be another important immobilization manner of heavy metals that cannot be ignored. It may be considered that the microbial behavior control the migration process of heavy metals because much of the mechanism can be ascribed to the metabolism of microbes in landfill, especially anaerobes. Unfortunately, to our best knowledge, information on the bio-immobilization of heavy metals in landfill is unavailable, except a few investigations concerning their behavior in landfill leachate. Mechanism of bio-immobilization is still considered unsatisfactory. Øygard et al. (2004) found that only a small extent of heavy metals will lead to discharge if MSW was deposited at well-constructed sanitary landfills. Suna Erses and Onay (2003) studied the attenuation of heavy metals in the methanogenic condition of landfill loaded with synthetic MSW. However, leachate and refuse are an inseparable part of the landfill system. In order to understand the bio-immobilization behavior of heavy metals in landfill system pertinently, much attention should be paid to the whole landfill system and the microbial behaviors together.

To protect the environmental quality of soil, groundwater, and surface water near the landfill site, it is necessary to make an accurate assessment of the heavy metal mobility. In our previous research (Long et al. 2009a, b), we found that the migration mechanisms of Cu and Zn, the two conventional heavy metals with the highest contents in MSW, are significantly different. In this study, we presented and discussed their fate from their total import amounts of bioreactor landfill system, their accumulated leaching amounts by leachate, and their significant retention by refuse and the relative microbes like SRB. It aims to present the bio-immobilization behavior of heavy metals in landfill and provide some reference suggestion for the manipulation of heavy metal pollution control after closure.

2 Experimental

2.1 Experimental setup

Two sets of simulated bioreactor landfill systems were used in this study. One was conventional bioreactor landfill system (CL) whose leachate was single-pass leaching, and the other was recirculated bioreactor landfill system (RL) in which leachate was recirculated. CL was a control system. Both bioreactor landfill systems were operated in room temperature. Complete configurations of the two bioreactor landfill systems are shown in Fig. 1. Each bioreactor landfill system had a diameter of 0.55 m and a height of 2.0 m. Both bioreactor landfill systems were constructed with watertight cement. Each bioreactor landfill system was equipped with five ports: The two inlet/outlet ports at the top lid were used for exporting gas and recycling leachate using a peristaltic pump, the two ports at the side were used for sampling of refuse from the top layers and the bottom layers, respectively, while the remaining one port at the bottom was used for leachate drainage and sampling. A 100-mm-thick layer of gravel was placed at the bottom of each bioreactor landfill system to simulate a leachate collection system and to prevent clogging of the leachate withdrawal outlets. MSW was loaded in 1,800-mm layers and compacted using a shovel and a sledgehammer. A second gravel layer was placed on the top of the MSW to simulate intermediate cover and upper drainage layer and further to provide even distribution of the recirculated leachate. The nominal size of the gravel used for both filter layers ranges from 10 to 40 mm. Finally, the two bioreactor landfill systems were sealed using construction-type sealant.

2.2 Characteristics of MSW

MSW used in this experiment was collected from the Kaixuan transport station of Hangzhou, Zhejiang, east China. In order to achieve a representative sample of solid waste that normally goes to a bioreactor landfill

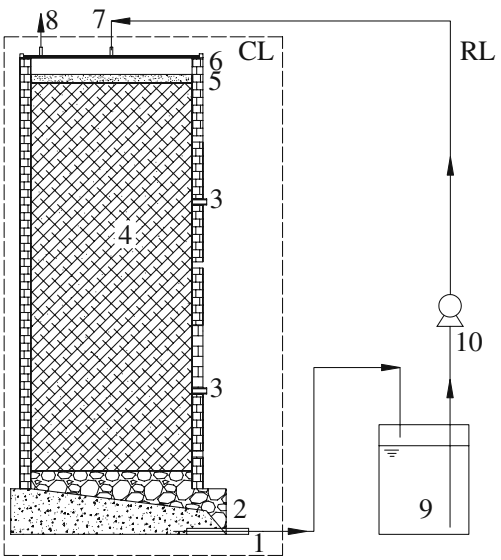

Fig. 1 Schematic of bioreactor landfill systems

1. Leachate outlet 2. Gravel layer 3. Refuse sampling port 4. Refuse 5. Sandy layer 6. Headspace 7. Vent-port 8. Gas outlet 9. Leachate collection tank 10. Peristaltic pump
The small fram part is the conventional bioreactor landfill system (CL), and the whole system is the recirculated bioreactor Landfill system (RL)

system, MSW was collected continuously at different periods in a day. Then, they were completely mixed manually. Moisture content of refuse was 54.0%. Visual inspection of the refuse showed the presence of a variety of food waste, plastic, paper, residue, timber, rubber, textile, and inorganic materials including glass containers and tin cans. The average wet density of the refuse compacted in each bioreactor landfill system was approximately 600 kg m^{-3}, and the total MSW amount loaded was 300 kg. Larger particles of the collected refuse were all shredded into 2 cm approximately, and the refuse were thoroughly mixed prior to loading. The characteristics of MSW utilized in this experiment are presented in Table 1.

2.3 Operation of simulated bioreactor landfill systems

In order to achieve the highest microbial activity during decomposition, the moisture content of the refuse was adjusted to 75% (Benson et al. 2007) by adding tap water to the two bioreactor landfill systems after loading. Leachate was collected and stored in sealed tank. Leachate of CL was discharged without further treatment, while that of RL was continuously recirculated back to the refuse using peristaltic pump with adjusted flow rates varying with leachate volume every day, except for the first 2 days when there was no leachate generation. The recirculation ratio was 100%.

2.4 Sampling and analytical methods

2.4.1 Background sampling

In order to get the background value of MSW sample, visual and separable components of MSW were separated exactly before deposition. After separation, their wet masses were weighted immediately. Then, all components (glass and metal were excluded) were dried at 105°C in a ventilated drying box until a constant weight was achieved for correction to dry mass. Finally, pseudototal contents of

Table 1 Components and moisture of test MSW

Component	Food waste	Plastic	Paper	Residue[a]	Glass	Textile	Rubber	Metal	Timber
%, *w*/*w*	61.50	11.60	10.30	7.10	6.40	1.30	0.60	0.60	0.60
Moisture content/%	75.61	40.67	58.34	36.40	–	3.45	40.72	–	41.06

[a] The residue fraction of MSW mainly including fine paper, dust, leftovers with the percentages of 70%, 20% and 10%, respectively

Cu and Zn in each MSW component were determined by digestion with aqua regia. In order to provide data against which the results of aqua regia digestion could be compared, each sample was handled in triplicate.

2.4.2 Sampling during landfill process

Leachate samples (~100 mL) were collected weekly from leachate outlet ports. In order to keep the balance of leachate volume in RL before recirculation, the same volume of tap water (~100 mL) was added into the leachate after sampling. Refuse was sampled biweekly from the refuse sample ports at the side of bioreactor landfill systems. The collected leachate was monitored on a regular basis to track the fate of Cu and Zn during stabilization process.

Leachate samples collected at the bottom of the CL and RL were analyzed for chemical oxygen demand (COD), pH, VFA, and concentration of Cu and Zn. COD was determined by potassium dichromate oxidation method, and VFA was measured by gas chromatograph with hydrogen flame detector (Agilent 6890N). All these analyses were performed in accordance with "Standard Methods for the Examination of Water and Wastewater" (China 1989). Cu and Zn analyses were performed using atomic absorption spectrophotometer (Shimadzu AA-650). Prior to analysis, each sample was digested with aqua regia according to the standard method (Dabek-Zlotorzynska et al. 2003). Namely, 1 g of homogenized air-dried refuse sample was weighed into the PTFE vessel, and then 7.0 mL of 12.0 mol l^{-1} HCl followed by 2.3 mL of 15.8 mol l^{-1} HNO_3, drop by drop, to reduce foaming, was added. The PTFE vessel was allowed to stand for 16 h (overnight) at room temperature for slow oxidation of the organic matter of the MSW. The temperature of the reaction mixture was slowly raised until reflux conditions were reached and maintained for 2 h. After cooling the PTFE vessel to room temperature, the digests were filtered into 100-mL volumetric flasks and diluted to the mark with distilled water. As for leachate, 10.00 mL of the sample was used for digestion with the procedure mentioned above. All analyses were carried out in triplicate to ensure the validity of the results.

Refuse sample were also used for analysis of the SRB growth. The population of viable SRB was determined by the most probable number (MPN) technique. The composition of the SRB culture medium were (per liter of water): yeast extract 1.00 g, NH_4Cl 1.00 g, $MgCl_2{\cdot}6H_2O$ 0.20 g, $CaCl_2{\cdot}2H_2O$ 0.10 g, KCl 0.10 g, cysteine HCl 0.25 g, resazurin 1.00 mg, and trace element solution 1.50 mL. The pH of the culture medium was adjusted to 7.2±0.2 with 6 N NaOH. The culture medium used was prepared anaerobically using the Hungate technique (Hungate 1969). Namely, the culture medium was boiled then cooled to room temperature under a stream of oxygen-free nitrogen gas and 4.50 mL aliquots were dispensed into 15-mL Hungate tubes. Finally, the tubes were autoclaved at 120°C for 30 min. The SRB growth was indicated by the turbidity of the culture medium and the detection of H_2S after 14 to 21 days culture (Widdel and Bak 1992).

3 Results and discussion

3.1 Total mass of Cu and Zn loaded in bioreactor landfill system

In order to evaluate the behavior and fate of Cu and Zn during decomposition in bioreactor landfill system, their total import mass in MSW were determined by monitoring their background contents in each MSW component before deposition. The visual and separable components of MSW were food waste, plastic, paper, residue, glass, textile, rubber, metal, and timber. Each component was separated exactly and the proportion could be calculated by 1.

$$P_i = \frac{M_i}{M_{MSW}} \times 100\% \quad (1)$$

where M_i and M_{MSW} were the wet masses of each component and the total MSW, respectively, and P_i was the proportion of each MSW component. The results of proportion and moisture content are showed in Table 1.

The Cu and Zn contents of each component of MSW are listed in Table 2. It showed that the variation of heavy metal content in MSW was high. The highest content of Cu and Zn, which accounted for 309.47±125.70 and 191.04±105.60 μg g^{-1} DW^{-1} (dry weight), respectively, were observed in plastic. Paper was also observed to have high levels of Cu and Zn. The lowest levels of Cu and Zn were observed in rubber, namely, 38.67±4.12 and 61.85±22.03 μg g^{-1} DW^{-1}, respectively. It suggests that the components like plastic and paper are important heavy metal sources of MSW. That is because some valuable

Table 2 Cu and Zn contents in different components of initial MSW (μg g^{-1} DW^{-1}, n=15)

Variable	Copper	Zinc
Food waste	51.31±3.93	108.9±24.6
Paper	165.3±146.7	184.3±124.4
Timber	92.61±4.84	166.4±45.8
Residue	61.13±30.29	85.06±60.14
Rubber	38.67±4.12	61.85±22.03
Textile	193.6±250.0	81.10±9.38
Plastic	309.5±125.7	191.0±105.6
Metal	159.4±13.81	107.3±5.0

components in MSW such as bulk metal or items containing high amount of heavy metal were sorted and picked out by household or MSW transport department before disposal. Even though, we still cannot neglect the heavy metal behavior in bioreactor landfill because many of them are "hidden" in different MSW components and still threaten the surrounding environment.

Therefore, the total mass of Cu and Zn loaded could be calculated by 2.

$$M_{Total} = \sum M_{MSW} \times p_{\mathrm{i}} \times (1 - \eta_i) \times X_{\mathrm{i}} \quad (2)$$

where η_{i} and X_{i} were the moisture content and selected heavy metal (Cu, Zn) content in each MSW component, respectively, and M_{Total} was the total import mass of select heavy metals (Cu, Zn) in MSW. In our experiment, the MSW mass loaded in each bioreactor landfill system was 300 kg. Supposing that the MSW used for deposition were mixed as homogeneously as possible, the total import masses of Cu and Zn in each bioreactor landfill system were 12.81 and 13.11 g, respectively. It suggested that the weight ratio of Cu and Zn in bioreactor landfill system were 0.00427% and 0.00437%, respectively.

3.2 Effluent mass of Cu and Zn from bioreactor landfill system

Since the landfill liners isolated the leachate from the surrounding environment, heavy metals are only discharged through the leachate outlet. In order to track the fate of Cu and Zn in the two different bioreactor landfill systems, their accumulated effluent masses should be computed. In our experiment, CL was a single pass reactor whose leachate was discharged periodically. Therefore, the accumulated effluent masses of Cu and Zn of CL were the sum of mass in each specific period, which could be calculated by 3.

$$M_{\mathrm{Accu}} = \sum_{i=1}^{n} V_i \times C_i \quad (3)$$

where M_{Accu} (mg) was the accumulated effluent mass of heavy metal, V_i (L) was the volume of leachate on day i, and C_i (mg L^{-1}) was the concentration of selected heavy metals (Cu, Zn) in leachate on day i. However, RL was a recirculated bioreactor landfill system whose leachate was recycled all along. Thus, the accumulated effluent masses of Cu and Zn of RL equaled the specific masses on day i, which could be calculated by 4.

$$M_{Accu} = V_i \times C_i \quad (4)$$

As Figs. 2 and 3 show, the effluent masses of Cu and Zn of the two bioreactor landfill systems were significantly different. The accumulated effluent masses of Cu and Zn in

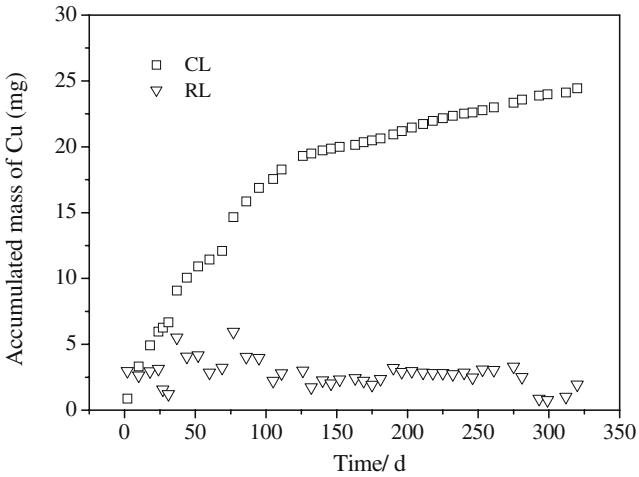

Fig. 2 Accumulated effluent mass of Cu leached out from bioreactor landfill systems

CL increased as time all along, while they still remain at a stable level except some fluctuation during the initial days in RL. During the first 10 days, the accumulated masses of Cu and Zn leached out from CL were 3.312 and 6.166 mg, while those from RL were 2.622 and 5.187 mg, respectively. In this period, the two bioreactor landfill systems experienced a fast decomposition phase called acidification phase when the soluble organic matter in MSW released into leachate. Like Fig. 4b shows, the COD concentration in leachate had a sharp rise. Meanwhile, VFA, hydrolyzed from easy degradable organic matter in leachate, was generated and pH decreased (Fig. 4a, c). Because of the generation of VFA, heavy metals in MSW started to release into leachate. However, heavy metals in MSW might still be kept at a balance of adsorption−desorption in this period, and there are no significant difference between CL and RL though leachate of RL was recirculated.

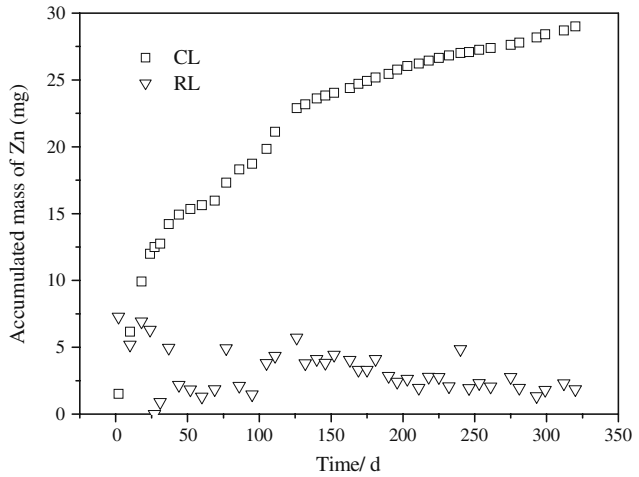

Fig. 3 Accumulated effluent mass of Zn leached out from bioreactor landfill systems

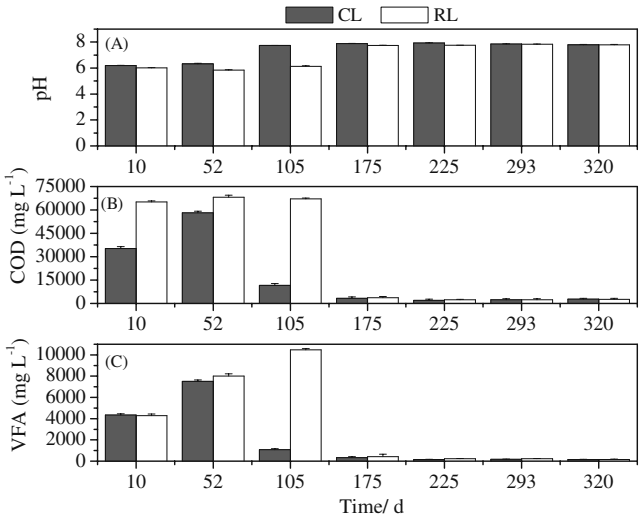

Fig. 4 Characteristics of leachate at different stages of landfill systems: pH (**a**), COD (**b**), VFA (**c**)

After 10 days' decomposition, it showed great change in the two bioreactor landfill systems. From day 10 to day 105, both of the accumulated effluent masses of Cu and Zn had a sharp rise in CL, which increased from 3.312 and 6.166 mg to 17.558 and 19.841 mg, respectively. However, they remain at a steady low level in RL which accounted for 2.234 and 3.810 mg, respectively. It suggested that Cu and Zn in RL had been "immobilized" in MSW during this period. We attributed that phenomenon to the degradation predominance of RL than CL, which could be confirmed from the results of COD, pH, and VFA of leachate. Like Fig. 4 shows, the COD in RL is still kept at a high level from day 10 (65,098.04 mg L^{-1}) to day 105 (67,134.27 mg L^{-1}), while it decreased fast except a highest level at day 52 (58,134.76 mg L^{-1}) in CL. It suggested that the biodegradation degree and speed were higher and faster in RL than CL. Meanwhile, the VFA concentration was also always higher in RL (4,280.3–1,0475.0 mg L^{-1}) than CL (4,340.1–1,075.2 mg L^{-1}).

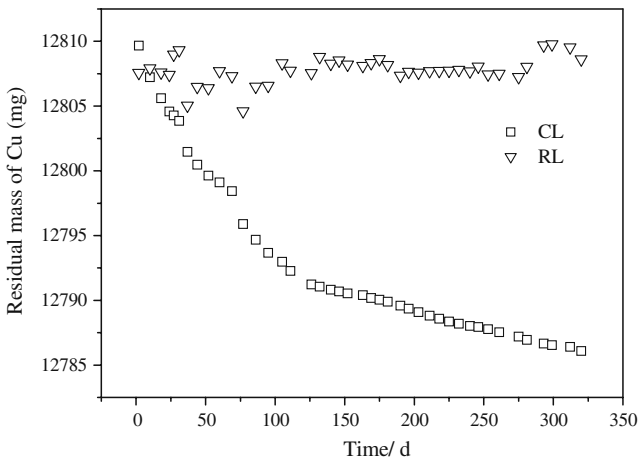

Fig. 5 Residual mass of Cu in bioreactor landfill systems

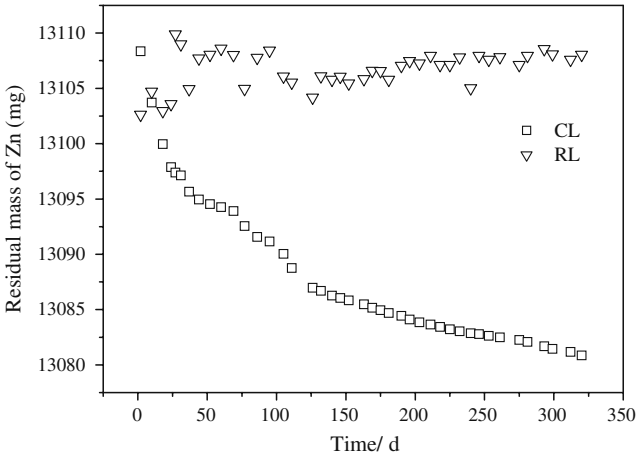

Fig. 6 Residual mass of Zn in bioreactor landfill systems

However, there were no great differences on pH in that process. It indicated that the acidogenic phase of the anaerobic degradation remained at the CL and RL together. Differently, much more organic matter in MSW was decomposed and the anaerobic digestion was more active in RL than CL, and heavy metals in MSW were then immobilized during the decomposition of MSW in RL. It was not like the first 10 days when heavy metals were mainly adsorbed onto the MSW surface and then desorbed into leachate again after the leachate recirculation. In this period, heavy metals had been immobilized and could not be released into leachate again though the pH of leachate recirculated was lower than the first 10 days in RL (Fig. 4a). We concluded that the complex between heavy metals and humus generated from the decomposition of MSW was the main reason.

At the end of the study, the accumulated effluent masses of Cu and Zn leached out from CL were 24.447 and 29.011 mg, while those from RL were 1.936 and 1.850 mg, respectively. With the action of leachate in RL, heavy metals had been immobilized into the MSW while released into the environment directly in CL whose leachate was single-pass.

3.3 Bio-immobilization of Cu and Zn in bioreactor landfill system

Based on the total import masses of Cu and Zn loaded in bioreactor landfill systems and their effluent masses from

Table 3 Growth of SRB in landfills at different stage (MPN g^{-1} DW^{-1})

Refuse	Day10	Day105	Day320
CL top layer	1.1×10^{9}	1.6×10^{10}	1.4×10^{10}
CL bottom layer	1.6×10^{9}	3.8×10^{11}	2.0×10^{11}
RL top layer	1.4×10^{9}	1.6×10^{11}	2.8×10^{12}
RL bottom layer	2.0×10^{9}	5.6×10^{13}	1.0×10^{13}

leachate, the residual masses of Cu and Zn in bioreactor landfill could be calculated by 5.

$$M_{Rsi} = M_{Total} - M_{Accu} \quad (5)$$

where M_{Rsi} was the residual masses of Cu and Zn in bioreactor landfill. Like Figs. 5 and 6 show, the residual masses of Cu and Zn in CL decreased as time, while they remain at a steady level in RL all along. After day 105, Cu and Zn in RL were almost immobilized due to the leachate recirculation. The increasing effluent masses of Cu and Zn in CL confirm that heavy metals in landfill like CL are a continuous pollution source (Flyhammar and Hakansson 1999; Flyhammar et al. 1998). However, this phenomenon could be controlled by leachate recirculation like RL because of the immobilization.

In order to explore the immobilization mechanism of heavy metals in the bioreactor landfill system, the microbial activity in MSW was studied. Heavy metals could complex with humus generated by the degradation of organic matter in MSW like the following reaction:

$$M^{2+} + \mathrm{RCOOHCOH} \longrightarrow \mathrm{RCOO} - \mathrm{M} - \mathrm{CO} \quad (6)$$

Moreover, groups such as –O–, $–NH_2$, –N=N–, and –CO– that are always contained in humus could also complex with heavy metals by the reaction mentioned above. Among the microbiological processes happening in the bioreactor landfill system, humus containing such groups was generated by microorganisms like acidogenic bacteria (AB) by the following reaction:

$$\mathrm{RCOH} + \mathrm{H_2O} \xrightarrow{\mathrm{AB}} \mathrm{RCOO} - + \mathrm{H_2} \quad (7)$$

However, compared with the microbiological processes initiated by other microorganisms which promoted the immobilization of heavy metals, SRB is a more critical candidate. SRB typically oxidize organic compounds using sulfate as their terminal electron acceptor. Hydrogen sulfide (H_2S), produced as one of the major end-products of their metabolism, has a strong affinity for heavy metals and readily forms insoluble metallic disulfide by the following reactions:

$$2\mathrm{CH_2O} + \mathrm{SO_4^{2-}} \xrightarrow{\mathrm{SRB}} \mathrm{H_2S} + 2\mathrm{HCO_3^-} \quad (8)$$

$$M^{2+} + \mathrm{H_2S} \longrightarrow \mathrm{MS_{(S)}} + 2\mathrm{H^+} \quad (9)$$

The difference on decomposition between the two bioreactor landfill systems was mainly attributed to the difference on microbial activity. Additional moisture can stimulate microbial activity by providing better contact between insoluble substrates, soluble nutrients, and microorganisms (Barlaz et al. 1990). Thus, the microbial activity in RL could be maintained and stimulated because the humidity of MSW could be supplied by leachate recirculation. Therefore, the organic matter in MSW could hydrolyze and ferment continuously. Moreover, some hard degradable organic matter in MSW could also be decomposed after the degradation of easily degradable organic matter. However, the microbial activity in CL gradually weakened because the surrounding environment tends to dry from the top layers to the bottom layers as the leachate streamed out. Therefore, much organic matter in CL could not be decomposed except for some easily degradable ones. As Table 3 shows, the SRB growth had significant difference between the two bioreactor landfill systems at different stages. The SRB growth in RL was obviously better than CL, which accounted for a superiority of two orders of magnitude in the bottom layers of the two bioreactor landfill systems in the later stage. Therefore, we could conclude that the microbial activity dominates the behavior of heavy metal in a bioreactor landfill system like RL. It is also confirmed by Flyhammar (1997) that "heavy metal is a kind of biologically mediated substance." The leachate recirculation guaranteed that the microbial activity and heavy metals were then immobilized into the MSW. In other accurate words, this immobilization is a "bio-immobilization."

4 Conclusion

The background analysis indicated that MSW in landfill is a threat to the environment because much of the heavy metal is "hidden" in different components. The weight ratio of Cu and Zn in landfill amounts to 0.00427% and 0.00437%, respectively. The accumulated effluent masses of Cu and Zn in CL increased all along, while they still remain at a stable level after day 105 in RL. Microbes like SRB mediate the behavior of Cu and Zn in bioreactor landfill system. Cu and Zn were bio-immobilized in a bioreactor landfill system with leachate recirculation like RL.

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