

# Detoxification of Electroplating Sludge by Bioleaching: Process and Kinetic Aspects

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## Abstract

The presence of significant amounts of heavy metals in industrial sludge poses a severe threat to the environment and human health. In this study, bioleaching of heavy metals from electroplating industrial sludge was investigated using indigenous *Acidithiobacillus ferrooxidans* as the bacterial agent. The effect of sludge loading on the efficiency of heavy metal removal by bioleaching was studied. The efficiency of bioleaching was assessed based on media acidification, oxidation-reduction potential, and concentration of heavy metals in the aqueous solution. Experimental results showed that the sludge loading had great impact on the bioleaching process. At sludge loading of 1% (w/v), maximum removal of 96.31% and 84.4% was achieved for the heavy metals Zn and Ni, respectively. Bioleaching data were subjected to first-order-based kinetic studies for rate constant and further shrinking core model analysis was applied. It was found that the rate constants for Zn and Ni bioleaching were maximum at the treatment with lower sludge loading. The kinetic analysis using the shrinking core model revealed that chemical reaction step controls the overall rate of the bioleaching process. Such a kinetic study will be helpful in designing the sludge detoxification process by bioleaching.

**Keywords:** electroplating sludge, *A. ferrooxidans*, bioleaching, rate kinetics, shrinking core model

## Introduction

Electroplating is the application of metal coating to a metallic or other conducting surface by an electrochemical process. Articles are electroplated to alter their appearance, provide protective coating, give them specific mechanical properties, and attain special surface properties [1]. The electroplating process generates huge quantities of wet sludge containing heavy metals as pollutants at the wastewater treatment unit [2, 3]. The major heavy metals present in the sludge are cadmium, chromium, lead, copper, zinc, and nickel [4, 5]. Electroplating sludge is categorized as hazardous waste by statutory authorities and is processed for metal recovery by suitable technologies before disposal [6-8]. Improper disposal of industrial sludge may contami-

nate surface water and groundwater with heavy metals and put the surrounding environment under risk and spoil human health [9-11]. Hence, electroplating sludge should be treated for removal of the heavy metals before considering any disposal methodology.

Currently, various chemical and biological methods are available to detoxify industrial sludge, and selection of a suitable process depends on both technical and economic feasibility [12]. Owing to the consumption of a large amount of inorganic acids, the chemical leaching process is often more expensive than the biological process, and thus paves the way for developing the biological leaching (bioleaching) process [13, 14]. In the bioleaching process, the filamentous fungi and lithotrophic bacteria from *Acidithiobacillus* genus are used as biological agents [15, 16]. In comparison, the efficiency of removing heavy metals is found to be less for fungal bioleaching than for bacte-

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rial bioleaching [17]. Bioleaching through bacterial activity is carried out usually by either direct or indirect mechanism [18]. In direct mechanism, non-soluble metal sulfides are oxidized into water-soluble metal sulfates (Eq. 1) by chemolithotrophic bacteria such as *Acidithiobacillus ferrooxidans*, *A. thiooxidans*, *A. caldus*, *Sulfobacillus acidophilus*, and *Acidiphilium acidophilum* [19, 20]. In indirect mechanism, elemental sulfur ( $S^0$ ), is oxidized first to sulfuric acid (Eq. 2) by sulfur-oxidizing bacteria and then dissolution of metals by sulfuric acid takes place (Eq. 3) [21]:



...where M is bivalent metal.

The indirect mechanism is often considered for the removal of heavy metals from sludge using sulfur-oxidizing bacteria. Though numerous works have been published on different parameters of bioleaching [22, 23] on sludge, only a few have looked into the bioleaching kinetics [24, 25]. The kinetics for rate and determination of rate-controlling step are very important in thorough understanding of the bioleaching process [26]. It owns a vital part to represent the process mathematically. Thus, it is necessary to investigate and analyze the kinetics of the bioleaching process in the direction of designing the sludge detoxification process. The objective of this work was to study the effect of sludge loading (SL) on bioleaching of heavy metals (Zn and Ni) from electroplating industrial sludge and to study the kinetics for rate and rate-controlling step of the bioleaching process using isolated *A. ferrooxidans*.

## Materials and Methods

### Sludge Collection and Characterization

For this study, heavy metal-bearing sludge was collected from an effluent treatment plant of the industrial electroplating sector (Chennai, India). The top surface of the sludge bed has more waterlogged phase with presence of chemically oxidized water-soluble compounds that cannot provide original property of the sludge. So the sludge sample was collected at a depth of 2-5 cm from the surface of the sludge bed because there will not be a remarkable difference in the physiochemical properties of the sludge sample at this depth to bottom surface. It can be considered as representative of generated sludge. The collected sample was stored using a polyethylene bag at 4°C before use for experiments to avoid change in its properties. It was air-dried at room temperature overnight. Total metal concentration in the sludge was determined after acid digestion with a mixture of concentrated  $HNO_3$ ,  $HClO_4$ , and  $HF$  [27]. The concentration of the dissolved metals in the sludge was determined after membrane filtration (0.45  $\mu m$  pore size), and analysis was conducted using an atomic absorption spectrometer (AA200 model; PerkinElmer; USA). Ionic

activity and electrical conductivity of the extract collected from dry sludge to water in the ratio of 10:25 were measured using a calibrated pH meter (Eutech Instruments, Singapore) and a conductivity meter (Elico, India) [28]. The presence of organic matter in the sludge was determined using Walkley-Black method with standard 1 N  $K_2Cr_2O_7$  and Ferrouin indicator. Total nitrogen content was estimated using micro-Kjeldahl distillation apparatus. Available phosphorus in the sludge was determined using the micro-vanadate-molybdate method after extraction with 0.5 M sodium bicarbonate. Calcium, magnesium, and potassium were determined using the flame photometer (CL378 model; Elico; India) after ammonium acetate extraction [29]. Soluble sulfate was estimated using a UV-visible spectrophotometer (U2900 model; Hitachi; Japan) after precipitation as barium sulfate according to the American Public Health Association (APHA) standard.

### Microorganism and Sludge Acclimatization

The sulfur-oxidizing bacteria *A. ferrooxidans* were isolated from water samples collected from acid mine drainage in Chitradurga copper mine (Karnataka, India). They were screened using elemental sulfur as the key nutrient in the medium [30] with the following chemical composition:  $S^0$  (10  $g \cdot l^{-1}$ ),  $MgSO_4 \cdot 7H_2O$  (0.5  $g \cdot l^{-1}$ ),  $(NH_4)_2SO_4$  (3  $g \cdot l^{-1}$ ),  $K_2HPO_4$  (0.5  $g \cdot l^{-1}$ ),  $Ca(CO_3)_2$  (0.01  $g \cdot l^{-1}$ ), and  $KCl$  (0.1  $g \cdot l^{-1}$ ). A brief literature survey showed that the optimal pH value of *A. ferrooxidans* is between 2 and 4 [31]. So the media pH was initialized to 3 using sulfuric acid for stimulating bacterial growth. The isolate was subcultured several times in the same medium for further activation. To acclimatize the culture to sludge, we added 0.25% (w/v) dry sludge as a supplement to the subculture medium at room temperature (28°C). The flasks were shaken at 150 rpm in a horizontal rotary shaker. The decrease in pH was monitored until it stagnated during growth. Two more subcultures were carried out with 0.25% (w/v) sludge as a supplement. A portion of this culture was further cultivated in the medium with 0.5% (w/v) dry sludge under similar conditions (28°C and 150 rpm) to produce mild-acclimatized culture. A portion of this mild-acclimatized culture was further acclimatized with 0.75% (w/v) and 1% (w/v) dry sludge to produce required acclimatized culture to sludge. The sludge-acclimatized culture was used as inoculum for bioleaching experiments.

### Bioleaching Experiments

The bioleaching studies were conducted in 250 ml Erlenmeyer flasks, each containing 90 ml medium, 10 ml inoculum, and predetermined amounts of SL. In the flask, SLs were 1.0%, 2.0%, 3.0%, 4.0%, and 5.0% (w/v). All flasks were incubated in a rotary shaker at 28°C and 150 rpm. Control experiments without the addition of inoculum were also maintained in 1% SL for comparison. To the medium, 5% (v/v) alcoholic thymol solution (1% (w/v) thymol crystal in alcohol) was added as bacterial germicide in control experiments. During bioleaching studies, pH and

oxidation-reduction potential (ORP) were monitored using a calibrated pH meter and Pt-Ag/AgCl electrode, respectively, at 24 h intervals. At every 48 h interval, 5 ml samples were periodically withdrawn and centrifuged at 3,000 rpm for 20 min. The supernatant was filtered using Whatman filter paper and preserved at 4°C before determining the concentration of leached Zn and Ni by atomic absorption spectrometry. A fresh nutrient solution without elemental sulfur was added to compensate for the media loss due to sample collection and evaporation. Metal bioleaching efficiency, denoted by (%), was calculated using the following equation:

$$\eta\% = \left( \frac{M_0 - M_{\text{soln}}}{M_T} \right) \times 100 \quad (4)$$

...where  $M_0$  and  $M_{\text{soln}}$  are the solubilized metal concentration in aqueous phase at zero time and time  $t$ , respectively.  $M_T$  is the total metal concentration in the primary sludge. All experiments were carried out in triplicate and mean values with standard deviation of parameters being expressed as results.

### Kinetic Studies for Rate Constant and Rate-Controlling Step

Rate of bio-solubilization of heavy metal by bioleaching can be described by the following empirical equation [32]:

$$\frac{dC_M}{dt} = k_m(C_{M,0} - C_{M,t}) \quad (5)$$

Integrating the above first-order equation between limits of initial and final values of metal concentration and time (at  $t = 0$ ,  $C_M = 0$  and at  $t = t$  h,  $C_M = C_{M,t}$ ) results in the following equation:

$$\ln \left( \frac{C_{M,0}}{C_{M,0} - C_{M,t}} \right) = k_m t \quad (6)$$

...where  $C_{M,0}$  and  $C_{M,t}$  are the total concentrations of metal available in the primary sludge and concentrations of metal in the aqueous phase of leached solution at time  $t$  during the process.  $k_m$  is the bioleaching rate constant and is obtained from the slope of the plot,  $\ln(C_{M,0} / (C_{M,0} - C_{M,t}))$  vs time. The analysis of sludge bioleaching mechanism is of immense importance for designing and further application of the process. Thus, the rate-controlling step of the reaction has been analyzed using the shrinking core model (SCM) of fluid-particle reaction kinetics [33]. According to the SCM, steps involved to control the overall reaction rate and its respective mathematical models in terms of conversion and leaching time are given in Table 1, where  $X_M$  is the fraction of leached metal in aqueous phase and  $k_{\text{obs}}$  the observed kinetic constant applicable to the respective model. On the basis of the regression analysis from the plots  $[1 + 2(1 - X_M) - 3(1 - X_M)^{2/3}]$  vs time,  $[1 - (1 - X_M)^{1/3}]$  vs time, and  $[X_M]$  vs time, the rate-controlling step was identified for the respective metal bioleaching [34].

Table 1. Mathematical models of rate-controlling steps.

Controlling step	Mathematical model
Diffusion through the ash layer	$1 + 2(1 - X_M) - 3(1 - X_M)^{2/3} = k_{\text{obs}} t$
Chemical reaction	$1 - (1 - X_M)^{1/3} = k_{\text{obs}} t$
Diffusion through liquid film	$X_M = k_{\text{obs}} t$

Table 2. Physico-chemical properties of sludge sample.

Sl. No.	Selected parameters	Composition
1	pH	8.2±0.24
2	Conductivity	3.7 cmol
3	Total nitrogen	3978±67 mg/kg
4	Total available phosphorus	2452±46 mg/kg
5	Sulfate	520±58 mg/kg
6	Organic mater	4.1±0.11%
7	Calcium	21,520±176 mg/kg
8	Magnesium	9560±243 mg/kg
9	Potassium	284±36 mg/kg
12	Zinc	42,180±685 mg/kg
13	Nickel	20,160±430 mg/kg

± indicates the standard deviation of data represent mean value of five samples.

## Results and Discussion

### Characteristics of Microorganism and Sludge

The bacterium *A. ferrooxidans* is gram-negative, non-sporulating rod (0.5-0.6 m wide and 1.0-2.0 m long with rounded ends) capable of oxidizing iron and sulfur and occurring singly or in pairs. All the mentioned characteristics were observed during the isolation of the strain. The scanning electron microscopy image of the isolate is given in Fig. 1. Table 2 lists the characteristics of electroplating the industrial sludge sample on a dry basis. The characterization study of the sludge revealed its alkaline nature. The sludge was rich in nitrogen (3,978 mg·kg<sup>-1</sup>) and phosphorus (2,452 mg·kg<sup>-1</sup>), and also contained moderate levels of potassium (284 mg·kg<sup>-1</sup>) that could be used by *A. ferrooxidans* culture during bioleaching. Calcium and magnesium concentrations were 21,520 and 9,560 mg·kg<sup>-1</sup>, respectively. Because the presence of organic matter in the sludge was comparatively low (4.1 mg·kg<sup>-1</sup>), the risk of inhibition to culture growth can be ignored. The analysis showed that the sludge was enriched with heavy metals (42,180 and 20,160 mg·kg<sup>-1</sup> for Zn and Ni, respectively). These heavy metal contents are extremely high, posing a serious threat to the environment and human health.

### Effect of Sludge Loading on Bio-Acidification During Bioleaching

The effect of pulp density on pH during sludge bioleaching is shown in Fig. 2. In the absence of bacteria in control experiments, a marginal decrease in pH (3.0-2.63) was observed due to the chemical oxidation of elemental sulfur. Apparent pH reduction was observed while conducting bioleaching experiments. At the end of the bioleaching period (480 h), a decrease in pH value from 3 to 1.17, 1.47, 1.60, 1.87, and 2.03 was found for treatments with 1%, 2%, 3%, 4%, and 5% SL. A decrease in pH value at 1% SL was an indication of the good bacterial activity with respect to other SL treatments due to lower sludge toxicity [35]. From the dynamics of bio-acidification, it is clear that the decline in the rate of pH took place in the order of 1% > 2% > 3% > 4% > 5% SL. Therefore, it is concluded that bioleaching with different concentrations of electroplating sludge with similar initial pH shows a difference in bio-acidification due to heavy metal toxicity.

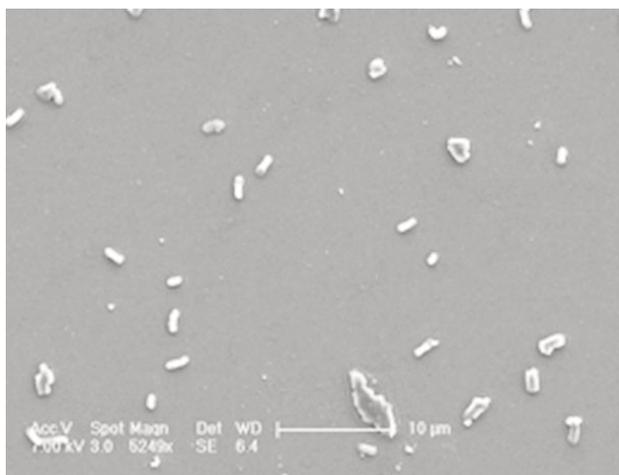


Fig. 1. SEM image of indigenous *A. ferrooxidans*.

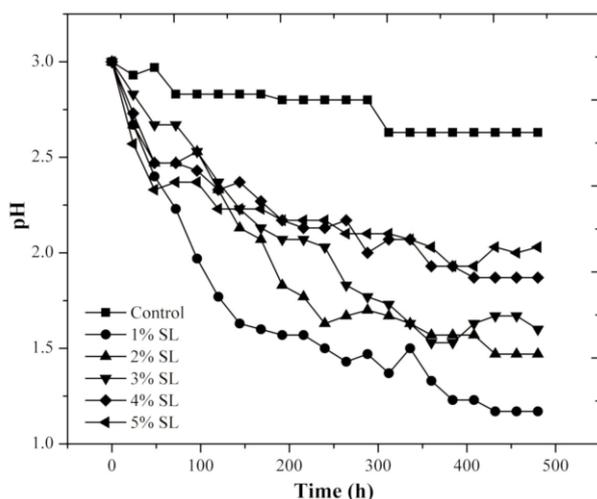


Fig. 2. pH variation in function of time for different sludge loadings during bioleaching.

### Effect of Sludge Concentration on Oxidation-Reduction Potential during Bioleaching

The low pH value coupled with a high oxidizing environment is a favorable condition for an effective bioleaching process. In addition to bio-acidification, bio-oxidation of elemental sulfur contributes to an increase in ORP of the bioleaching medium. The increase in ORP can be attributed to the increase in the  $[\text{SO}_4^{2-}][\text{H}^+]/\text{O}_2$  ratio, which can occur by bacterial catalysis [36]. The variation in ORP during the bioleaching process is shown in Fig. 3. In the control experiment, the change in ORP was from 166 to 176.5 mV. Significant change in ORP of the bioleaching medium was observed in experiments with varying SLs (from 1% to 5%). At the end of day 20, the flask with 1% SL showed considerable increase in ORP (from 173 to 630 mV). It was also observed that ORP increased from 185, 196, 218, and 199 mV to 587, 524, 522, and 483 mV for the respective experiments with 2%, 3%, 4%, and 5% SLs. The increase in ORP showed a similar trend as decreases in pH with respect to SL. The rate of ORP increase took place in the order of 1% > 2% > 3% > 4% > 5% SL, and it is well supported by the pH profiles.

### Effect of Sludge Loading on Heavy Metal Bioleaching

Typical heavy metal bioleaching curves for Zn and Ni at different SLs are shown in Figs. 4 a) and b). From the experimental runs, it is evident that the bioleaching of heavy metals can be strongly influenced by SL. Bioleaching efficiency for Zn was the highest in all experiments with chosen SL because Zn can form into highly soluble  $\text{ZnSO}_4$  with sulfate. After 20 days of treatment, the bioleaching efficiencies of Zn were 96.31%, 94.46%, 89.18%, 85.41%, and 79.03% at the experiments with 1%, 2%, 3%, 4%, and 5% SL, respectively. The removal efficiencies of Ni were obtained as 84.40%, 80.47%, 75.81%,

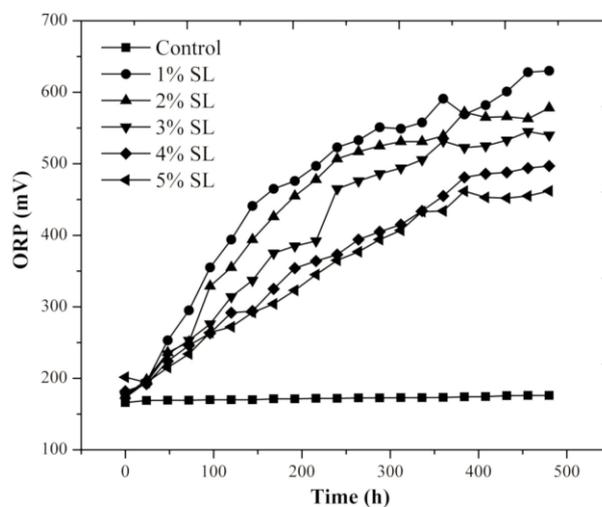


Fig. 3. ORP variation in function of time for different sludge loadings during bioleaching.

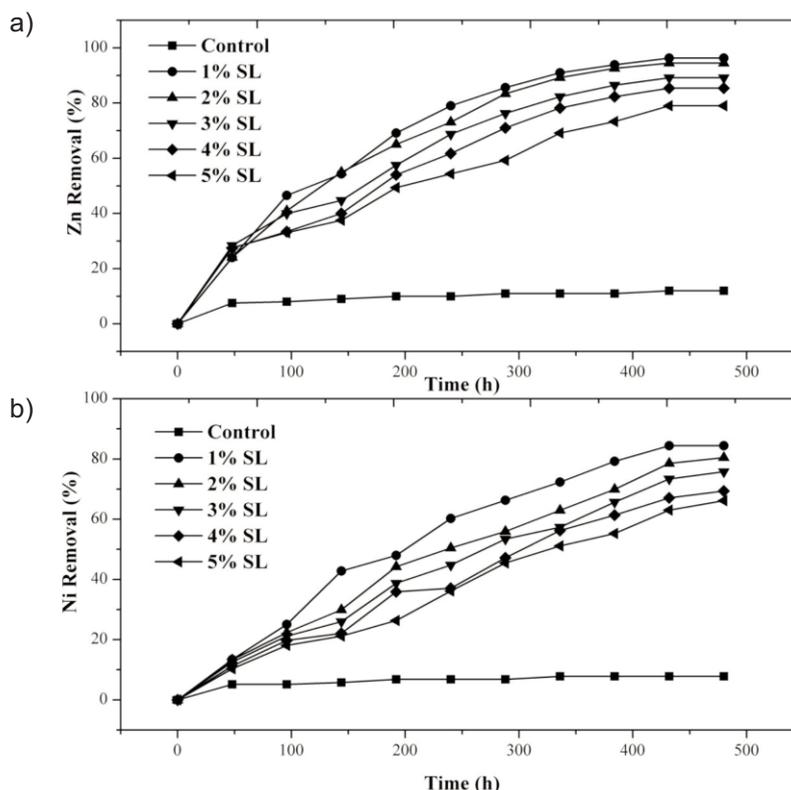


Fig. 4. a) Bioleaching of Zn in function of time for different sludge loadings. b) Bioleaching of Ni in function of time for different sludge loadings.

69.38%, and 66.14% at the experimental runs with 1%, 2%, 3%, 4%, and 5% of SL, respectively. The bioleached residue obtained from the experiment with 5% SL was subjected to energy-dispersive X-ray spectroscopic (EDX) and Fourier transform infrared spectroscopic (FTIR) analyses. The spectra of EDX and FTIR analyses are given in Figs. 5 and 6. Results from the EDX analysis showed that elements O, Na, Mg, Al, Si, S, K, Ca, Cr, Ni, Zn, and Fe were at weight percent of 52.62, 1.85, 0.85, 6.88, 24.96, 0.47, 1.05, 10.47, 0.09, 0.05, 0.65, and 0.05, respectively, and atomic percent of 68.97, 1.68, 0.74, 5.34, 16.23, 0.31, 0.56, 5.48, 0.04, 0.02, 0.21, and 0.36, respectively. This confirmed the reduction in heavy metal contents in treated sludge.

An interferogram of FTIR spectra (transmittance (T %) plotted against the wavenumber (cm<sup>-1</sup>)) of bioleached sludge showed significant adsorption peaks at different wavenumbers, as shown in Fig. 6. This indicates the presence of different functional groups at leach residue resulting from reaction between chemicals used for media preparations and sludge components through bacterial catalysis. The broad adsorption band in the range of 600-700 cm<sup>-1</sup> is assigned to Ni-O stretching vibration mode, which shows the broadness of adsorption band in the sludge. The broad adsorption band at 3,442 cm<sup>-1</sup> is attributed to O-H stretching vibrations of coordinated water, and the weak band near 1,635 cm<sup>-1</sup> is assigned to H-O-H bending vibrations [37]. These observations show the effect of hydration on structure and OH molecules present in the samples oxidized to form water molecules in order to reduce the intensity of hydroxides.

The removal efficiency of Zn from the sludge was higher than that of Ni. It has been reported that the bioleaching behavior of metals strongly depends on their chemical forms in the original sludge. The experimental data show that the removal efficiencies of heavy metal with respect to concentration of sludge took place in the order of 1% > 2% > 3% > 4% > 5% SL, supporting the observations of Akcil et al. [38] and Bakhtiari et al. [39]. High SL causes higher shear stress, high toxicity, high mechanical damage to cells, and less oxygen mass transfer, which could result in reducing the bioleaching efficiency [40]. Therefore, the better

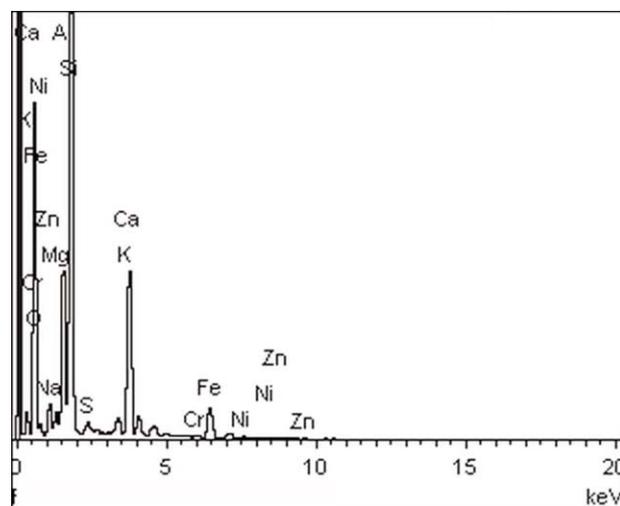


Fig. 5. EDX spectrum of bioleached residue.

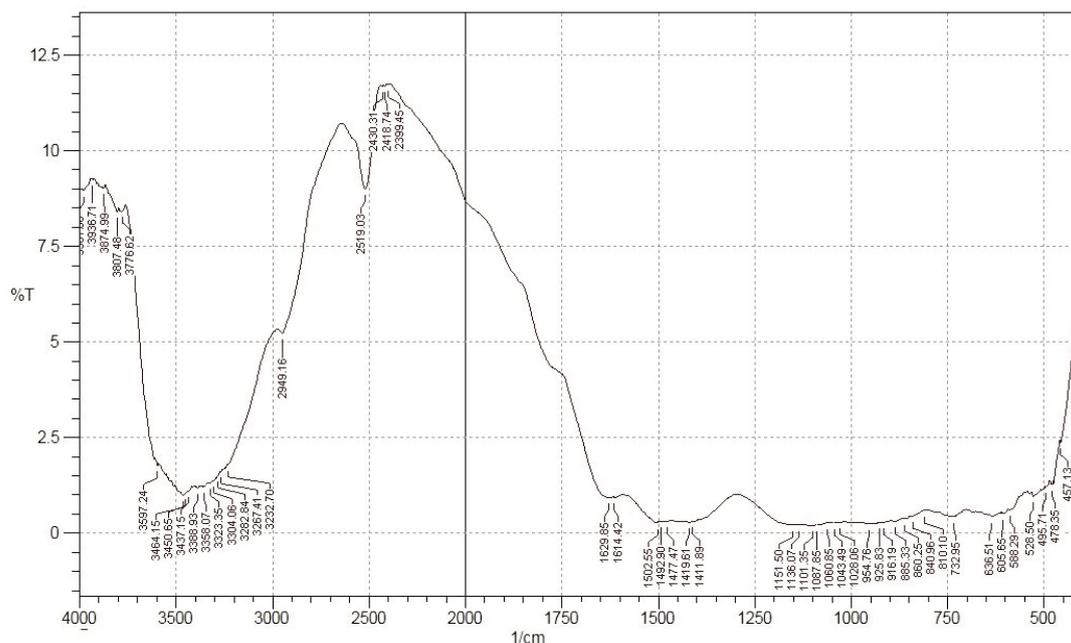


Fig. 6. FT-IR spectrum of bioleached residue.

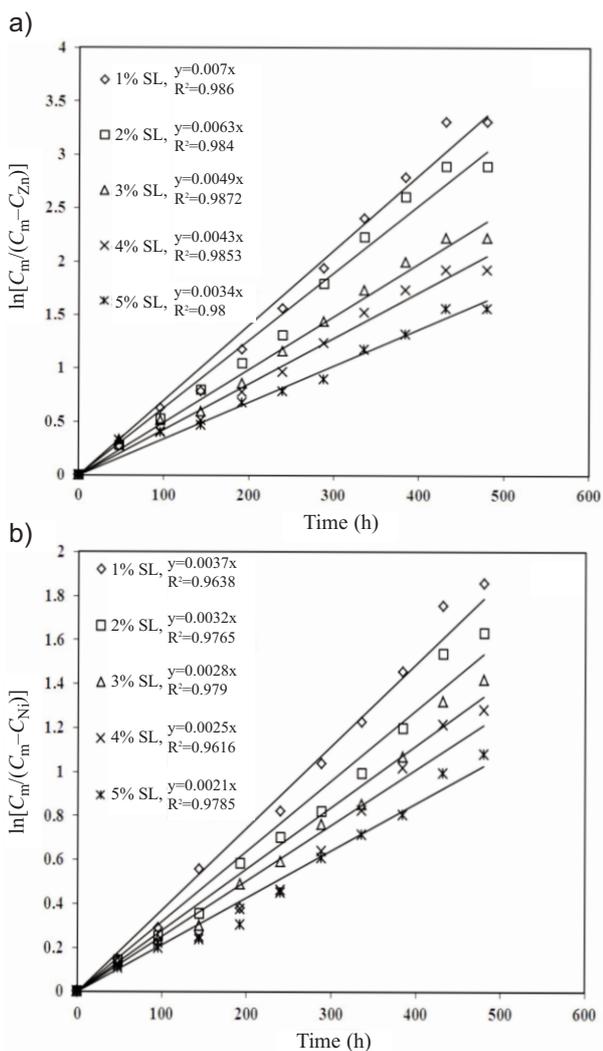


Fig. 7. a) Plot for kinetic rate constant of Zn bioleaching. b) Plot for kinetic rate constant of Ni bioleaching.

Table 3. Rate constant values and regression coefficients of Zn and Ni bioleaching.

Sludge composition	Zn		Ni	
	$k_m$ -value	$R^2$	$k_m$ -value	$R^2$
1% SL	0.007	0.986	0.0037	0.9638
2% SL	0.0063	0.984	0.0032	0.9765
3% SL	0.0049	0.9872	0.0028	0.979
4% SL	0.0043	0.9853	0.0025	0.9616
5% SL	0.0034	0.98	0.0021	0.9785

heavy metal solubilization requires treatment, preferably with lower sludge concentration. However, further efforts should be made to improve the efficiency of bioleaching at a high concentration of sludge.

### Kinetic Study of Bioleaching

Figs. 7 a) and b) show the fitting of the experimental results to Eq. (6) for Zn and Ni. The values of rate constant ( $k_m$ ) and corresponding correlation parameter ( $R^2$ ) are summarized in Table 3 for the respective metals. The values of rate constant attained at experiments with 1%, 2%, 3%, 4%, and 5% of SL were, respectively, 0.007, 0.0063, 0.0049, 0.0043, and 0.0034  $h^{-1}$  for the removal of Zn, and 0.0037, 0.0032, 0.0028, 0.0025, and 0.0021  $h^{-1}$  for the removal of Ni. It is evident that the concentration of sludge strongly affects the rate of metal bioleaching. Various rate-controlling steps of fluid-particle reaction kinetics, such as ash layer diffusion, chemical reaction, and diffusion through liquid film, were examined. Figs. 8 a) and b), 9 a) and b),

Table 4. Regression coefficient values from the graphical fitting of different controlling step models.

Sludge loadings	Ash layer diffusion control		Chemical reaction control		Liquid film control	
	Zn	Ni	Zn	Ni	Zn	Ni
1% SL	0.967	0.930	0.979	0.991	0.7389	0.9193
2% SL	0.957	0.770	0.977	0.956	0.7768	0.9859
3% SL	0.957	0.819	0.967	0.975	0.788	0.9874
4% SL	0.946	0.828	0.971	0.978	0.8358	0.9895
5% SL	0.943	0.858	0.958	0.989	0.8221	0.9871

and 10 a) and b) show the fitting of the experimental data to ash layer control, chemical reaction control, and liquid film control model for the metals Zn and Ni. Among the plots, the best fit was observed at the plot  $[1 - (1 - X_M)^{1/3}]$  vs time. The kinetic data (Table 4) show a good fit to the chemical reaction-controlled SCM. The rate-controlling factor is a chemical reaction between sludge components and sulfuric acid.

### Conclusions

The removal efficiencies of Zn and Ni from the electroplating industrial sludge using the isolate *A. ferrooxidans* under the chosen experimental conditions were evaluated. The bioleaching data for different concentrations of sludge were observed. Owing to less toxicity, less shear stress, and

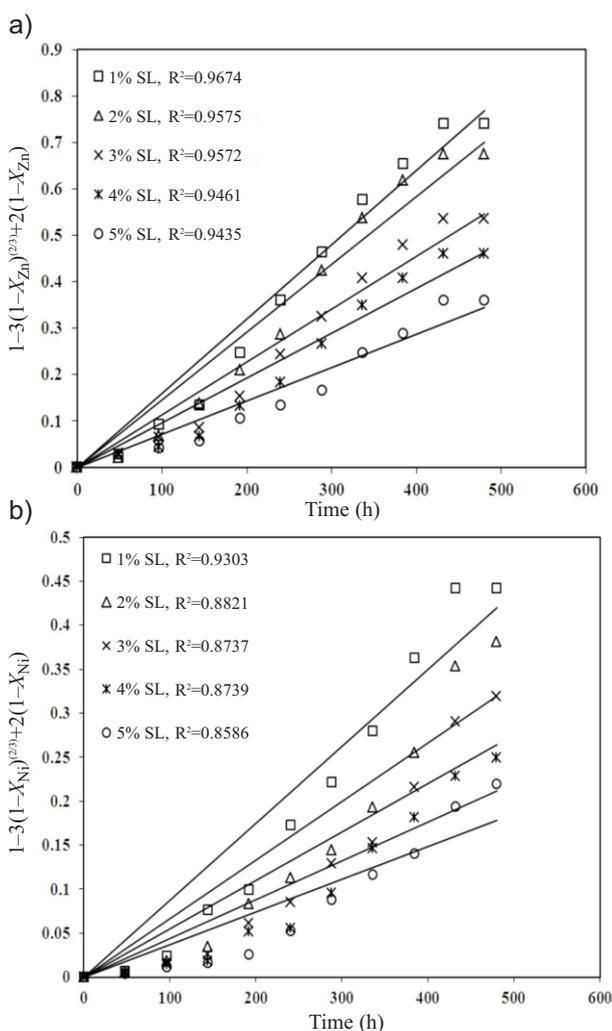


Fig. 8. a) Fitting of data to ash layer diffusion control model for Zn bioleaching. b) Fitting of data to ash layer diffusion control model for Ni bioleaching.

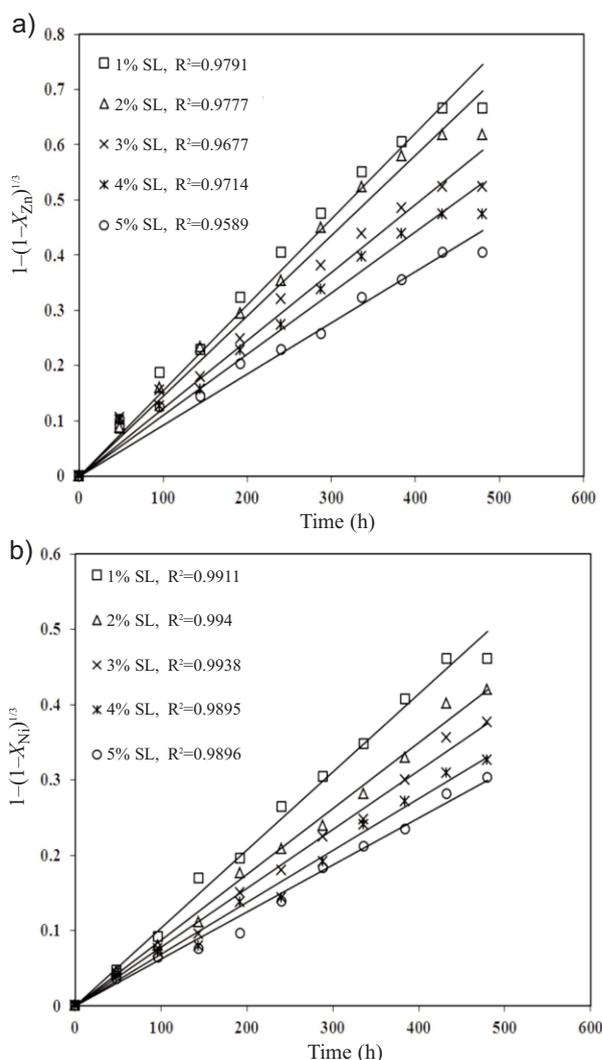


Fig. 9. a) Fitting of data to chemical reaction control model for bioleaching of Zn. b) Fitting of data to chemical reaction control model in bioleaching of Ni.

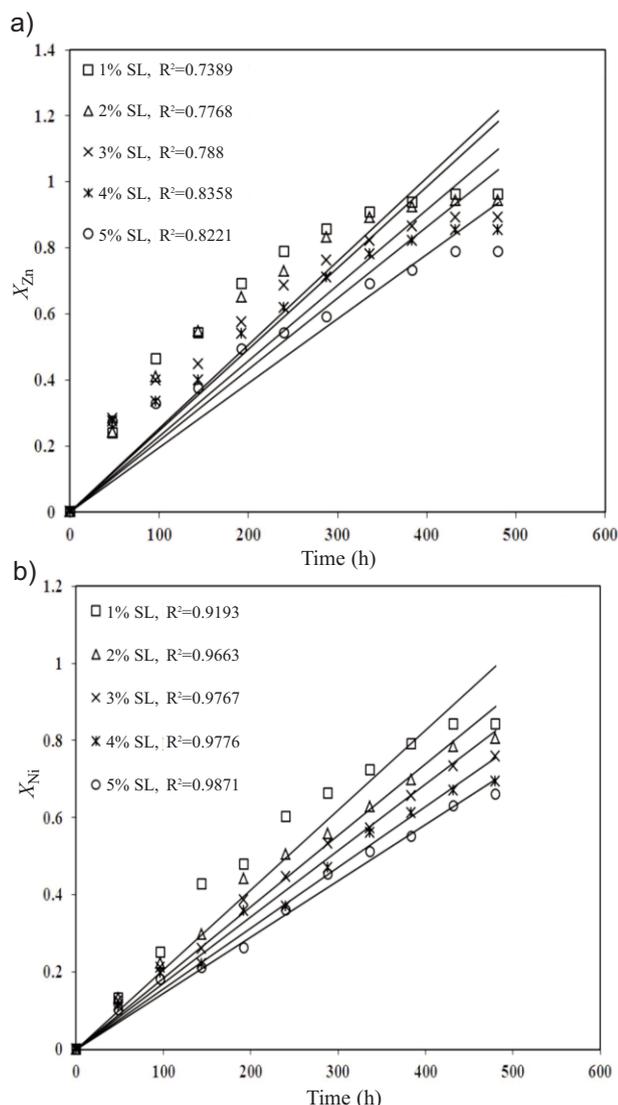


Fig. 10. a) Fitting of data to liquid film control model in bioleaching of Zn. b) Fitting of data to liquid film control model in bioleaching of Ni.

better mass transfer effects, the lower sludge concentration becomes preferable for the effective bioleaching of heavy metals. Maximum removal efficiencies of Zn and Ni (96.31% and 84.40%, respectively) were achieved while using 1% (w/v) SL. The bioleaching kinetics was studied for reaction rate constants of Zn and Ni removal from the sludge. It is apparent that the values of bioleaching rate constant were high at the treatment with 1% SL. On the basis of the SCM, the controlling step for the bioleaching reaction was identified as chemical reaction between sulfuric acid and sludge components. This study proved that it is feasible to detoxify the electroplating sludge containing heavy metals using the bioleaching process.

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