Transformation of heavy metals from sewage sludge during bioleaching

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Abstract: Bioleaching experiment was carried out in 80L SBR reactor with sewage sludge collected from each treatment step of the wastewater treatment plant (WWTP) system, to investigate the transformation of heavy metals during bioleaching. The corresponding changes in pH, oxidation-reduction potential (ORP) and the concentration of Zn, Cu and Pb in extracellular polymeric substances (EPS) were also studied. The results showed that the physical and chemical properties of sewage sludge could affect the sludge acidification and raise the ORP by oxidizing ferrous sulfate. The highest total concentration of Zn-EPS, Cu-EPS, and Pb-EPS was found in secondary sludge (SS), primary sludge (PS) and aerobic sludge (OS), respectively. Content of Pb in LB-EPS was more than in TB-EPS during 9 days bioleaching. Concentration of Cu and Zn in LB-EPS was better in the early leaching period while that in TB-EPS was at the end. Most of Zn existed in their forms of Fe-Mn oxides-bound in raw sludge (50.87%-61.79% of the total), followed by the organic oxide bound. The organic oxide bound was the predominant fraction of Cu (50.14-70.15% of the total) and Pb (41.28-61.94% of the total) in all original sludge samples. After bioleaching, Pb in primary sludge (PS) remained as the residual fraction, while the Fe-Mn oxides bound fraction in aerobic sludge (OS), anaerobic sludge (AS) and secondary sludge (SS). Zn existed as a high available fraction (F_{1+2}) in primary sludge (PS), aerobic sludge (OS) and anaerobic sludge (AS) but the residual fraction in secondary sludge (SS) after bioleaching. For Cu in all bioleached sludge, the predominant fraction was the residual fraction (average 32.71% of the total).Significant differences of the formation of heavy metals were observed in different sludge system during bioleaching, suggesting that the species of sludge significantly affected the distribution of various fractions of the metals in bioleaching.

1. Introduction

During the conventional treatment process of municipal wastewater, a large amount of toxic heavy metals such as copper, zinc, chromium, lead and cadmium accumulates in sewage sludge, which limits land application [1,2].Therefore, the effective removal of enriched heavy metals from sewage sludge has been a crucial problem. As an emerging technology for removal of heavy metals from sewage sludge, bioleaching has advantages of low cost and high removal efficiency, and has drew much attention in decades [3]. It has been widely accepted that toxic effects of heavy metals depend on not only the total concentration but also bioavailability which is relative to specific chemical forms or combinations of heavy metals in different environmental phase [4,5]. The environmental behaviors of heavy metals in wastewater treatment include dissolution-precipitation, cation exchange, adsorption-desorption, complexation and other reactions, which results in complicated chemical forms in sludge [6] .However, the releasing characteristics of heavy metals in sewage sludge is not identical. The different chemical forms of heavy metals do not only affect the efficiency of bioleaching but also the bioavailability of heavy metals after bioleaching [7].Chen and others investigated the transformation of heavy metal forms during sewage sludge bioleaching and showed that exchangeable forms of Cu, Zn and Pb were transformed from sulfide precipitate form, carbonate precipitate form and organically bound, respectively [8].The research report mainly focuses on parameters of bioleaching process such as initial pH, type and concentration of substrates and physiochemical characteristics of treated sludge like dewatering performance and fertilizer effect of subsequent application [9,10,11]. However, few papers concentrate on the leaching mechanism of sewage sludge, especially transformation and heavy metals distribution during bioleaching. The aim of this work is to investigate the dynamic transformation of heavy metals from sewage sludge during bioleaching process, which is of great help to the theoretical basis for developing better mechanism and technology of bioleaching from sewage sludge. It also can provide evidence on the safe disposal of bioleached sludge.

2. Materials and Methods

2.1 Sewage sludge sampling

Sewage sludge was from Qilidian wastewater treatment plant (WWTP) in Guilin, China. The wastewater was originated from domestic and industrial sources, and treated by adopted oxidation ditch process. Four types of sludge were collected as primary sludge (PS), aerobic sludge (OS), anaerobic sludge (AS) and secondary sludge (SS). Samples were air-dried at ambient temperature,and grinded by an agate mortar. Samples were then passed through a mesh sieve100 and stored at 4 °C for measurement.

2.2 Inoculum preparation and bioleaching experiment

The inoculum was prepared with 10g/L (w/v) of $FeSO_4 \cdot 7H_2O$ in four 80L SBR reactors with 50L PS, OS, AS and SS, respectively. When pH of sludge reduced from the initial value 7.02-7.49 to 2-3, the 10L culture (20%, v/v) was transferred into another four fresh samples of 50L corresponding sludge. This procedure was repeated three times to obtain prepared inoculum for the bioleaching experiment [12]. Cultivation of mixed inoculums lasted for 15 days.

The bioleaching experiment was conducted in four 80L SBR reactors with 50L sewage sludge (PS, OS, AS, SS) collected from each treatment step of the wastewater treatment plant (WWTP) system. Then each reactor was added 10 L inoculum (inoculum ratio, 20%, v/v) and ferrous sulfate (concentration, 10 g/L, w/v). The bioleaching experiment was at 26°C and 0.5 m^3/h of aeration intensity. Due to water evaporation loss, distilled water was replenished based on weight loss daily during the bioleaching process. The pH and ORP were measured at the interval of two days followed by withdrawing a sludge sample from each reactor for chemical analyses. The Bioleaching experiment lasted for 9 days. The equipment for the bioleaching experiment reactor mainly included 80L cylindrical container, electric paddle stirrer, gas meter and aeration pump et al.

A comparative analysis was focused on the transformation of heavy metals (Zn, Cu and Pb) from primary sludge (PS), aerobic sludge (OS), anaerobic sludge (AS) and secondary sludge (SS) during bioleaching. The corresponding changes in pH, oxidation-reduction potential (ORP) and the concentration of heavy metals in EPS were also studied.

2.3 Analysis method

Total solid content, organic matter content, total nitrogen (TN), total phosphorus (TP) and total potassium content (TK)of the sludge were determined according to the standard methods (CJ/T 221-2005). For total heavy metal determination, sludge samples were subjected to microwave digestion (HNO_3-HCl) and heavy metals in the digested liquid were determined by using ICP-AES (Optima 700 DV). The loosely bound（LB） fraction and tightly bound（TB） fraction of extracellular polymeric substances(EPS) in the sludge was extracted by the physical method [13], in which the extraction of LB was mainly through ultrasound and oscillation after normal saline digestion, while TB mainly adopted heat extraction.

For exploration of different chemical forms of heavy metals in the sewage sludge during bioleaching process, the selective sequential extraction procedure is followed, as shown in Table 1 [14].

(i) Exchangeable. The sludge sample was extracted at room temperature for 1 h with 8 mL of 1M

$MgCl_2$(pH 7.0) with continuous agitation.

(ii) The Carbonates bound. The residue from (i) was leached at room temperature with 8 mL of 1 M NaOAc was adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained and took 6 hours necessary to complete extraction.

(iii)The Fe-Mn Oxides bound. The residue from (ii) was extracted with 20 mL of 0.04 M NH_2OH-HCl in 25% (v/v) HOAc. The latter experiment was performed at 96°C with occasional agitation and it needed 6hours to complete dissolution of the free iron oxides.

(iv) The Organic Matte bound. The residue from (iii) were added 3 mL of 0.02 M HNO_3 and 5 mL of 30% $H_2O_2$and was adjusted to pH 2 with HNO_3, the mixture was heated to 85°C for 2 h with occasional agitation. A second 3mL aliquot of 30% H_2O_2 (pH 2 with HNO_3,) was then added and the sample was heated to 85°C for 3h again with intermittent agitation. After cooling, 5 mL of 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added and the sample was diluted to 20 mL and agitated continuously for 30 min.

(v) Residual. The residue from (iv) was digested with a HNO_3-HCl mixture according to the procedure described above for total metal analysis.

Table1 Sequential selective extraction procedure

Reagent	Extraction time(h)	Extracted metal form
1M $MgCl_2$	1h	Exchangeable
1M NaOAc	6h	Carbonate
0.04M NH_2OH-HCl	6h	Fe-Mn oxides bound
0.02M HNO_3+30%H_2O_2,3.2M NH_4OAc	6h	The sulfide and organic bound
Residul	-	Residual

3 Results and discussion

3.1 Sludge properties

Table 2 Characteristics of original sewage sludge

		pH	Heavy metal(mg/kg)			Nutrient element(g/kg)			Organic matter(g/kg)
			Zn	Cu	Pb	TN	TP	TK	
PS	raw	7.14	740.75	408.75	91.75	42.59	29.53	6.81	445.73
	bioleached	2.37	286.67	153.28	32.85	25.41	16.32	4.16	278.54
OS	raw	7.38	774.75	385.25	83.81	60.37	37.42	7.46	706.52
	bioleached	2.46	306.80	139.85	28.66	34.67	21.63	4.69	449.91
AS	raw	7.49	780.01	303.05	92.25	58.41	35.64	7.07	689.87
	bioleached	2.41	290.16	93.34	27.31	32.89	20.00	4.56	445.59
SS	raw	7.02	810.92	497.68	109.78	50.25	29.87	8.23	513.29
	bioleached	2.01	283.01	149.30	30.63	27.42	16.43	4.92	315.21
GB4284-84	pH<6.5		500	250	300				
	pH≥6.5		1000	500	1000				

Physiochemical characteristic properties of sewage sludge shown in Table 2. The average content of total nutrient (TN+TP+TK) of sewage sludge is 93.41 g/kg (78.93-101.12g/kg) with high value of fertilizer. Concentrations of Zn and Pb are both higher than the limited standard of heavy metals in sewage sludge in agriculture (GB4284-1984, pH<6.5), which should be paid more attention for the safety of land utilization. The averagely removal rate of heavy metals (Zn、Cu and Pb) is 62.6%、66.35% and 67.98% (291.66、133.94 and 29.86 mg/kg), respectively after bioleaching. Meanwhile, the content of organic matter and NPK stillsatisfy the minimum requirements of the agricultural sludge though some losses. Sludge has high agricultural value and is suitable for the land utilization.

3.2 pH and ORP

Change profiles of pH and ORP with different sludge during bioleaching process is shown in

Fig.1.The increase in ORP coupled with a low pH value during bioleaching is mainly due to the hydrolysis of ferric ion via biological oxidation, which is an obvious indicator of substantial growth of microorganisms [15].With the addition of substrates and inoculum, pH in PS, OS, AS and SS decreases fast from the initial value 7.14, 7.38, 7.49 and 7.02 to 3.03, 4.11, 4.15 and 4.22 on the first day and then shows a gradual fall in following days and finally down to 2.37, 2.46, 2.41 and 2.01,respectively on the 9th day. Compared with other runs, pH of PS has a faster decrease in first three days, which may be due to the existence of a large number of inorganic components in PS [16]. The pH in OS and SS decrease at the similar rate, which indicates that anaerobic or aerobic treatment forbio-sludge does not significantly affect acidification process of bioleaching.

After 9 days of bioleaching, ORP of mixed liquor increase from the initial value 113,101, 95 and 128 mV to 552, 522, 517 and 608 mV for PS, OS, AS and SS, respectively, which is attributed to oxidation of ferrous sulfate. The ORP shows a rapid increase in the first three days and a flat growth follows in the end [17].

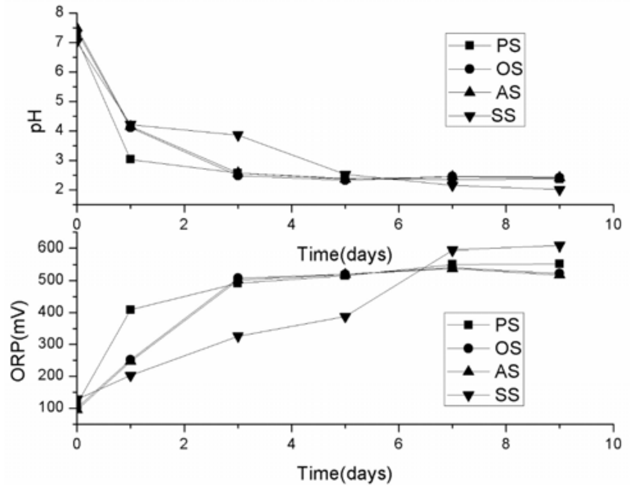

Fig. 1 Change profiles of pH and ORP in sewage sludge during bioleaching

3.3 Heavy metals in EPS

Extracellular Polymeric Substances (EPS) is referred to the secretion of microorganism under specific environmental conditions [18]. EPS could be separated into loosely bound fraction (LB) and tightly bound fraction (TB). The former combines with the cell body is not so tight, while the latter is opposite [19]. It is well known that EPS mediated the contact of microorganisms to material surfaces, and plays an important role in the dissolution of heavy metals via an "EPS contact leaching mechanism" [20]. Changes of heavy metals (Zn、Cu and Pb) in EPS during bioleaching process are shown in Fig. 2.

There is a gradual increase for both Zn-EPS and Cu-EPS in first 5 days. The change tendency contributes to two reasons. Firstly, fractional heavy metal dissolves into the liquid as free form was reabsorbed at the EPS secreted by leaching microbial. On the other hand, microbial cell accumulated heavy metals is hydrolyzed in increasing acidic mixed liquor; and then the released heavy metal is detained simultaneously for the EPS chelate complex [21]. However, there appears a downward trend of Pb-EPS during 6-9 days after beginning. It may be related to the releas of heavy metals combination resulted from the biodegradation of EPS. The highest concentration of heavy metals in EPS of all runs is 260.27, 66.71 and 11.66 mg/kg for Zn、Cu and Pb, respectively. Compared with Cu-EPS in PS and Pb-EPS in OS, Zn-EPS in SS showed the better adsorption ability. During bioleaching in each sludge system, total concentration of Pb in LB-EPS is slightly higher than the TB-EPS. For both Cu and Zn, a better content in LB-EPS is in the early leaching stage while in the TB-EPS is in the end.

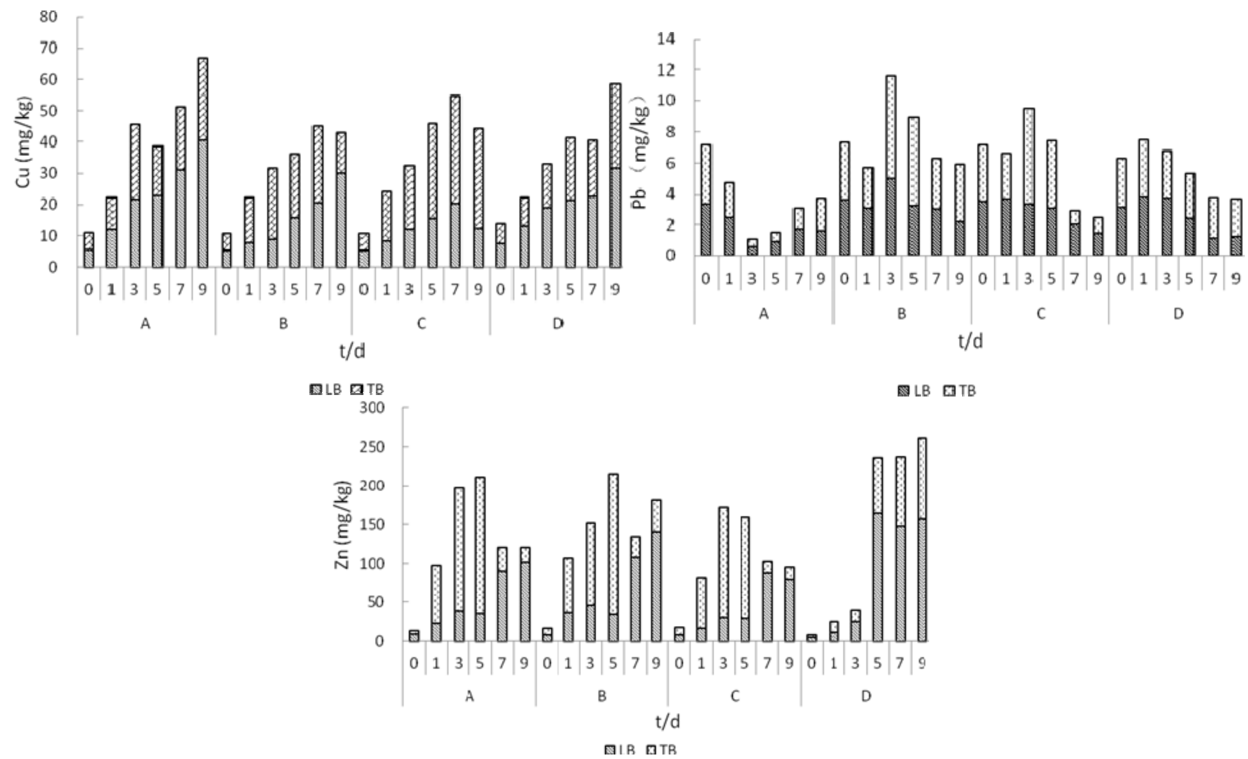

Fig. 2 Content of Zn, Cu and Pb in EPS during bioleaching
: A for PS, B for OS, C for AS, D for SS

3.4 Chemical forms of heavy metals

F1 represents the fraction of adsorbed metals, which is easily affected by the ionic composition of water. F2 is susceptible to change of pH. F3 in sludge is susceptible to the anoxic condition. F4 represents the fraction of organic matter and sulfide bound and may get extracted under oxidizing conditions. The residual fraction(F5) represents the most stable form of metals remaining in the sludge after extraction of the fraction F1, F2, F3 and F4 [22].So chemical forms can be sorted roughly as following based on the morphological stability: F5> F4> F3> F2> F1.

Fig.3 presents variation of chemical forms of heavy metals (Zn、Cu and Pb) in different sludge (PS, OS, AS and SS) during whole 9 days of bioleaching process. In raw sludge, the predominant fraction of Zn is F3 (50.87%-61.79% of the total), followed by the F4 fraction (15.98-21.01%). For Zn, the sum of the first three fractions (F1+F2+F3) accounts for 65.66-76.28% of the total concentration, which implies the relatively high mobility and bioavailability. This is similar with the research from Wang Chao and others, in which 58.5%-77.5% of the total Zn in sludge remained as more mobile chemical forms [23]. F4 is the predominant fraction (50.14-70.15% of the total) for Cu in all original sludge samples, which represented the portion of metals of the organic matter and sulfides bound. It is reported that Cu in sludge had a strong tendency to remain as sulfide minerals or chelate associating with organic matter of sludge [24]. The second most important fraction of Cu is F5 (14.53-32.44%), which indicated the presence of residual fraction of Cu in the sludge. Combination of F4 and F5 accounts 75.69-85.16% of the total Cu, which suggests that solubilization of Cu would need more highly oxidizing and acidic conditions than that Zn and Pb. Among chemical forms of Pb, F4 is the predominant fraction, which equals 41.28-61.94% of the total, which was similar to thepublishedresult in another literature [25].

Taking considering changes of different chemical forms of Zn in different sludge system, the exchangeable fraction (F1) is gradually increased in PS and SS during bioleaching process of 9 days, but an unobvious regularity in OS and AS. This difference may be attributed to variation of physicochemical properties of OS and AS. Active sludge is formed mostly by floating microorganism with greater surface area than PS and SS [25]. Another interesting observation is a slightly decrease of carbonate bound (F2) of Zn with a small proportion in SS but sharply rised in PS, AS, OS. The residual fraction (F5) of Zn has a drastic reduction in PS、OS and AS, but an increase in SS. The continually low pH condition combines with highly oxidizing environment enhanced the liberation of organically bound (F4) of Cu. It is reported that Cu was hard to be dissolved into organic matter due to its tough affinity, which a strong acidic conditions should be required [26]. Significant differences of Fe-Mn oxides fraction (F3) of Cu is observed between SS and other sludge during bioleaching process, which suggess that the thickening treatment of sludge significantly influenced transformation of chemical forms. In the exchangeable of Pb, slightly increases during the first 7days and suddenly decreasessince the 7th day was observed in PS, AS and SS. For all the four sludge, the carbonate fraction (F2) and Fe-Mn oxides fraction (F3) of Pb show a slight change during the running, while the organically fraction (F4) has obvious increase because of the oxidizing condition [27].

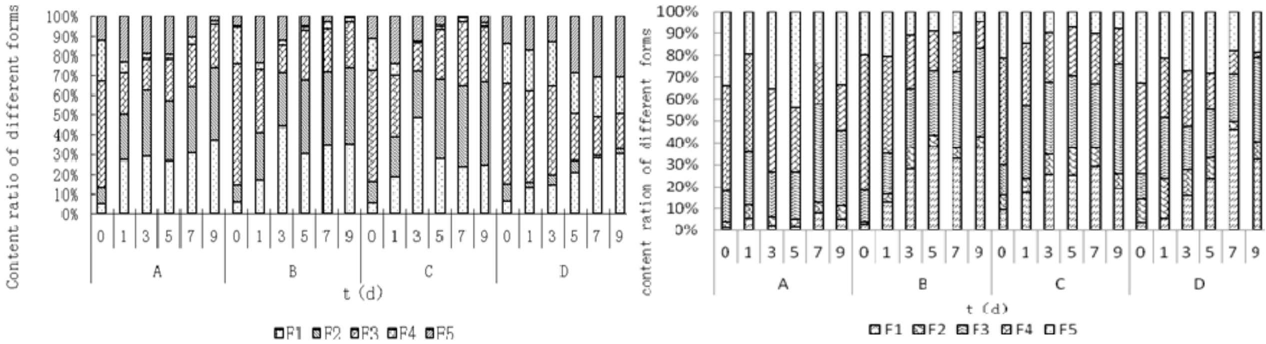

Fig. 3 Chemical forms of Zn, Cu and Pb during bioleaching
: A for PS, B for OS, C for AS, D for SS

After bioleaching, the distribution of heavy metaland chemical fraction in bioleached sludge vary from one metal to another. For Cu in all bioleached sludge, the predominant fraction is the residual fraction (average 32.71% of the total).Likewise, Pb in PS remains as the residual fraction after bioleaching, while Fe-Mn oxides bound in OS,AS and SS. Zn presents in a high available fraction(F_{1+2}) in PS, OS and AS, however, as the residual fraction in SS.

Based on above results, it is observed that sludge characteristics and chemistry of metals can significantly affect the transformation of heavy metals during bioleaching process.

4.Conclusions

(1) Sludge collected from different treatment steps of WWTP is suitable for the land utilization after bioleaching for its high value of fertilizer. The bioleaching technologyhas a good removal efficiency of Zn, Cu and Pb with 62.6%、66.35% and 67.98% of removal rate, respectively.

(2) pH in PS,OS,AS and SS decreases slightly from an initial value 7.14,7.38,7.49 and 7.02 to 2.37,2.46,2.41 and 2.01,respectively after 9 days with the addition of substrates and inoculum. The pH and ORP in PS change more quickly in first three days than other sludge. There is little difference of changes of pH and ORP between OS and AS from the third day.

(3) The content of EPS of Zn and Cu increase gradually in first 5 days, while no obvious regulation in Pb-EPS.A better adsorption ability for Zn-EPS, Cu-EPS and Pb-EPS is in SS, PS and OS, respectively. Content of Pb in LB-EPS is more than in TB-EPS during 9 days. For Zn and Cu, a better concentration is in LB-EPS in the early leaching period while that of TB-EPS is at the end.

(4) In raw sludge, the predominant fraction of Zn is Fe-Mn oxides fraction, and that of Cu and Pb is organic fraction in all sludge system. After bioleaching, Pb in PS remained as the residual fraction, while Fe-Mn oxides fraction in OS,AS and SS. Zn presents in a high available fraction(F_{1+2}) in PS,OS and AS, and the residual fraction in SS. For Cu in all bioleached sludge, the predominant fraction is the residual fraction (average 32.71% of the total). The species of sludge has a great effect on the transformation of heavy metals during bioleaching process.

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