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# Assessment of recoverable forms of sulfur particles used in bioleaching of contaminated sediments

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#### Abstract

The use of recoverable sulfur particles will enhance the feasibility and reduce the cost of bioleaching process. Three different forms of sulfur particles, powder, pastilles and pellets were used to study the utilization and recovery of sulfur, used as energy source for thiobacilli in the bioleaching process. The Langmuir isotherm was used to explain the adsorption equilibrium existing between the sorbed and suspended bacteria and the maximum adsorption capacity obtained from the Langmuir isotherm was utilized to determine the specific surface area of the sulfur particles. The specific surface area of sulfur particles was found to be the determining factor in the bioleaching process and not the particle size. The rates of pH reduction, sulfate production and metal solubilization increased with increasing specific surface area of the particles. The pH reduction and metal solubilization were significantly enhanced by the reuse of recovered sulfur particles. The efficiency of metal solubilization with recovered sulfur pastilles was comparable to that with sulfur powder. This study revealed the practicability of reusing the recovered sulfur pastilles in the bioleaching process.

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#### 1. Introduction

In industrialized and densely populated areas, bottom sediments in rivers act as a sink for the heavy metals contained in industrial wastewaters and municipal sewage. For maintaining the water quality and managing waterways, the sediments in water bodies are dredged regularly. The sediments dredged from the contaminated sites usually contain high concentrations of heavy metals that may pose potential hazards to human health and environment if disposed on land. This necessitates the removal of heavy metals from the contaminated sediments before land application. The bioleaching process has been recognized as a better

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alternative to physical and chemical procedures for the removal of heavy metals from contaminated sediments [1–5]. Aerobic bacteria, belonging to genus *Thiobacillus*, are commonly used in the bioleaching process. These gram-negative, non-spore forming, rod-shaped bacteria are chemoautotrophic obtaining their energy from the oxidation of elemental sulfur or reduced inorganic sulfur. They can tolerate high concentrations of heavy metals and hydrogen ions, in which other bacteria cannot survive [6].

When insoluble elemental sulfur is used as substrate in the bioleaching process, the microbial oxidation of sulfur by thiobacilli is believed to take place by the adsorption and growth of bacteria on the surface of sulfur [7]. The adsorption of bacteria to solid substrate plays a vital role in the bioleaching process by enhancing the sulfur oxidation rate [8]. Therefore, sulfur powder, which provides larger surface area for the adsorption of

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thiobacilli is commonly used as substrate in the bioleaching process [9,5,1-4]. However, about 60-70% of the sulfur powder added is not utilized during the bioleaching process [10]. The unused and unrecoverable sulfur powder remaining in the treated sediments increases the operational costs of the bioleaching process and causes acidification of the disposal land. Therefore, it is necessary to use recoverable forms of sulfur as substrate for thiobacilli in the bioleaching process. For assessment of recoverable forms of sulfur particles as substrates for thiobacilli in the bioleaching process, the performance of sulfur pastilles, sulfur pellets and commercially available sulfur powder were compared in the present work. In addition, adsorption experiments were also conducted with these different forms of sulfur particles (powder, pastille and pellet) to investigate the influence of adsorption of thiobacilli on sulfur particles in the bioleaching process.

## 2. Materials and methods

#### 2.1. Microorganisms and media

Thiobacillus thiooxidans (CCRC 15612) and Thiobacillus thioparus (CCRC 15623) obtained from the Culture Collection and Research Center (CCRC) of the Food Industry Research and Development Institute (FIRDI) [11] (Hsinchu, Taiwan) were used throughout this study. These bacteria were routinely cultured in two basal media, medium 317 for T. thiooxidans and medium 318 for T. thioparus. Medium 317 was composed of (in g/l): (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.3; K<sub>2</sub>HPO<sub>4</sub>, 3.5; MgSO<sub>4</sub> · 7H<sub>2</sub>O, 0.5; CaCl<sub>2</sub>, 0.25 and tyndallized sulfur powder, 5.0. The pH of the medium was adjusted to 4.5 using 1 N H<sub>2</sub>SO<sub>4</sub>. Medium 318 contained (in g/l):  $(NH_4)_2SO_4$ , 0.3; K<sub>2</sub>HPO<sub>4</sub>, 4.0; KH<sub>2</sub>PO<sub>4</sub>, 1.5; MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.5 and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O, 10.0. The pH was adjusted to 7.0 using 1 N H<sub>2</sub>SO<sub>4</sub>. The cultures were incubated in 500 ml flasks shaken at 200 rpm and maintained at a temperature of 30°C.

# 2.2. Adsorption experiments

Three different forms of sulfur particles, commercially available sulfur powder (200–300 µm in diameter), sulfur pastilles and sulfur pellets were used in the adsorption experiments. The sulfur pastilles (1 cm in diameter by 0.3 cm in thickness) were prepared by solidifying melted elemental sulfur in a stainless steel mold at room temperature [12]. The sulfur pellets (2–4 mm in diameter) were prepared by solidifying melted elemental sulfur in water [13]. In the adsorption experiments, 0.5, 1.0, and 2.0 g each of the three forms of sulfur particles were added to 100 ml of the basal medium inoculated with 5 ml of bacterial suspension (*T. thioparus* or *T.* 

thiooxidans) in 250 ml flasks, separately. To evaluate the adsorption of thiobacilli on sulfur particles during the bioleaching process, the pH was adjusted to 7, 6, and 5 for the basal medium inoculated with *T. thioparus* (less-acidophilic), and 4, 3, and 2 for the one inoculated with *T. thiooxidans* (acidophilic). The flasks were mounted on a rotary incubator shaker set at 200 rpm and maintained at 30°C for 5 h to accomplish adsorption equilibrium. At equilibrium, the bacterial cells in the liquid were enumerated and subtracted from the initial concentration of cells in the liquid to obtain the concentration of adsorbed bacterial cells.

## 2.3. Bioleaching experiments

The sediments for the bioleaching experiments were obtained from the lower reaches (near Nan Ding Bridge) of Ell-Ren River in Taiwan, one thought to be heavily polluted by heavy metals. In preparation for the bioleaching experiments, the subculture of thiobacilli was acclimated to the test environment of contaminated sediments and elemental sulfur. The mixed inoculum composed of 1% (v/v) of 5-day old subculture of *T. thiooxidans* and *T. thioparus* was transferred into 500 ml shaker flasks containing 150 ml of autoclaved suspension of the contaminated sediments (solid content: 2% (w/v)) and 0.5% (w/v) of tyndallized elemental sulfur. The shaker was set at 200 rpm at 30°C. The acclimation was continued until the pH of the sediments dropped to 2.0.

The bioleaching experiments were carried out in a completely mixed batch (CMB) reactor maintained at 30°C, mixed mechanically at 200 rpm and aerated with an air diffuser at a rate of 1.21/min. The innoculum, 5% (v/v) growing mixed culture of thiobacilli, obtained from the acclimation process was added to 31 of the sediment (solid content: 2% w/v) along with the different forms of sulfur particles (powder, pastille and pellet). The quantities and forms of sulfur particles added to the reactor, and the experimental conditions maintained during testing are summarized in Table 1. The first set of bioleaching experiments, designated as Run 1, was carried out using 5% (w/v) of fresh sulfur particles as the substrate. After completion of the run, the sulfur particles, except sulfur powder, were recovered from the sediments by a sieve with a mesh size of 2 mm. The recovered sulfur pastilles and pellets were washed with deionized water before reusing for the next set of bioleaching experiments (Run 2). To compensate for the losses during recovery, the sulfur pastilles and pellets were replenished to 5% (w/v) with fresh, tyndallized sulfur particles (pastille and pellet) before the subsequent run. Run 2 was conducted under the same test conditions as Run 1. The procedures were repeated for Run 3. The bioleaching experiments were terminated when the pH dropped to about 2.5. The progress of the

Table 1 Details of sulfur particles used in the bioleaching experiments

Experiment	Amount	Form	Sulfur particles added
Run 1	0.5% (w/v)	Powder	Fresh sulfur particles
	0.5% (w/v)	Pastille	
	0.5% (w/v)	Pellet	
Run 2	0.5% (w/v)	Pastille	Sulfur particles recovered from Run 1 <sup>a</sup>
	0.5% (w/v)	Pellet	_
Run 3	0.5% (w/v)	Pastille	Sulfur particles recovered from Run 2 <sup>a</sup>
	0.5%  (w/v)	Pellet	•

<sup>&</sup>lt;sup>a</sup>The deficiency of sulfur particles was complemented with fresh sulfur particles to 5% (w/v).

bioleaching experiments was monitored by periodic sampling of the sediment suspension for pH, sulfate and soluble heavy metals (Cu, Zn, Pb, and Ni).

## 2.4. Analyses

The cell numbers in the liquid were counted using a Levy's hemacytometer mounted on a microscope with a contrast phase arrangement. Several counts were conducted for each flask until reproducible results, with a variation equal to or less than 5% was obtained. The characteristics of the contaminated sediments such as total solids, organic matter [14] and pH [15] were determined. The total heavy metal concentration in the sediments was determined by HF-HNO<sub>3</sub>-HCl digestion method [16]. An on-line monitor (Tank, model RD-500) was used to measure the variation in pH during the bioleaching process. The sediment suspension taken from the reactor was filtered through a 0.45 µm membrane, and the filtrate was analyzed for sulfate concentration [14] and heavy metals. The heavy metal concentration was determined with a flame atomic absorption spectrophotometer (AAS) equipped with a graphite burner (Model Z-8100, Hitachi). The analyses indicated that the contaminated sediment used in the experiments had the following characteristics: total solids 72.14% (w/w), organic matter 2.07% (w/w), pH 7.85, Cu  $138 \mu g/g$  dry weight, Zn  $881 \mu g/g$  dry weight, Pb 201 μg/g dry weight and Ni 227 μg/g dry weight.

#### 3. Results and discussion

## 3.1. Adsorption of bacteria on sulfur particles

The representative kinetic data for adsorption of *T. thioparus* and *T. thiooxidans* on sulfur particles under different pH values are shown in Fig. 1. The concentration of free bacteria in the liquid phase decreased with time indicating greater adsorption of bacteria to sulfur particles. The concentrations of *T. thioparus* and *T. thiooxidans* adsorbed on sulfur particles appeared to be stable after 4 and 2 h, respectively. The adsorption of *T.* 

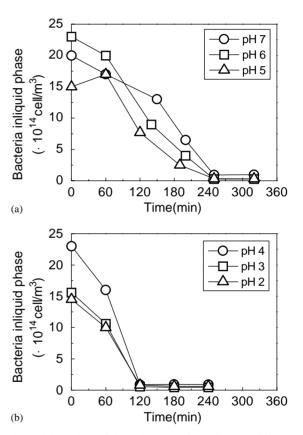


Fig. 1. Adsorption of bacteria on sulfur pellets at different pH values (a) *T. thioparus* (pH 5–7) and (b) *T. thiooxidans* (pH 2–4).

thioparus and *T. thiooxidans* to sulfur particles was found to reach equilibrium within 4 and 2 h. The concentrations of adsorbed *T. thioparus* and *T. thiooxidans* on sulfur particles were similar at the observed adsorption equilibrium. It was further noted that the maximum adsorption capacities of *T. thioparus* and *T. thiooxidans* were not significantly affected by pH. Blais et al. [9] found the generation time of *T. thioparus* to be between 6.7 and 8.8 h and that of *T. thiooxidans* to range

from 8.8 to 10.4 h in bioleaching of metals from sewage sludges. Chen and Lin [4] have also reported generation times of 9.1 and 12.2 h for *T. thioparus* and *T. thiooxidans*, respectively. It was concluded that the duration of bacterial adsorption on sulfur particles was significantly less than the generation time of these bacteria. Therefore, bacterial growth during adsorption equilibration was considered insignificant in the study.

Fig. 2 illustrates representative data for the adsorption equilibrium of thiobacilli on sulfur particles. The concentration of adsorbed bacteria per unit weight of sulfur particles approached a limiting value as the concentration of bacteria in the liquid phase increased. The equilibrium data in Fig. 2 was described by the Langmuir isotherm (Eq. (1)). The results of other adsorption experiments in this study also showed similar trends.

$$X_{\mathbf{A}} = \frac{K_{\mathbf{A}} X_{\mathbf{A} \mathbf{M}} X_{\mathbf{L}}}{1 + K_{\mathbf{A}} X_{\mathbf{L}}} \tag{1}$$

where  $X_A$  is the amount of bacteria adsorbed per unit weight of sulfur particles (cell/kg),  $X_{AM}$  is the maximum adsorption capacity (cell/kg),  $X_L$  is the concentration of

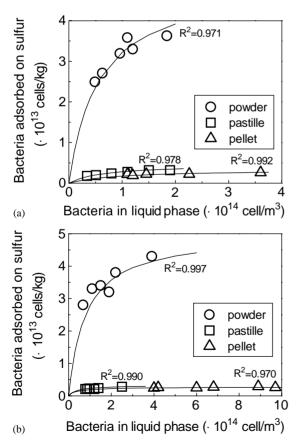


Fig. 2. Equilibrium adsorption isotherm for bacteria on different forms of sulfur particles (a) *T. thioparus* at pH 7 and (b) *T. thioparus* at pH 4.

bacteria in the liquid phase (cell/ $m^3$ ), and  $K_A$  is the adsorption equilibrium constant (m³/cell). The estimated values for parameters,  $X_{AM}$  and  $K_{A}$ , for adsorption of T. thioparus and T. thiooxidans on sulfur particles at different pH values are summarized in Table 2. The equilibrium constant,  $K_{A}$  in the Langmuir isotherm, represents the equilibrium between adsorption and desorption reactions. The value of  $K_A$  ranged from  $1.09 \times 10^{-13}$  to  $9.26 \times 10^{-14}$  m<sup>3</sup>/cell for T. thioparus and  $1.52 \times 10^{-13}$  -2.82 ×  $10^{-14}$  for *T. thiooxidans*. The form of sulfur particles and pH values used in the study did not have an appreciable affect on the value of  $K_A$ . The X<sub>AM</sub> values for T. thioparus and T. thiooxidans on sulfur pastilles were greater than those on sulfur pellets. However, the  $X_{AM}$  values of sulfur powder were about 10 times higher than those of sulfur pastilles and pellets suggesting the availability of larger surface area for adsorption of thiobacilli. The  $X_{AM}$  values for T. thioparus and T. thiooxidans on sulfur particles did not vary significantly in the pH range of 7-2. Therefore, pH had no apparent effects on the adsorption of thiobacilli on sulfur particles.

The surface characteristics of sulfur particles are vital in interpreting bacterial adsorption and bioleaching of metals from the sediments. Since elemental sulfur sublimes under vacuum, the surface area of sulfur particles cannot be directly measured by the specific surface area analyzer of BET. On the other hand, the Langmuir isotherm, which is the simplest theoretical adsorption model, can be applied when adsorption is limited to a single molecular layer on the solid [17]. Based on this adsorption theory, the maximum adsorption capacity,  $X_{\rm AM}$ , is a function of the specific surface area, which was determined by the following equation:

$$S_0 = \frac{X_{\text{AM}}S}{10^{11}},\tag{2}$$

where  $S_0$  is the specific surface area of the sulfur particle  $(cm^2/g)$ , and S is the surface area of a single molecule of adsorbate, which is bacterium (µm2). The bacteria inoculated in this study were rod-shaped cells of T. thioparus and T. thiooxidans. Based on the dimensions reported by Blais et al. [9],  $(0.3-0.4 \times 0.8-1.2 \,\mu\text{m})$  for T. thioparus and  $0.4-0.5 \times 1.2-2.0 \,\mu\text{m}$  for T. thiooxidans) the surface areas of the bacterial cells were calculated as  $0.35 \,\mu\text{m}^2$  for T. thioparus and  $0.56 \,\mu\text{m}^2$  for T. thiooxidans. The surface areas of sulfur pastilles and pellets calculated by Eq. (2) and by the particle size method, proposed by Bryant et al. [12], Laishley et al. [13] and Ravishankar et al. [10], were found to differ much (Table 3). The existence of micropores on sulfur pastilles and pellets could have resulted in an underestimation of surface areas by the particle size approach. Thus, the particle size method was found to be inadequate in determining the surface areas of sulfur particles in this study. During the preparation stage, since sulfur

Table 2
Estimated parameters of Langmuir isotherm for adsorption of thiobacilli on sulfur particles under different pH values

Microorganism	pН	Form	Size	X <sub>AM</sub> (cells/kg)	$K_{\rm A}~({\rm m}^3/{\rm cells})$	Reference
T. thioparus	7	Powder	200–300 μm (d) <sup>a</sup>	$5.00 \times 10^{13}$	$1.81 \times 10^{-14}$	This study
•		Pastille	$1.0 \mathrm{cm}  (\mathrm{d}) \times 0.3 \mathrm{cm}  (\mathrm{t})^{\mathrm{b}}$	$3.30 \times 10^{12}$	$1.58 \times 10^{-13}$	•
		Pellet	2–4 mm (d)	$3.30 \times 10^{12}$	$1.09 \times 10^{-13}$	
	6	Powder	200–300 μm (d)	$5.00 \times 10^{13}$	$1.61 \times 10^{-13}$	
		Pastille	$1.0  \text{cm}  (d) \times 0.3  \text{cm}  (t)$	$2.50 \times 10^{12}$	$5.46 \times 10^{-13}$	
		Pellet	2–4 mm (d)	$2.50 \times 10^{12}$	$9.26 \times 10^{-14}$	
	5	Powder	200–300 μm (d)	$2.50 \times 10^{13}$	$1.89 \times 10^{-14}$	
		Pastille	$1.0  \text{cm}  (d) \times 0.3  \text{cm}  (t)$	$3.30 \times 10^{12}$	$1.30 \times 10^{-14}$	
		Pellet	2–4 mm (d)	$2.50 \times 10^{12}$	$6.22 \times 10^{-13}$	
T. thiooxidans	4	Powder	200–300 μm (d)	$5.00 \times 10^{13}$	$2.37 \times 10^{-14}$	
		Pastille	$1.0  \text{cm}  (d) \times 0.3  \text{cm}  (t)$	$3.30 \times 10^{12}$	$2.76 \times 10^{-13}$	
		Pellet	2–4 mm (d)	$2.50 \times 10^{12}$	$2.37 \times 10^{-13}$	
	3	Powder	200–300 μm (d)	$5.00 \times 10^{13}$	$2.19 \times 10^{-14}$	
		Pastille	$1.0  \text{cm}  (d) \times 0.3  \text{cm}  (t)$	$1.11 \times 10^{13}$	$2.31 \times 10^{-14}$	
		Pellet	2–4 mm (d)	$5.00 \times 10^{12}$	$2.82 \times 10^{-14}$	
	2	Powder	200–300 μm (d)	$5.00 \times 10^{13}$	$2.03 \times 10^{-14}$	
		Pastille	$1.0  \text{cm}  (d) \times 0.3  \text{cm}  (t)$	$5.00 \times 10^{12}$	$1.52 \times 10^{-13}$	
		Pellet	2–4 mm (d)	$3.30 \times 10^{12}$	$2.46 \times 10^{-13}$	
T. ferrooxidans	2	Powder	25-63 μm (d)	$4.88\times10^{13}$	$2.15 \times 10^{-15}$	Konishi et al. [7]

<sup>&</sup>lt;sup>a</sup> Diameter.

Table 3
Specific surface area of sulfur particles

Form	Size	Specific surface area determined by Eq. (2) $(cm^2/g)^a$	Specific surface area calculated by particle size [10] $(cm^2/g)^b$
Powder	200–300 μm (d) <sup>c</sup>	213	121
Pastille	$1.0  \text{cm}  (d) \times 0.3  \text{cm}  (t)^d$	23	5
Pellet	2–4 mm (d)	15	10

<sup>&</sup>lt;sup>a</sup>The mean value of specific surface of sulfur particles under different pH values.

pastilles and pellets were cooled in air and water, respectively, sulfur pastilles contained more micropores and possessed larger surface area than sulfur pellets [10]. As observed from the results, the method developed in this study for the determination of specific surface areas of sulfur particles was more reliable.

## 3.2. pH and sulfate variations in bioleaching

The variation of pH during the bioleaching process with different forms of sulfur particles is illustrated in Fig. 3(a). It took 14, 26, and 52d for sulfur powder, pastilles, and pellets, respectively, to decrease the pH value to 2.5. The rates of pH reduction were in the order: powder > pastille > pellet. Greater the surface area of sulfur particles, higher the number of sites available to thiobacilli for absorption, increasing the oxidation rates

of sulfur. Fig. 3(b) shows the sulfate production during bioleaching with different forms of sulfur particles. The rate of sulfate production was highest for sulfur powder and lowest for sulfur pellets. The differences in the rates of pH reduction and sulfate production with various forms of sulfur particles showed better correlation to specific surface areas of sulfur particles than the size of the particles. Furthermore, as calculated on the basis of sulfate production, only 20-30% of the initial supply of sulfur particles is utilized for the bioleaching process with the possibility of recovering and reusing the excess. The smaller size of sulfur powder (200-300 µm) makes recovery of unutilized sulfur from the treated sediment a difficult proposition. For this reason, the use of larger sized sulfur pastilles and pellets is favorable for the recovery of unutilized sulfur from the bioleaching process.

<sup>&</sup>lt;sup>b</sup>Thickness.

<sup>&</sup>lt;sup>b</sup>Surface area was calculated using density of sulfur as 2 g/cm<sup>3</sup>.

<sup>&</sup>lt;sup>c</sup>Diameter.

<sup>&</sup>lt;sup>d</sup>Thickness

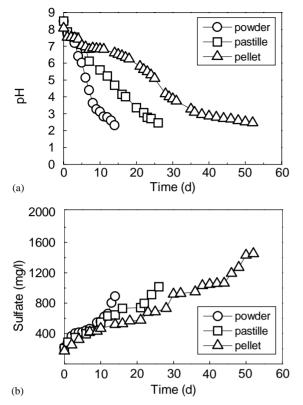


Fig. 3. Variations of pH and sulfate during bioleaching with fresh sulfur particles (Run 1) (a) pH and (b) sulfate.

## 3.3. Metal solubilization in bioleaching

The solubilization of heavy metals from the contaminated sediments during bioleaching is shown in Fig. 4. An initial lag phase was observed for heavy metal solubilization from sediments with sulfur pellets in concordance with the lower rate of pH reduction in this system (Fig. 3(a)). The solubilization efficiencies of heavy metals were in the range 95-96% for Cu, 72-81% for Zn. 16-60% for Pb. and 10-47% for Ni. It was found that the solubilization efficiency of Pb was significantly influenced by the forms of sulfur particles (Fig. 4(c)). The solubilization efficiency of Pb was lower than Cu and Zn since it formed less soluble PbSO<sub>4</sub>  $(K_{\rm sp}=1.62\times 10^{-8})$  in the presence of sulfate [1]. The solubilization efficiency of Pb decreased with increasing sulfate concentration. Also, an increase in the specific surface area of sulfur particles resulted in greater rates of metal solubilization. Thus, it may be said that the rate of acidification and metal solubilization depended on the specific surface area of sulfur particles in the bioleaching process.

## 3.4. Reuse of recoverable sulfur particles in bioleaching

The acidification of sediments was faster in the bioleaching process with recovered sulfur particles (Runs 2 and 3) than that with fresh sulfur particles (Run 1). The pH reduction in the bioleaching process with recovered sulfur particles compared to fresh sulfur

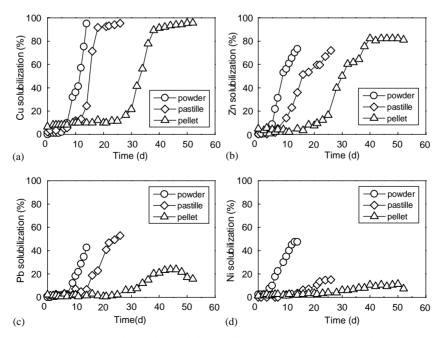


Fig. 4. Metal solubilization during bioleaching with fresh sulfur particles (Run 1) (a) Cu, (b) Zn, (c) Pb, and (d) Ni.

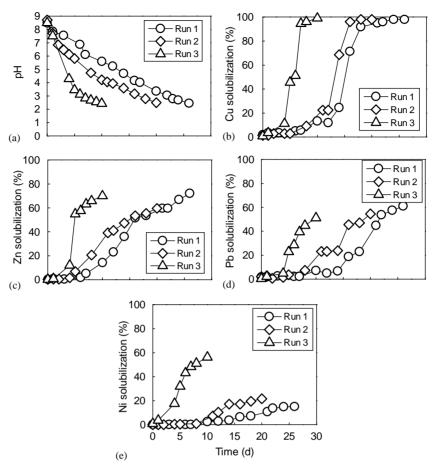


Fig. 5. Variations of pH and metal solubilization during bioleaching with recovered sulfur pastilles (a) variation of pH, (b) solubilization of Cu, (c) solubilization of Zn, (d) solubilization of Pb, and (e) solubilization of Ni.

particles is shown in Figs. 5(a) and 6(a). Since the sulfur particles recovered form the bioleaching process contained a significant number of acclimated bacteria adsorbed on them, the time required for bioleaching was reduced with recovered sulfur [10]. For sulfur pastilles, the pH value dropped to 2.5 on the 20th day and 10th day, respectively, for Run 2 and Run 3 as compared to 26 d for Run 1 (Fig. 5(a)). However, with recovered sulfur pellets, the pH reduction was slower for Run 3 in comparison to Run 2 (Fig. 6(a)). The sulfur pellets used in this study were not firm enough and frangible because sulfur pellets were prepared by cooling melted sulfur in water. Therefore, the percentage of sulfur pellets recovered from the bioleaching experiment was sometimes less. In the bioleaching experiments, the recovery percentages of sulfur particles were calculated as follows:

Recovery percentage (%) = 
$$\frac{W_1}{W_0(1-P)} \times 100\%$$
, (3)

where  $W_0$  is the weight of sulfur particles added in the bioleaching experiment (g) that equals  $15 \,\mathrm{g}; \,W_1$  is the weight of recovered sulfur particles from the previous bioleaching experiment (g); and P is the ratio of sulfur oxidized into sulfate to sulfur added, i.e., sulfate (mg/l)/ 1000/15. The recovery of sulfur pellets decreased from Run 1 (73%) to Run 2 (55%) (Table 4), thus requiring a larger quantity of fresh sulfur pellets to maintain the desired sulfur concentration (0.5% (w/v)) in Run 3. This resulted in a drop in the pH reduction rate for Run 3. Since metal solubilization in the bioleaching process is highly dependent on pH [4], the solubilization of heavy metals from contaminated sediments exhibited similar trends to pH variation with recovered sulfur particles (Figs. 5 and 6). The rate of metal solubilization was enhanced by reuse of recovered sulfur particles in the bioleaching process. Though sulfur powder showed better rates of acidification and metal solubilization than sulfur pastilles and pellets (Figs. 3 and 4), the recovery of sulfur powder from treated sediments was

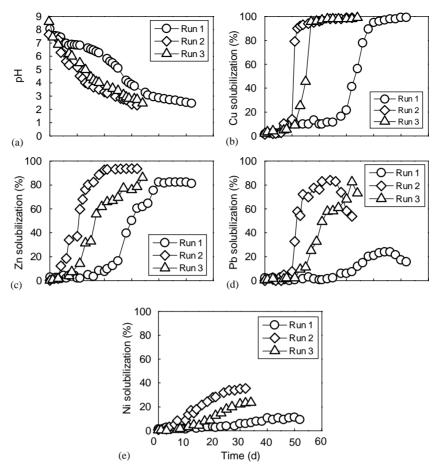


Fig. 6. Variations of pH and metal solubilization during bioleaching with recovered sulfur pellets (a) variation of pH, (b) solubilization of Cu, (c) solubilization of Zn, (d) solubilization of Pb, and (e) solubilization of Ni.

Table 4
Oxidation and recovery of sulfur particles in the bioleaching process

Form	Run 1		Run 2		Run 3	
	Oxidation (%)	Recovery (%)	Oxidation (%)	Recovery (%)	Oxidation (%)	Recovery (%)
Powder	18	_	_	_	_	
Pastille	24	75	24	75	35	72
Pellet	32	73	23	55	19	70

minimal. The acidification and solubilization rates for sulfur pastilles and pellets could be enhanced by recovery and reuse. The sulfur pastilles were recovered better from the sediments than sulfur pellets and the subsequent reuse of recovered sulfur resulted in higher rates of pH reduction and metal solubilization with pastilles. In bioleaching experiments of Run 3 (Fig. 5), the pH reduction and metal solubilization rates with recovered sulfur pastilles approached those with sulfur

powder (Figs. 3(a) and 4). With emphasis on recovery and reuse, sulfur pastilles showed a superior performance in the bioleaching process.

## 4. Conclusions

In the bioleaching process, the adsorption equilibrium of *T. thioparus* and *T. thiopxidans* on sulfur particles was

described by the Langmuir isotherm. The maximum adsorption capacity obtained from the isotherm was used for determining the specific surface area of sulfur particles. This method overcame the difficulty in measuring the specific surface area of sulfur particles with the BET analyzer due to sublimation of elemental sulfur. It was found that the specific surface area of sulfur particles did not always depend on the particle size but on the quantity of micropores in sulfur particles. So the process performance was not clearly interpreted by the size of sulfur particles. In the bioleaching process, some significant relationships between pH reduction, sulfate production, metal solubilization and specific surface area of sulfur particles were observed. The results suggested that reuse of recovered sulfur particles would improve the process performance. In the reuse of sulfur pastilles, the pH reduction and metal solubilization rates were comparable to those for sulfur powder. The use of recoverable sulfur pastilles can offer distinct advantages in the bioleaching process.

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