



Enhancement of metal bioleaching from sewage sludge by cotton stalk

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ABSTRACT

It was found that the distribution of heavy metals in liquid and solid phases at the end of bioleaching of sewage sludge could be described by adsorption isotherm model. Cotton stalk could be used to improve heavy metal leaching efficiency in bioleaching of sewage sludge. Amended with 5 g/L cotton stalk in late bioleaching, leaching efficiency increased from 56.75, 56.42, and 62.28 to 73.18, 81.34, and 82.39% for copper, lead, and chromium, respectively, with 6% pulp density. Relationship between heavy metals in liquid phase and that adsorbed onto cotton stalk could be described by Freundlich equation. Adsorption onto cotton stalk lowered heavy metal concentration in liquid phase. Consequently, more heavy metals were released from sewage sludge. The increased section of heavy metals released from sludge was mainly attributed to mobile fractions. Content of heavy metals in stable fractions was left unchanged. Mobility of residual heavy metals in sludge after bioleaching with treatment was also lowered greatly.

Keywords: Bioleaching; Leaching efficiency; Adsorption; Cotton stalk

1. Introduction

Bioleaching has been proven to be the most promising method to remove heavy metals from sewage sludge for a long time [1]. To remove heavy metals from sewage sludge as much as possible, many efforts have been carried out on optimizing bioleaching process [1–5]. However, bioleaching is influenced by many interacting factors such as origin of sludge, temperature, pulp density, aeration, and pre-acidification. This fact makes bioleaching process optimization troublesome and far from practical application.

Some bioleaching strategies could also enhance heavy metal leaching efficiency in laboratory. Continuous bioleaching is an effective technique to enhance leaching efficiency [1,6]. In continuous bioleaching, the wastewater produced in bioleaching process is

replaced by fresh water partly and continuously to keep the heavy metal concentration in water phase at a low level. So, more heavy metals can be solubilized from sludge than that in batch bioleaching. For the huge water consumption and wastewater production, continuous bioleaching is definitely not suitable for practical application.

However, the high leaching efficiency in continuous bioleaching implies that more heavy metals might be released from sewage sludge if the heavy metal concentration in water phase could be held at a low level. It is known that adsorption can lower heavy metal concentration in liquid phase. Biomass is well known as an adsorbent for heavy metals [7–9]. At the same time, heavy metals in biomass can be recovered easily which makes biomass more feasible than other adsorbents in application [10–12].

In this paper, adsorption of heavy metals from wastewater in bioleaching onto cotton stalk and the enhancement in leaching efficiency were investigated. Variation in speciation of heavy metals in sewage sludge after bioleaching treated with adsorption was also investigated to evaluate the mechanism of enhancement.

2. Materials and methods

2.1. Materials

Sewage sludge was an activated municipal sludge provided by Zhifang sewage treatment plant in Wuhan City, Hubei Province, China. Initial pH of sewage sludge was 8.1 and moisture content which was investigated with 80°C for 16 h was 87.3%. It contained 358 ± 1.2 mg/kg copper, 220 ± 2.3 mg/kg zinc, 237 ± 5.9 mg/kg lead, and 46 ± 0.8 mg/kg chromium in dry weight, respectively, and traced other heavy metals (<10 mg/kg).

Cotton (*Gossypium* spp.) stalk was the stem of cotton from farm around Wuhan City, Hubei Province, China. It was reaped and crushed into fragments of 0.5 cm wide and around 5 cm long by machine. Crushed cotton stalk was then dried under the sun for 7 d to reduce the moisture content (decreased from 21.2 to 5.6%).

2.2. Apparatus and procedures

2.2.1. Bioleaching

Batch bioleaching was carried out in 2.5 L flasks. Different amounts of sewage sludge were added to 1 L deionized water with 1.1 g/L elemental sulfur as energy resource. Rotation was 220 rpm and the temperature was 30°C. Evaporation was compensated by deionized water per 48 h. Pulp density ranged from 3.5 to 6.5% w/v in dry weight with a 0.5% degree. When the pH finally stabilized at around 2.0 for 6 h, bioleaching reached the endpoint. The flask was then left standing for another 2 h to separate solid and liquid phases. Sediment was centrifuged for 15 min at 3,000 rpm. The final sediment is the acidified sludge. Moisture content of acidified sewage sludge was all around 82.6%. The water after bioleaching was acidified with wastewater which contained all the heavy metals that leached out from sewage sludge.

2.2.2. Bioleaching amended with cotton stalk

Cotton stalk was added when pH stabilized at around 2.0 for 2 h. After bioleaching reached the

endpoint, cotton stalk was removed and the leaching efficiency was investigated. In this experiment, 4 h was ample for cotton stalk to establish adsorption equilibrium.

2.2.3. Speciation of heavy metals

Heavy metals in sewage sludge and acidified sewage sludge were extracted by HCl:HNO₃:HClO₄ (3:1:1). Heavy metals in biomass were extracted by HNO₃:HClO₄ (3:1). Speciation of metals was determined by a sequential extraction procedure, which was based on the method reported by Tessier et al. [13]. In this procedure, five fractions of metal bound in 1 g sludge were selected. Exchangeable (S1) fraction was extracted at room temperature for 1 h with 8 mL of magnesium chloride solution at pH 7.0. Then, bound to carbonates (S2) fraction was extracted from residue at room temperature with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid. The residue was further treated with 20 mL of 0.3 M Na₂S₂O₄ + 0.175 M Na-citrate + 0.025 M H-citrate to extract bound to iron and manganese oxides (S3) fraction. Bound to organic matter (S4) fraction was extracted by two steps. The residue was treated with 3 mL of 0.02 M HNO₃ and 5 mL of 30% H₂O₂ adjusted to pH 2 with HNO₃ at 85 ± 2°C with occasional agitation for 2 h. Then, a second 3-mL aliquot of 30% H₂O₂ (pH 2 with HNO₃) was compensated. The solution was further treated at 85 ± 2°C for 3 h with intermittent agitation, and finally treated with 5 mL of 3.2 M NH₄OAc in 20% (v/v) HNO₃ diluted to 20 mL and agitated continuously for 30 min. Residual fraction (S5) was extracted from the final residue with HCl: HNO₃: HClO₄ (3:1:1) mixture.

The determination of heavy metals was carried out by a TAS-986 Flame Atomic Absorption Spectrometer. Detection limitation of the spectrometer is 0.006 mg/L. It measures the sample for five times and presents the mean value with four decimal accuracy in mg. Determination of Cr and fractions of metals was carried out by ICP.

2.2.4. Adsorption model

Adsorption investigation was carried out at 220 rpm, 30°C.

Kinetic experiments were performed to assess the uptake rates and contact times needed for completion of adsorption reactions in treatment systems. Pseudo-first-order Eq. (1) and pseudo-second-order Eq. (2) were used to study the adsorption kinetics.

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (1)$$

$$t/q_t = 1/k_2q_e^2 + 1/q_e t \quad (2)$$

In these equations, k is the equilibrium rate constant of adsorption, q_e is the amount of metal ions adsorbed at equilibrium, and q_t is the amount of metal ions on the surface of the adsorbent at time t (mg/g).

The most commonly used isotherm equations in modeling adsorption are Langmuir (3) and Freundlich (4) equations. They may be written as:

$$1/q_e = 1/k_L q_m c_e + 1/q_m \quad (3)$$

$$\ln q_e = \ln k_f + 1/n \cdot \ln c_e \quad (4)$$

where q_e is the amount of metal ions adsorbed per specific amount of adsorbent (mg/g), c_e is the equilibrium concentration (mg/L), q_m is the amount of metal ions required to form a monolayer (mg/g), k_L is the Langmuir equation parameter, k_f and $1/n$ are Freundlich equation parameters.

3. Results and discussion

3.1. Bioleaching and heavy metal adsorption onto acidified sewage sludge

Bioleaching could reach the endpoint in 6 d in this experiment. In a pulp density range from 4.0 to 6.0%, leaching was efficient (Table 1) and fertilizer value loss varied little (approximately 21% loss for nitrogen and 44% loss for phosphorus). When pulp density was lower than 4.0% in this experiment, mass loss and fertilizer value loss (higher than 43% for nitrogen and 61% for phosphorus) were high. The more, because little sewage sludge could be treated in a given volume of bioreactor and period, the low pulp density was not feasible in application. When pulp density was higher than 6.5%, sewage sludge couldn't be acidified

effectively and only little heavy metals were solubilized except chromium. The most suitable pulp density for the experimental sewage sludge with the given bioleaching conditions was 6.0%.

Sewage sludge and its derivate had been proven to be excellent adsorbents for heavy metals [14]. For the competition by hydrogen ion, their adsorption capacity for heavy metals would be heavily weakened under acid condition. However, they might still be capable to adsorb heavy metals, because there were always some residual heavy metals in sewage sludge after bioleaching. With the result in Table 1, a series of distributions of heavy metals in solid and liquid phases of bioleaching could be achieved and treated as q_e and c_e , respectively. Fitting of them to adsorption isotherm equations was presented in Table 2; it could be found that the distributions of heavy metals at different pulp densities could be described by Freundlich equation. It implied that acidified sewage sludge might be considered as adsorbent for heavy metals at the end of bioleaching to study the leaching efficiency.

To verify the adsorption capacity of acidified sewage sludge to heavy metals, adsorption of heavy metals onto dry acidified sewage sludge (after bioleaching with 6% pulp density) in standard solution at pH 2.0 (H_2SO_4) was also investigated (Table 2). The investigation was carried out in 250 mL flasks with 100 mL standard solution and 1 g dry acidified sewage sludge for 4 h. Results revealed that acidified sewage sludge was indeed an adsorbent for heavy metals and the adsorption could be described by Freundlich equation. It meant that adsorption might be an important factor influencing leaching efficiency. The adsorption analysis might be helpful to determine the suitable pulp density of bioleaching in practical application.

3.2. Adsorption of heavy metals onto cotton stalk

According to the adsorption mechanism, another adsorbent might cause desorption of heavy metals from

Table 1
Bioleaching of sewage sludge at different pulp densities

| Pulp density (%) | Period (h) | Final pH | Mass loss (%) | Metal leaching efficiency (%) | | | |
|------------------|------------|-------------|---------------|-------------------------------|--------------|--------------|--------------|
| | | | | Cu | Zn | Pb | Cr(III) |
| 3.5 | 96 | 1.57 ± 0.01 | 34.2 ± 5.94 | 76.25 ± 0.23 | 81.24 ± 0.07 | 62.38 ± 0.03 | 86.74 ± 1.27 |
| 4.0 | 144 | 2.01 ± 0.01 | 11.52 ± 1.22 | 64.73 ± 1.24 | 48.72 ± 2.11 | 46.55 ± 1.25 | 80.33 ± 2.33 |
| 4.5 | 144 | 1.98 ± 0.02 | 11.46 ± 1.03 | 63.44 ± 1.78 | 45.13 ± 1.87 | 52.41 ± 1.47 | 78.16 ± 1.41 |
| 5.0 | 144 | 1.97 ± 0.01 | 12.31 ± 2.02 | 60.78 ± 1.44 | 41.63 ± 2.41 | 55.53 ± 2.63 | 70.61 ± 1.29 |
| 5.5 | 144 | 2.0 ± 0.03 | 10.57 ± 0.55 | 59.83 ± 2.21 | 39.38 ± 0.99 | 53.85 ± 1.35 | 66.28 ± 1.57 |
| 6.0 | 144 | 2.1 ± 0.02 | 11.25 ± 0.97 | 56.75 ± 1.37 | 36.19 ± 1.52 | 56.42 ± 1.22 | 62.28 ± 1.24 |
| 6.5 | 192 | 3.4 ± 0.1 | 2.35 ± 0.1 | 0 | 27.55 ± 4.25 | 9.24 ± 3.61 | 58.44 ± 0.94 |

Table 2
Adsorption of heavy metal onto acidified sewage sludge

| | | At different pulp densities (%) | | | | | | In standard solution at different concentration (mg/L) | | | | | |
|----|-----|---------------------------------|--------------|--------------|---------------|----------------|---------------|--|--------------|--------------|--------------|--|--|
| | | Pulp density (%) | c_e (mg/L) | q_e (mg/g) | Freundlich | Langmuir | Concentration | c_e (mg/L) | q_e (mg/g) | Freundlich | Langmuir | | |
| Cu | 4.0 | 9.27 | 0.1427 | 0.1427 | R^2 0.8981 | R^2 0.9006 | 1 | 0.84 | 0.016 | R^2 0.9785 | R^2 0.9801 | | |
| | 4.5 | 10.22 | 0.1478 | 0.1478 | $1/n$ 0.6772 | q_m 0.4675 | 2 | 1.74 | 0.026 | $1/n$ 0.7492 | q_m 0.132 | | |
| | 5.0 | 10.88 | 0.1601 | 0.1601 | k_f 0.0313 | k_l 0.0467 | 5 | 4.52 | 0.048 | k_f 0.0172 | k_l 0.0028 | | |
| | 5.5 | 11.78 | 0.1608 | 0.1608 | | | 10 | 9.21 | 0.079 | | | | |
| | 6.0 | 12.19 | 0.1745 | 0.1745 | | | 15 | 13.55 | 0.145 | | | | |
| Zn | 4.0 | 4.29 | 0.0850 | 0.0850 | R^2 0.9574 | R^2 0.9696 | 1 | 0.93 | 0.007 | R^2 0.9584 | R^2 0.9679 | | |
| | 4.5 | 4.47 | 0.1023 | 0.1023 | $1/n$ 5.2227 | q_m -0.0268 | 2 | 1.89 | 0.011 | $1/n$ 1.202 | q_m 0.323 | | |
| | 5.0 | 4.58 | 0.1220 | 0.1220 | k_f 4.22e-5 | k_l -0.1776 | 5 | 4.74 | 0.026 | k_f 0.0059 | k_l 0.0024 | | |
| | 5.5 | 4.77 | 0.1367 | 0.1367 | | | 10 | 9.13 | 0.087 | | | | |
| | 6.0 | 4.78 | 0.1582 | 0.1582 | | | 15 | 13.29 | 0.171 | | | | |
| Pb | 4.0 | 4.41 | 0.0954 | 0.0954 | R^2 0.7572 | R^2 0.701 | 1 | 0.51 | 0.049 | R^2 0.8664 | R^2 0.8036 | | |
| | 4.5 | 5.59 | 0.0955 | 0.0955 | $1/n$ 0.3498 | q_m 0.1511 | 2 | 1.37 | 0.063 | $1/n$ 0.7324 | q_m 0.201 | | |
| | 5.0 | 6.58 | 0.1002 | 0.1002 | k_f 0.0547 | k_l 0.3557 | 3 | 1.97 | 0.103 | k_f 0.069 | k_l 0.024 | | |
| | 5.5 | 7.02 | 0.1121 | 0.1121 | | | 4 | 2.47 | 0.153 | | | | |
| | 6.0 | 8.02 | 0.1164 | 0.1164 | | | 5 | 3.18 | 0.182 | | | | |
| Cr | 4.0 | 1.48 | 0.0068 | 0.0068 | R^2 0.8341 | R^2 0.8616 | 1 | 0.97 | 0.003 | R^2 0.9804 | R^2 0.9903 | | |
| | 4.5 | 1.62 | 0.0085 | 0.0085 | $1/n$ 6.9406 | q_m -1.85e-3 | 2 | 1.93 | 0.007 | $1/n$ 1.0963 | q_m -0.226 | | |
| | 5.0 | 1.62 | 0.0128 | 0.0128 | k_f 4.14e-4 | k_l -0.5286 | 5 | 4.87 | 0.013 | k_f 0.003 | k_l -0.001 | | |
| | 5.5 | 1.68 | 0.0159 | 0.0159 | | | 10 | 9.65 | 0.035 | | | | |
| | 6.0 | 1.72 | 0.0195 | 0.0195 | | | 15 | 14.34 | 0.066 | | | | |

q_e : By difference.

acidified sewage sludge. Lignocellulose had been proven to be an efficient adsorbent for heavy metals [15,16]. There was 5,000,000 ton of cotton stalk produced as biomass waste in China yearly. Cotton stalk was a cheap lignocellulose, capable to adsorb heavy metals [17,18]. In this experiment, adsorption capacity of heavy metals onto cotton stalk was investigated at the first. Amount of cotton stalk was counted in dry weight.

Acidified wastewater from bioleaching with 6.0% pulp density was used to investigate the adsorption of heavy metals onto cotton stalk. Concentrations of copper, zinc, leads and chromium in acidified wastewater were 12.19, 4.78, 8.02, and 1.72 mg/L, respectively. Adsorption of copper onto 0.25 g cotton stalk in 1 L acidified wastewater was 1.00, 1.28, 1.52, 1.68, 1.92, 2.20, and 2.24 mg/g at 30, 60, 90, 120, 150, 180, and 210 min, respectively. The adsorption of copper could be described by pseudo-second-order equation with 0.9644 for R^2 and 2.99 mg/g for q_e . For lead, the adsorption was 30.68, 39.12, 44.08, 45.12, 45.40, and 45.48 mg/g at 30, 60, 90, 120, 150, and 180 min, respectively. Parameters for pseudo-second-order equation were 0.998 (R^2) and 49.26 mg/g (q_e). Because the amount of chromium was little in acidified wastewater, its adsorption onto cotton stalk was not investigated. At the same time, no adsorption of zinc onto cotton stalk was detected.

Well-fitting of pseudo-second-order equation to adsorption process meant more factors influencing the adsorption other than concentration of metals [19]. Especially, adsorption in individual metal standard solution in pH 2.0 H_2SO_4 demonstrated the same results except higher q_e s (3.45 mg/g for copper and 60.24 mg/g for lead).

The abundant $-OH$ group on biomass didn't take part in the adsorption under the acid condition (Fig. 1). Adsorption capacity was mainly attributed to the free carboxyl group on lignin at $1,733\text{ cm}^{-1}$ [7].

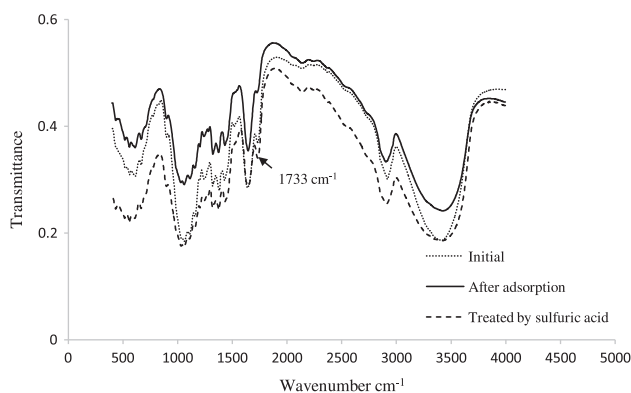


Fig. 1. FTIR spectra of cotton stalk samples.

Because there were few free carboxyl groups on lignocelluloses, adsorption capacity of lignocelluloses in acid solution was poor. Meanwhile, normally, metal adsorption onto lignin was thought to be strongly pH dependent. Because of the competition with H^+ , adsorption would be weakened with the decrease in pH. It made the adsorption under acid condition much lower than that in neutral solution [8,20]. However, it could also be found that peaks at $1,733\text{ cm}^{-1}$ strengthened after treatment with pH 2.0 H_2SO_4 for 2 h. It meant that acid treatment could produce free carboxyl group on lignocellulose. According to existing researches, moderate acid treatment could break the cross-linking in lignocellulose by partly hydrolyzing hemicellulose and release the groups on lignin [21,22]. Acid treatment should attribute to adsorption at the same time.

Adsorption equilibrium investigation was performed with different amounts of cotton stalk. Results were presented in Table 3. Correlation coefficients obtained from Langmuir equation were high. However, the values of q_m did not fit the adsorption data. Freundlich equation could be used to describe the adsorption with $1/ns$ higher than 0.5, which fit the long adsorption period.

Copper and chromium sorption observed were lower than their sorption onto lignin in neutral condition [7]. In contrary, adsorption of lead was higher which might be more complex than other metals. Given the metal concentration in acidified wastewater, adsorption capacity of cotton stalk was considerable. Compared with existing chemical method to enhancing leaching efficiency in bioleaching [23], adsorption by cotton stalk would produce no secondary pollution and can be easy to recover heavy metals. It might be a feasible method in application.

3.3. Bioleaching amended with cotton stalk

Enhancement in 6% pulp density bioleaching amended with cotton stalk was investigated. It can be found in Table 4 that leaching efficiency increased with the increase in cotton stalk amount. When the amount of cotton stalk was 5 g, leaching efficiency was the highest.

Adsorption of heavy metals onto cotton stalk could still be described by Freundlich equation. The adsorption lowered metal concentration in acidified wastewater. Consequently, more metal residual in sewage sludge could be solubilized. It could be confirmed by the metal equilibrium concentration in acidified wastewater, and q_e here were higher than those in Table 3. More cotton stalk would lead to more solubilization.

Table 3
Adsorption of metals onto cotton stalk and the fitting to isotherm model

| | Amount of cotton stalk (g) | c_e (mg/L) | q_e^* (mg/g) | Freundlich | | Langmuir | |
|----|----------------------------|--------------|----------------|------------|--------|----------|--------|
| Cu | 0.25 | 11.63 | 2.24 | R^2 | 0.8802 | R^2 | 0.9059 |
| | 0.5 | 11.24 | 1.90 | $1/n$ | 0.668 | q_m | 4.35 |
| | 0.75 | 10.83 | 1.82 | k_f | 0.3858 | k_l | 0.07 |
| | 1 | 10.43 | 1.76 | | | | |
| | 2 | 8.97 | 1.61 | | | | |
| | 5 | 5.79 | 1.28 | | | | |
| Pb | 0.25 | 0.81 | 45.52 | R^2 | 0.8839 | R^2 | 0.9274 |
| | 0.5 | 0.67 | 23.04 | $1/n$ | 1.6307 | q_m | -48.78 |
| | 0.75 | 0.53 | 15.55 | k_f | 52.23 | k_l | -0.506 |
| | 1 | 0.37 | 11.82 | | | | |
| Cr | 0.25 | 0.1878 | 6.12 | R^2 | 0.8383 | R^2 | 0.8901 |
| | 0.5 | 0.1623 | 3.11 | $1/n$ | 2.7162 | q_m | -1.92 |
| | 0.75 | 0.1529 | 2.09 | k_f | 463.91 | k_l | -3.77 |
| | 1 | 0.1173 | 1.60 | | | | |

*By difference.

Table 4
Leaching efficiency of bioleaching with 6% pulp density amended with cotton stalk

| | Amount of cotton stalk (g) | c_e (mg/L) | q_e (mg/g) | Freundlich | | Langmuir | | Leaching efficiency (%) |
|----|----------------------------|--------------|--------------|------------|---------|----------|---------|-------------------------|
| Cu | 0.5 | 11.65 | 2.27 | R^2 | 0.9131 | R^2 | 0.9328 | 59.52 |
| | 0.75 | 11.37 | 2.01 | $1/n$ | 1.0699 | q_m | -31.45 | 59.95 |
| | 1 | 11.13 | 1.95 | k_f | 0.1522 | k_l | -5.32 | 60.89 |
| | 1.25 | 10.97 | 1.88 | | | | | 62.01 |
| | 3 | 9.15 | 1.67 | | | | | 65.92 |
| | 5 | 8.37 | 1.47 | | | | | 73.18 |
| Pb | 0.5 | 0.6843 | 15.25 | R^2 | 0.9336 | R^2 | 0.8936 | 58.43 |
| | 0.75 | 0.5521 | 12.17 | $1/n$ | 1.592 | q_m | -7.2516 | 68.07 |
| | 1 | 0.4257 | 9.34 | k_f | 32.3172 | k_l | -64.52 | 68.68 |
| | 1.25 | 0.3224 | 7.26 | | | | | 66.09 |
| | 3 | 0.2545 | 3.55 | | | | | 76.68 |
| | 5 | 0.2164 | 2.27 | | | | | 81.34 |
| Cr | 0.5 | 0.172 | 3.1 | R^2 | 0.9568 | R^2 | 0.9192 | 62.39 |
| | 0.75 | 0.155 | 2.31 | $1/n$ | 2.2482 | q_m | -0.7682 | 68.38 |
| | 1 | 0.120 | 1.82 | k_f | 175.02 | k_l | -3.1087 | 70.29 |
| | 1.25 | 0.110 | 1.48 | | | | | 71.01 |
| | 3 | 0.087 | 0.69 | | | | | 78.15 |
| | 5 | 0.074 | 0.44 | | | | | 82.39 |

Amended with cotton stalk, variation in leaching efficiency of bioleaching with 6% pulp density could not be described by adsorption isotherm equation any more. It definitely meant that the adsorption equilibrium of heavy metals onto acidified sewage sludge was disturbed by cotton stalk and the enhancement in leaching efficiency was caused by desorption of heavy metals from acidified sewage sludge. The more, almost all the $1/n$ s of Freundlich equation in Table 2 were higher than 0.5. It meant the decrease in metal concentration in liquid phase would lead to more

release of metals from sludge. This procedure would undoubtedly benefit from the adsorption of metals onto cotton stalk.

3.4. Speciation of heavy metals after bioleaching and the leaching efficiency

However, when amount of cotton stalk was higher than 5 g, no great enhancement in solubilization could be detected. More factors than adsorption influenced the distribution of heavy metals at the end of bioleach-

ing. Speciation of heavy metals in sludge would vary after bioleaching as presented in Fig. 2. Metal had a characteristic fractionation profile independent of the operating conditions after bioleaching [24,25]. Chen et al. found that the speciation was just dependent on the final pH in bioleaching [26]. Speciation of residual heavy metals in acidified sewage sludge varied little in the pulp density with the range of 4.0–6.0%, because the final pH was almost the same. In sequential extraction procedure, S1, S2, and S3 fractions were thought to be mobile and might endanger the environment. S4 and S5 fractions were stable and would be safe in environment [13,27]. After bioleaching, proportion of mobile fractions increased greatly. Though the total heavy metals content decreased, heavy metals risk was not completely eliminated [28]. Former research had revealed that the S1 fraction was easy to be exchanged [26]. According to the mechanism of sequential extraction procedure, S2 and S3 fractions could be also exchanged at the end of bioleaching because the bioleaching conditions were much more strenuous than the extraction conditions [29]. Sequential extraction investigation revealed that the contents of S1, S2, and S3 fractions of heavy metals in acidified sewage sludge decreased with increase in cotton stalk, and the distribution of these fractions became irregular. Contents of S4 and S5 fractions remained constant. Definitely, because only part of heavy metals in acidified sewage sludge participated in adsorption and desorption, variation of heavy metals in acidified sewage sludge to that in acidified wastewater could not

be described by the adsorption isotherm equation when amended with cotton stalk.

Normally, leaching efficiency was calculated by the ratio of metals in acidified wastewater to the initial amount. Leaching efficiency in Table 4 was calculated in this way with the addition of metals adsorbed onto cotton stalk. If the moisture content of acidified sewage sludge was treated as a part of acidified wastewater, leaching efficiency should be 90.03, 82.01, and 83.55% for copper, lead, and chromium, respectively.

On the other hand, leaching efficiency can also be calculated by the difference between heavy metals in acidified sewage sludge and the initial amount. Leaching efficiency calculated in this way was 56.73, 57.82, and 58.91% for copper, lead, and chromium, respectively. Acidified sewage sludge could be further centrifuged for 15 min at 12,000 rpm, and the moisture content could be lowered to 73.6%. Leaching efficiency would increase to 64.31, 66.2, and 70.23% for copper, lead, and chromium, respectively. Contents of S4 and S5 fractions remained constant in the treatment. The rise should be attributed to S1, S2, and S3 fractions. With mass loss, if remnant metals in acidified sewage sludge was only S4 and S5 fractions, the maximum leaching efficiency could be 82.7, 84.74, and 92.46% for copper, lead, and chromium, respectively. The values were close to those calculated in the first method. Definitely, during drying, heavy metals initially in acidified wastewater bound in acidified sewage sludge [30] was transformed to be the integral part of S1, S2, and S3 fractions.

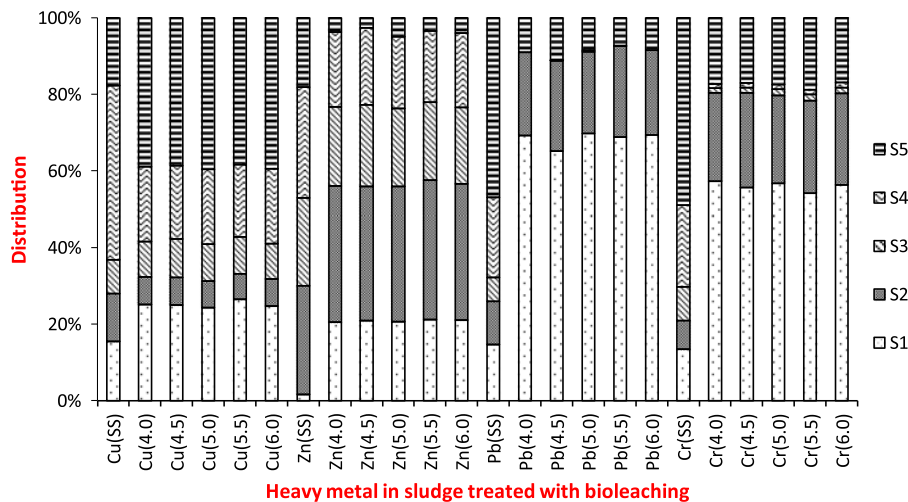


Fig. 2. Speciation of heavy metals in initial sewage sludge (SS) and the acidified sewage sludge after bioleaching at different pulp densities (%).

In the investigation on bioleaching of soil, it was thought that most of the remnant heavy metals were bound either to residual fraction or to other stable fractions [31]. The same thing happened in this experiment. The highest metal leaching efficiency in Table 4 was close to the theoretical value calculated in second method. It could be concluded that the enhancement was caused by the release of mobile fractions with the competition with cotton stalk.

Because acidified sewage sludge was normally high in moisture content, potential heavy metals risk was definitely higher than the calculation [30]. It was impossible to dewater sewage sludge after bioleaching completely. Lowering heavy metals concentration in acidified wastewater by adsorption could undoubtedly reduce the potential risk which would be feasible in application.

4. Conclusion

Sewage sludge at the end of bioleaching could be treated as adsorbent for heavy metals to investigate the leaching efficiency. With competition from cotton stalk, more heavy metals could be released from sewage sludge and leaching efficiency of heavy metals could be enhanced. Because the enhancement was mainly caused by the release of heavy metals in mobile fractions, cotton stalk treatment made the sewage sludge after bioleaching safer than before.

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List of symbols

| | | |
|-----------------|---|---|
| $k_{1/2}$ | — | the equilibrium rate constant of adsorption |
| q_e | — | the amount of metal ions adsorbed at equilibrium (mg/g) |
| q_t | — | the amount of metal ions on the surface of the adsorbent at time t (mg/g) |
| t | — | time (min) |
| c_e | — | the equilibrium concentration in liquid phase (mg/L) |
| q_m | — | the amount of metal ions required to form a monolayer (mg/g) |
| k_L | — | langmuir equation parameter |
| k_f and $1/n$ | — | freundlich equation parameters |

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