



Bioleaching of heavy metals from sediment: significance of pH

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Abstract

Bioleaching process, which causes acidification and solubilization of heavy metals, is one of the promising methods for removing heavy metals from contaminated sediments. The solubilization of heavy metals from contaminated sediments is governed by the sediment pH. In the present study, the significance of pH in bioleaching of heavy metals from contaminated sediment was evaluated at different solid contents of sediments in a bench-scale reactor. Results showed that a temporal change of pH in the bioleaching process was effected by the buffering capacity of the sediment particulates. The variations of pH in this bioleaching process were calculated by a modified logistic model. It was observed that solubilization of heavy metals from sediments is highly pH-dependent. In addition, a non-linear equation for metal solubilization relating pH value in the bioleaching process was established. This allows an easier and faster estimate of metal solubilization by measuring pH in the bioleaching process. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Bioleaching; Contaminated sediment; Heavy metal; pH; Thiobacilli

1. Introduction

Due to heavy industrialization, sediments in most rivers of Taiwan are contaminated with heavy metals. Land spreading is an attractive and economical method for the final disposal of these contaminated sediments. The disposal of heavily contaminated sediments on land may pose a potential hazard to human health and to the environment. Therefore, it is necessary to remove the heavy metals from the sediments before being spread on land. The treatment of metal contaminated sediments can be achieved by either physical or chemical methods. Although these physical or chemical treatment techniques have been extensively applied in practice, they show some limitations such as low efficiency and high cost (Rulkens et al., 1995). The bioremediation of heavy

metals has received a great deal of attention in recent years, not only as a scientific novelty but also for its potential application in industry (Stoll and Duncan, 1996). For example, a variety of bioleaching processes have been successfully applied to remove heavy metals from ores, industrial wastes, and sewage sludges (Bosecker, 1986; Blais et al., 1992; Sreekrishnan et al., 1993; Ahonen and Tuovinen, 1995). Bioleaching with sulfur-oxidizing bacteria is one of the promising methods for removing heavy metals from contaminated aquatic sediments.

Thiobacillus, which plays a role in bioleaching process includes *T. ferrooxidans*, *T. thiooxidans*, and *T. thioparus* (Blais et al., 1992). Although *T. ferrooxidans* and *T. thiooxidans* have been extensively used in bioleaching process, it requires an initial acid addition to lower the pH of the system to 4.0 or below, at which the acidophilic *T. ferrooxidans* or *T. thiooxidans* can grow. Thus, the operational cost of bioleaching process by *T. ferrooxidans* is high. Furthermore, *T. ferrooxidans* oxidize sulfur compounds slowly compared to

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T. thiooxidans (Wong and Henry, 1988). Recently, an economical bioleaching process using a mixed culture of less-acidophilic and acidophilic thiobacilli, *T. thioparus* and *T. thiooxidans*, at neutral pH has been reported (Blais et al., 1992).

The main mechanisms involved in bioleaching of heavy metals by *T. thiooxidans* and *T. thioparus* can be explained by the following equations (Rulken et al., 1995):

(1) *direct mechanism*



(2) *indirect mechanism*



where M is a bivalent metal.

The bioleaching of heavy metals from contaminated sediments is a complex process. Various physicochemical and biological parameters such as nature of contaminated particles, temperature, oxygen and carbon dioxide, pH, oxidation–reduction potential (ORP), composition of the medium, bacterial strain and cell concentration affect the bioleaching process (Wong and Henry, 1988; Battaglia et al., 1994). Sreekrishnan et al. (1993) found that sludge pH is the single most important parameter that influences metal solubilization during the metal bioleaching of sewage sludge. Tichy et al. (1993) reported that production of acid is the limiting step in the bioleaching process using sulfur as the substrate. Although it was found metal solubilization in the bioleaching process is related to pH value in these studies, they all belong to qualitative investigations of the relationship between pH and metal leaching. The purposes of this study are to quantitatively investigate the relationship between pH and metal solubilization and to provide a better understanding of significance of pH in bioleaching process for the treatment of contaminated sediments.

2. Materials and methods

2.1. Microorganisms

Two cultures used throughout this study, *T. thiooxidans* (CCRC 15612) and *T. thioparus* (CCRC 15623), were obtained from Culture Collection and Research Center of the Food Industry Research and Development Institute (FIRDI), Hsinchu, Taiwan. The cultures were maintained for subculture in shaker flasks at 200 rpm and at 30°C before being used in leaching experiments.

Two media were used for growing the thiobacilli. Medium 317, for *T. thiooxidans*, was composed of (in g/l) $(\text{NH}_4)_2\text{SO}_4$ 0.3; K_2HPO_4 3.5; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.5; CaCl_2 0.25 and tyndallized sulfur powder 5.0. The pH was adjusted to 4.5 with 1 N H_2SO_4 . The composition of medium 318, for *T. thioparus*, was $(\text{NH}_4)_2\text{SO}_4$ 0.3; K_2HPO_4 4.0; KH_2PO_4 1.5; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.5 and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ 10.0. The pH was adjusted to 7.0 with 1 N H_2SO_4 (FIRDI, 1994).

2.2. Bioleaching experiments

The sediment samples used in the experiments were taken from lower reaches (near Nan Ding Bridge) of Ell Ren River, which is heavily polluted by heavy metals in Taiwan (Fig. 1). Before the leaching experiments, the subculture of thiobacilli was acclimated to contaminated sediment. In this acclimation process, 5-day old mixed culture of *T. thiooxidans* and *T. thioparus* (1% v/v) was transferred to 150 ml autoclaved sediment (2% w/v) containing tyndallized elemental sulfur (0.5% w/v). The mixture was incubated at 30°C in a 500 ml shaker flask at 200 rpm. The growth of thiobacilli in sediments was monitored by measuring the decrease in pH during sulfur oxidation (Blais et al., 1992).

The bioleaching experiments were carried out in a completely mixed batch (CMB) reactor at 200 rpm and aerated with an air diffuser at the rate of 1.2 l/min. The cell concentrations of *T. thioparus* and *T. thiooxidans* in the inoculum are about 5×10^5 and 7×10^7 cfu/ml. A 5% (v/v) growing mixed culture inoculum of thiobacilli obtained from the acclimation process was added to 3 l of sediments with different solids contents (total solids (TS) (w/v): 1%, 2%, 4% and 7%) containing 0.5% (w/v) tyndallized elemental sulfur. Temperature was maintained at 30°C. A control test was conducted without addition of bacteria inoculum and the other conditions were the same as those of the experiment of 1% total solids. The reaction process was monitored by periodic sampling and analysis of the sediment suspension for pH, ORP, sulfate and soluble heavy metals (Cu, Mn, Zn, Pb, Ni and Cr). The concentrations of *T. thioparus* and *T. thiooxidans* in the sediment were measured by a plate count method with the modified thiosulfate agar medium of medium 317 and medium 318 (Blais et al., 1992).

2.3. Metal sulfides oxidation

The oxidation of metal sulfides in the bioleaching process was tested with a 230 mesh fraction of copper sulfide (CuS), lead sulfide (PbS) and zinc sulfide (ZnS) powder. The bioleaching experiment of metal sulfide was carried out in the CMB reactor with a mixture of these three metal sulfides (CuS 0.33%, PbS 0.33% and ZnS 0.33%) as substrate (1% w/v). The metal solubilization

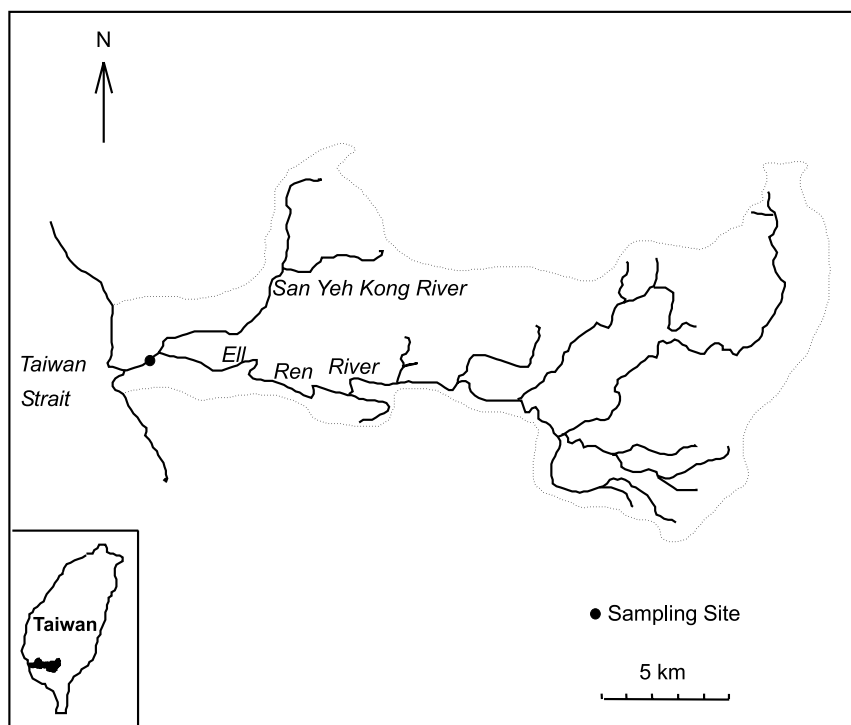


Fig. 1. Map of study area and sampling site.

from sulfides was measured. The CMB reactor containing metal sulfides was incubated for a period of 25 d under the same conditions as the previous bioleaching experiments.

2.4. Chemical analyses

The moisture content and volatile solids of the sediment samples were determined using Standard Methods (APHA, 1995) and the pH value was measured by the procedures recommended by LaBauve et al. (1988). In bioleaching experiments, ORP and pH in the reactor were measured with an on-line monitor (Tank, model RD-500). The sediment suspension taken from the CMB reactor was centrifuged at 10,000 rpm for 20 min. The supernatant was filtered through a 0.45 μm filter membrane and analyzed for the sulfate (APHA, 1995) and heavy metal (Zn, Mn, Cu, Pb, Ni, and Cr) concentrations. The heavy metal concentrations were determined using a flame atomic absorption spectrophotometer (AAS) equipped with a graphite burner (Model Z-8100, Hitachi). The composition of heavy metal in the sediment was determined by HF–HNO₃–HCl digestion method (30 min, 630 W CEM microwave system at 100% power) (USEPA, 1995). To ensure analytical quality, a standard reference material (SRM 2704, National Institute of Standards and Technology) was an-

alyzed with each batch of samples. Duplicate digestion experiments carried out to ascertain the reproducibility of the analyses show no significant differences (Table 1).

3. Results and discussion

3.1. pH variations in bioleaching

In bioleaching, elemental or reduced sulfur compounds are oxidized to sulfuric acid by the leaching bacteria, resulting in acidification of the sediments (decrease of pH) (Eq. (2)). Subsequently, protons released into the liquid phase can replace heavy metals adsorbed on the sediment particles (Eq. (3)). During this stage, thiobacilli oxidize metal sulfides to sulfate and the metals are solubilized (Eq. (1)). As time elapses, the concentrations of hydrogen ion and heavy metals increase. At high hydrogen ion and heavy metal concentrations, bacterial activity will be inhibited and sulfur oxidation will cease. Therefore, the pH of the sediment stabilizes at a particular limiting value. In this study, it is assumed that pH decreases exponentially at higher values and the rate of decline decreases as the pH approaches some limiting value. Thus, the modified logistic model for estimated pH in bioleaching can be expressed as (McGhee, 1991):

Table 1
The properties of sediment samples (mean \pm standard deviation ($n=12$))

Item	This study (Ell Ren River)	Reference material (Certified values)	Reference material (Analytical values)	Criteria for disposal of dredged sediment ^a
Moisture (w/w, %)	27.57 \pm 0.08	–	–	–
Volatile solids (w/w, %)	3.51 \pm 0.09	–	–	–
pH	7.85 \pm 0.10	–	–	–
Metal ($\mu\text{g/g}$)				
Mn	424 \pm 14	555 \pm 19	545 \pm 15	–
Zn	401 \pm 25	438 \pm 12	425 \pm 10	100
Cu	191 \pm 7	99 \pm 5	91 \pm 2	100
Pb	143 \pm 11	161 \pm 17	145 \pm 10	50
Ni	50 \pm 2	44 \pm 3	43 \pm 2	100
Cr	74 \pm 0	135 \pm 5	120 \pm 5	100

^a Interim criteria for in-water disposal of dredged sediments of Wisconsin (Sullivan et al., 1985).

$$\text{pH} = \frac{\text{pH}_{\text{lim}}}{1 + ae^{-bt}}, \quad (4)$$

where pH_{lim} is the limit of sediment pH in bioleaching, b the rate constant of pH change, a the constant, and t is the elapsed time. In Eq. (4), if the constant “ a ” is negative, the value of pH will decrease. Conversely, a positive constant “ a ” means that the value of pH will increase.

The results of pH variations during bioleaching for different sediment solids contents are illustrated in Fig. 2. The sediment pH dropped from 8.0 to about 2.4 at different sediment solids contents. The rate of decline of sediment pH decreased as the sediment solids content was increased, because sediment with higher solids content had a higher buffering capacity (Sreekrishnan et al., 1993). Thus, it required more time to reach pH_{lim} for sediments with higher solids content. *T. thioparus* used in this study was cultured at an initial pH between 5.9 and 9.0, and the maximum growth was attained between pH 6.0 and 8.0. Maximal growth of *T. thiooxidans* was observed between pH 2.5 and 4.0 (Blais et al., 1992),

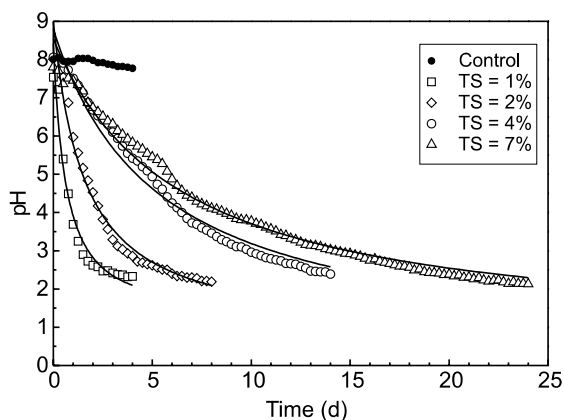


Fig. 2. Variation of pH in the bioleaching process (the solid lines were computed from the logistic model).

though they could grow between pH 1.5 and 5.5. The ability to resist low pH is an important physiological adaptation of thiobacilli since sulfuric acid is formed by the oxidation of elemental sulfur. However, the growth of acidophilic thiobacilli was inhibited at pH lower than 1.5 (Sreekrishnan et al., 1993). In Fig. 2, the solid lines representing the logistic model were calculated from Eq. (4). It was found that variations of sediment pH could be correlated with the logistic model, with the R^2 values ranged from 0.97 to 0.99. Table 2 lists the simulated values of pH limit and the constants of logistic model in bioleaching at solids contents between 1% and 7% (w/v). The rate constant (b) of decline of pH decreased with increasing sediment solids content. The pH limit estimated by the logistic model for bioleaching of sediments ranged from 1.10 to 1.64. The results of this study are concordant with previous studies. For example, Blais et al. (1992) demonstrated that sludge (total solids of 1.5%) inoculated with a mixed culture of *T. thioparus* and *T. thiooxidans* was acidified from pH of 7.1 to a final pH of 1.7 in 5 d. Garcia et al. (1995) reported that after sphalerite (ZnS) media (total solids of 2.5%) was inoculated with *T. thiooxidans*, the pH decreased to 1.1 in 32 d. Donati et al. (1996) found that the pH was lowered to 1.12 in bioleaching of covellite (CuS) (total solids of 0.1%) by *T. thiooxidans* in 46 d. Furthermore, from Eq. (4), the time needed to reach pH_{lim} in the bioleaching process can be estimated by the following equation:

$$\Delta t = \frac{-1}{b} \ln \left[\frac{1}{a} \left(\frac{\text{pH}_{\text{lim}}}{\text{pH}} - 1 \right) \right]. \quad (5)$$

From the results (Table 2), it was found that the time needed for the variation of pH (from 8.0 to 2.5) increased linearly with increasing solids content of the sediment in the bioleaching process (Fig. 3).

The bacterial populations of thiobacilli during the bioleaching process with sediment solids content of 4% are shown in Fig. 4. First, less-acidophilic *T. thioparus*

Table 2
The parameters of logistic model determined from bioleaching

Total solids (%)	pH _{lim}	<i>a</i>	<i>b</i> (d ⁻¹)	R ²
1	1.64 ± 0.13 ^a	-0.81 ± 0.02	0.33 ± 0.07	0.97
2	1.21 ± 0.13	-0.87 ± 0.02	0.09 ± 0.02	0.98
4	1.15 ± 0.14	-0.87 ± 0.03	0.03 ± 0.01	0.97
7	1.10 ± 0.10	-0.87 ± 0.01	0.02 ± 0.00	0.99

^a Mean ± standard deviation (based on the 95% calculated confidence level).

predominately grew and took responsibility for acidification of the sediment in the first stage of bioleaching. Then acidophilic *T. thiooxidans* activated when the sediment pH was reduced to 4, and kept producing acid. This acidification leads the number of *T. thioparus* to decrease. In Fig. 4, the exponential growth phase (linear range) of *T. thioparus* occurred between 1 and 3 d of reaction time, and *T. thiooxidans* proceeded from 3 to 7 d with sediment solids content of 4%. It can be found

that the maximum specific growth rate (*m*) of *T. thioparus* ($\mu = 0.076 \text{ h}^{-1}$) is greater than *T. thiooxidans* ($\mu = 0.057 \text{ h}^{-1}$). Blais et al. (1992) found that the maximum specific growth rate of *T. thioparus* was between 0.079 and 0.104 h⁻¹ and that of *T. thiooxidans* between 0.067 and 0.079 h⁻¹, which suggested that it made no difference for thiobacilli to grow in the sludge or sediment system.

3.2. Metal solubilization in bioleaching

The main characteristics of the sediment used in this study are listed in Table 1. On a dry weight basis, the organic content of the sediments equalled 3.5% (w/w) measured as volatile solids. The pH value was about 7.85. The concentrations of heavy metals, Zn, Mn, Cu, Pb, Ni, and Cr, were 401, 424, 191, 143, 50 and 74 µg/g, respectively. Lag phases were observed in the solubilization of some heavy metals especially at high solids contents and the rate of metal solubilization decreased with increasing solids contents (Fig. 5). Therefore, it took more time for sediments with higher solids contents to attain the final values of pH for reaching the ultimate metal solubilization due to higher buffering capacity. The ultimate solubilization efficiency of bioleaching of Cu was highest at 82–95% and that of Cr was lowest at 16–20% of the six metals in the sediment (Table 3). Most of the Cr (77%) exist in lattice-held fraction of the sediments; therefore, it requires highly acidic conditions to solubilize Cr from the sediments (Lin et al., 1999). Except for Pb and Ni, effects of solids content on the ultimate solubilization of Cu, Mn, Zn and Cr were not apparent. The ultimate solubilization efficiency of Pb (34–72%) decreased with increasing solids content (Table 3). The formation of PbSO₄, which has low solubility ($K_{sp} = 1.62 \times 10^{-8}$), resulted in a decreased solubilization efficiency of Pb at higher sediment solids contents due to the production of more sulfate.

3.3. Relationship between sediment pH and metal solubilization in bioleaching

Variations of pH, ORP and metal solubilization in the bioleaching experiments with metal sulfides over reaction time are shown in Table 4. The results suggest that acidification and metal solubilization are not

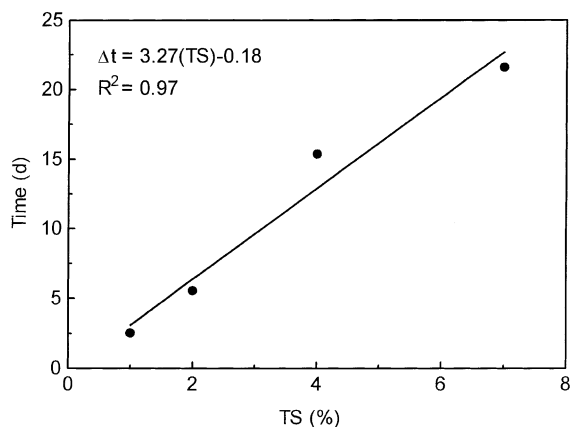


Fig. 3. The time needed for the variation of a certain range of pH (from 8.0 to 2.5) in the bioleaching process with different sediment solids concentrations.

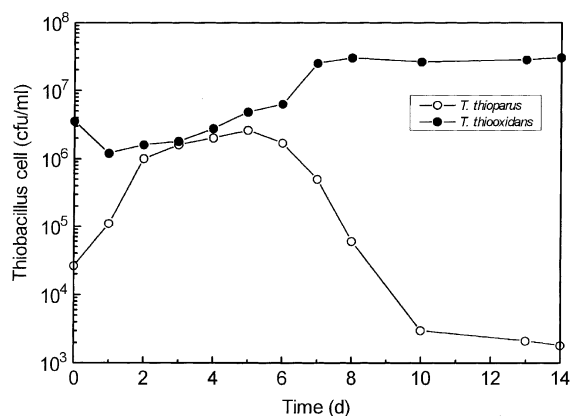


Fig. 4. The number of thiobacilli in the bioleaching process with sediment solids content of 4%.

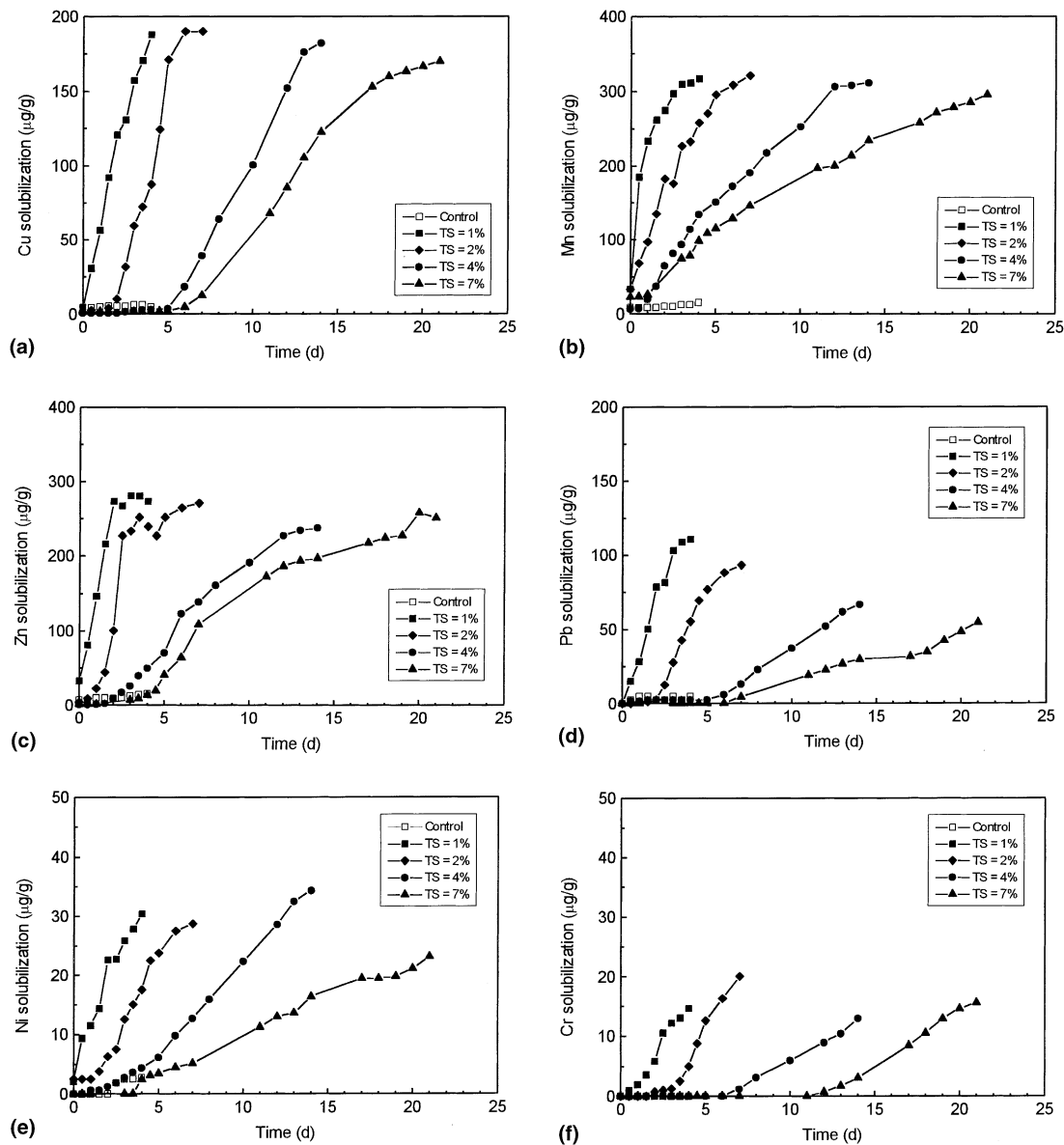


Fig. 5. Metal solubilization from sediment in the bioleaching process: (a) Cu, (b) Mn, (c) Zn, (d) Pb, (e) Ni and (f) Cr.

Table 3

The ultimate sulfate concentration and solubilization efficiency of bioleaching of heavy metals from sediment

Total solids (%)	Time ^a (d)	Sulfate (mg/l)	Solubilization efficiency (%)					
			Cu	Mn	Zn	Pb	Ni	Cr
1	3	759	82	73	70	72	52	16
2	6	1133	90	70	63	54	48	17
4	14	2150	95	73	60	47	65	18
7	20	3756	87	67	64	34	42	20

^a The reaction time for sediment to reach the pH = 2.4.

Table 4
Variation of pH, ORP and metal solubilization in the bioleaching experiment with metal sulfides

Time ^a (d)	Initial pH	Final pH	Initial ORP (mV)	Final ORP (mV)	Metal solubilization (%)		
					Cu	Pb	Zn
3	6.68	5.63	-103	-86	0.2	2.9	5.2
6	6.68	4.65	-103	-77	4.9	3.7	9.0
14	6.68	4.47	-103	-69	10.2	6.9	9.9
20	6.68	4.45	-103	-65	10.8	8.7	11.6

^a The reaction time to reach the final pH.

apparent after 3 d of reaction time when metal sulfide is used as substrate. However, the pH reduction in the CMB reactor resulted in little metal solubilization from metal sulfides after 20 d of reaction. The results of metal sulfide oxidation show that direct oxidation (Eq. (1)) of metal sulfides by thiobacilli is a secondary process and heavy metals are primarily solubilized by the indirect mechanism (Eq. (3)). Generally, the results obtained in the experiment of metal sulfide oxidation are in agreement with those of Tyagi et al. (1993). Tichy et al. (1993) suggested that acid production is the limiting step for bioleaching process when sulfur is used as the substrate. Therefore, it can be assumed that metal solubilization in microbial leaching process is controlled by the acidification from oxidation of elemental sulfur, i.e. indirect mechanism (Eq. (3)).

Eq. (3), a microscopic reaction, is not necessarily observed in the bioleaching process. The solid-liquid reaction is usually better described by a macroscopic proton exchange reaction of the form (Honeyman and Leckie, 1986):



with the corresponding reaction constant

$$K = \frac{[\text{sediment-}H_x][M]}{[\text{sediment-}M][H]^x}, \quad (7)$$

where sediment- H is any surface site unassociated with any metal ion of M , sediment- M (expressed as M_s) a metal/surface site complex, and x is the apparent ratio of moles of protons consumed per mole of metal ion released to the solution. Taking logarithms of both sides in Eq. (7), a linear expression is obtained (as shown in Fig. 6) and the number of protons participating in the reaction can be determined by the expression (Kedziorek and Bourg, 1996):

$$\log\left(\frac{[M_s]}{[M]}\right) = xpH - \log K' \quad (8)$$

with

$$K' = \frac{K}{[\text{sediment-}H_x]}, \quad (9)$$

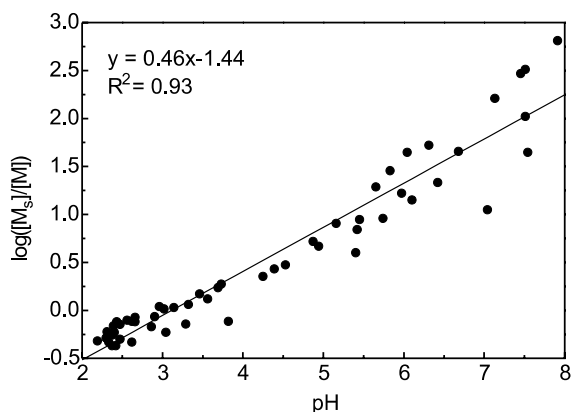


Fig. 6. Linear regression of $\log([M_s]/[M])$ of Zn as a function of pH.

where M_s and M are the concentrations of metal associated with sediment and metal solubilized from sediment, respectively. The term $\log([M_s]/[M])$ in Eq. (8) is determined experimentally. Rearranging Eq. (8) gives the following equation:

$$\begin{aligned} \frac{[M_s]}{[M]} &= \frac{[M_{s0}] - [M]}{[M]} = \frac{1 - ([M]/[M_{s0}])}{([M]/[M_{s0}])} = \frac{1 - E}{E} \\ &= 10^{xpH - \log K'}, \end{aligned} \quad (10)$$

where M_{s0} is the initial concentration of metal associated with sediment, and E is the efficiency of metal solubilization. Finally, an equation relating metal solubilization efficiency to the responding pH is obtained

$$E = \frac{10^{\log K' - xpH}}{1 + 10^{\log K' - xpH}}. \quad (11)$$

The data of x and K' obtained from the linear expression between the term $\log([M_s]/[M])$ and pH (Fig. 6) are shown in Table 5. The results of x data in Table 5 are in agreement with the values for solubilization of Pb (x : 0.4–0.7) from polluted river sediments, when subjected to acidification (Bourg and Loch, 1995). The values of x were found to be 0.5 ± 0.4 for Pb and 0.3 ± 0.1 for Ni in a study of acidification and solubilization of heavy metals from kaolinite (Kedziorek and Bourg, 1996).

Table 5
Parameters of efficiency equation in bioleaching of heavy metals from sediment

Metal	Efficiency parameter		R^2	n^a	Valid pH
	x	$\log K'$			
Cu	0.61	1.89	0.91	50	2.30 < pH < 5.37
Zn	0.46	1.44	0.93	56	2.30 < pH < 9.16
Mn	0.27	1.02	0.91	55	2.30 < pH < 7.44
Pb	0.59	1.39	0.84	38	2.30 < pH < 5.22
Ni	0.32	0.73	0.90	49	2.30 < pH < 7.02
Cr	0.78	1.15	0.85	31	2.30 < pH < 4.73

^a Sample size.

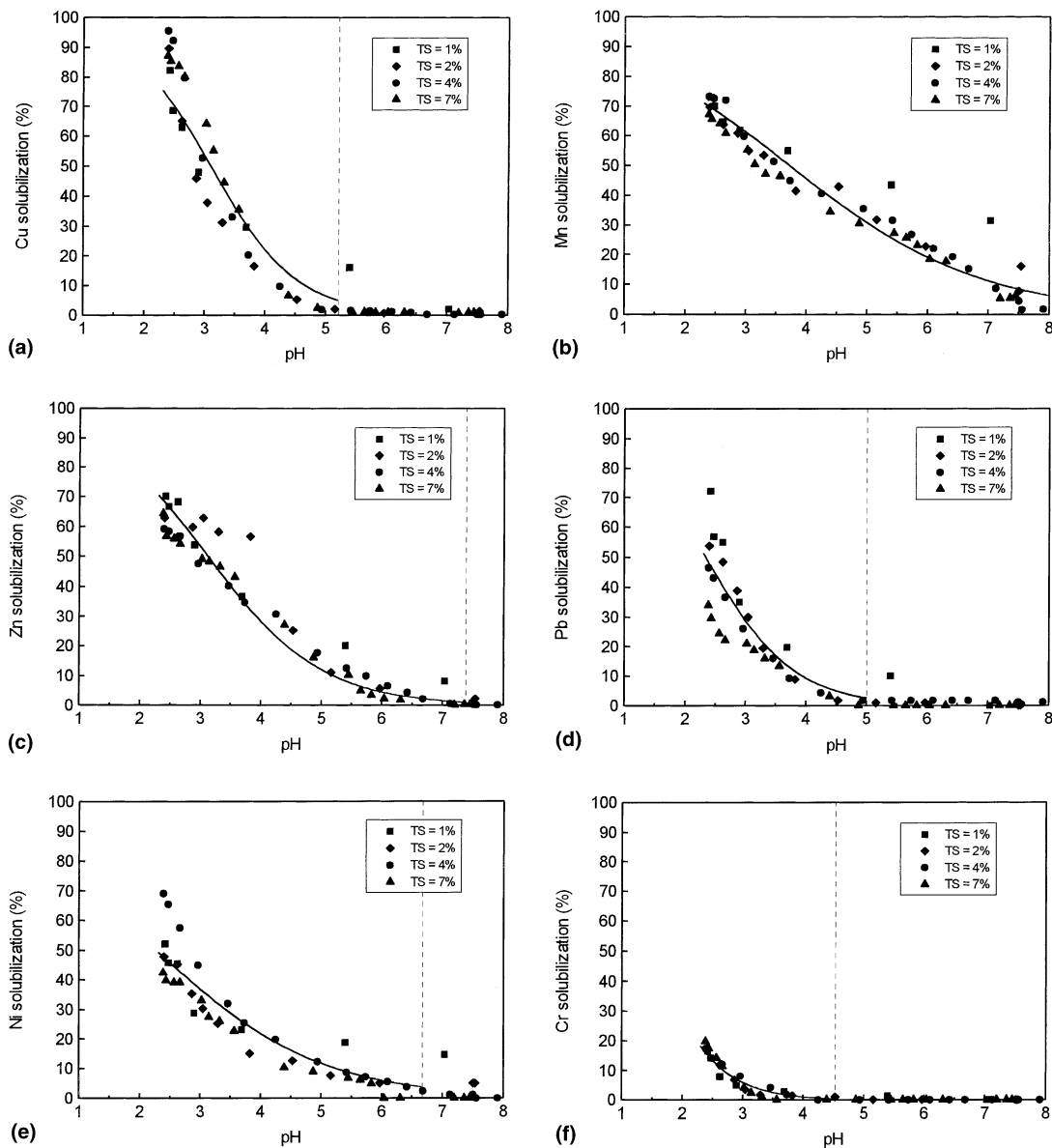


Fig. 7. The relationship between sediment pH and metal solubilization in the bioleaching process: (a) Cu, (b) Mn, (c) Zn, (d) Pb, (e) Ni and (f) Cr (the solid lines were computed from the efficiency equation and the dotted lines were the valid range of pH).

It was found that the solubilization percentage of heavy metals was constant at a given value of sediment pH (Fig. 7). To lower the sediment pH to the same level for higher solids contents, more acid needs to be produced and hence the thiobacilli take longer reaction time. This accounts for the lag time in metal solubilization for higher solids contents (Fig. 5). The solubilization of each metal will take place efficiently when pH value is under a certain limit (Fig. 7). These results demonstrate that pH is the predominant factor that determines the solubilization of heavy metals in bioleaching and solids content does not directly influence the process of metal solubilization.

The non-linear response of metals towards pH changes is also quite clear (Fig. 7) and the efficiency equation (11) was used to simulate the relationship between metal solubilization and sediment pH in the bioleaching process. The parameters of the efficiency equation referring to the data are presented in Table 5. The good fit of the efficiency equations to the data from experiments with different solids contents suggests that the efficiency equation is appropriate. The efficiency equation can predict metal solubilization in the bioleaching process over the pH range of interest for each heavy metal. In practice, it is much easier to measure pH by an on-line pH meter than to analyze concentration of solubilized metal in the bioleaching process. Moreover, the efficiency equation provides an easier and faster alternative to estimate metal solubilization during the bioleaching process.

4. Conclusions

The pH in bioleaching process of contaminated sediment depends on the buffering capacity of the sediment, which is affected by the solids content of the sediment. The logistic model similar to S-shaped curve of population growth illustrates the variations of pH in the bioleaching process. This modified logistic model may be combined with the efficiency equation for estimating the metal solubilization during the bioleaching process. The buffering capacity is slowly diminished by continuous production of acid from the oxidation of sulfur compounds by thiobacilli. When pH reaches a certain value metals will start solubilizing from the sediments. Therefore, a lag phase is observed in the solubilization of heavy metals from sediments with higher solids contents. The metal solubilization in the bioleaching process is highly dependent on the pH and its relationship with pH is non-linear. An efficiency equation which relates metal solubilization and pH value in the bioleaching process is decided in this study, which can be used to estimate metal solubilization easily by only measuring the pH value.

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