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Bioleaching kinetics and multivariate analysis of spent petroleum catalyst dissolution using two acidophiles

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1. Introduction

Due to the depletion of suitable ore, there has recently been increased effort to extract valuable metals from industrial wastes. In addition, the global production of wastes is constantly increasing, especially in industrialized countries. There are various types of waste generated by metallurgical and chemical processing industries. In the latter case, the catalysts containing heavy metals are one of the main sources of pollution. Large quantities of catalysts namely platinum/palladium, rhodium, vanadium, nickel, molybdenum, etc. are used in the refining industry to purify and up-grade various petroleum streams and residues [1]. The primary purpose of using these catalysts is to improve the process efficiency [2]. The catalyst materials, especially those used in petroleum refineries, usually contain chemicals such as metals, metal oxides, and metal sulfides, which aid in hydrocarbon transformation to produce a full range of transportation fuels [3]. These catalysts lose their activity with time, and when the same decreased to the acceptable level, they are regenerated and reused [4]. However, after a few cycles of regeneration and reuse, the catalysts are discarded because they are no longer useful for pretreatment. The quantity of spent catalysts discharged from different industries depends on the demand of fresh catalyst used. Currently, the quantity of spent petroleum

ABSTRACT

Bioleaching studies were conducted to evaluate the recovery of metal values from waste petroleum catalyst using two different acidophilic microorganisms, *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. Various leaching parameters such as contact time, pH, oxidant concentration, pulp densities, particle size, and temperature were studied in detail. Activation energy was evaluated from Arrhenius equation and values for Ni, V and Mo were calculated in case of both the acidophiles. In both cases, the dissolution kinetics of Mo was lower than those of V and Ni. The lower dissolution kinetics may have been due to the formation of a sulfur product layer, refractoriness of MoS₂ or both. Multivariate statistical data were presented to interpret the leaching data in the present case. The significance of the leaching parameters was derived through principle component analysis and multi linear regression analyses for both iron and sulfur oxidizing bacteria.

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catalysts generated worldwide is estimated to be in the range of from 150,000 to 170,000 tons/year [5]. The amount of spent catalyst that is discarded is always greater than that of the fresh catalyst due to the deposition of coke, sulfur and metals during the refining process. Waste catalysts are regarded as hazardous by the US Environmental Protection Agency (USEPA) due to the presence of appreciable concentrations of various heavy metals such as Ni, V, Mo, Co, and Al [6]. This is because these metals can be leached into the environment after disposal. In addition, the environmental laws concerning the disposal of spent catalysts have become increasingly stringent. As per Basel convention the waste catalyst cannot be exported to third world countries [7]. These stringent environmental regulations have led to a concerted effort to treat waste catalysts in a meaningful way that enables recovery of the valuable metals values through economically sustainable techniques.

Traditionally, metal recovery from the spent petroleum catalyst has been conducted using a combination of pyro- and hydro techniques [8–10]. Pyro-techniques involve calcination processes that are otherwise energy intensive and also emit SO_2 to the atmosphere. Chemical leaching processes entail the use of acids in large-scale operations that generate large volumes of potentially hazardous waste and gaseous emissions.

Recently, bioleaching has been found to be a novel approach for the recovery of metal from various solid industrial wastes. Bioleaching is based on the ability of some microorganisms to transform solid compounds to extractable entities [11]. During the growth process of bacteria and fungi, metabolites are formed

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which are able to extract valuable metals from waste materials due to their acidic nature or their ability for complex formation. For example, Acidithiobacillus ferrooxidans and Leptospirillum ferrooxidans have been used to recover valuable metals from coal liquefaction catalysts [12]. In addition, there has been a series of studies conducted to evaluate the recovery of metals from another coal liquefaction catalyst containing NiMo/Al₂O₃ using A. ferrooxidans, Sulfolobus and thermophilic cultures [13-15]. Briand et al. [16], used Acidithiobacillus thiooxidans to treat spent vanadiumphosphorus catalyst. Recently, Mishra et al. [18] studied the use of acidophilic sulfur oxidizing bacteria to extract valuable metals such as Ni, V and Mo from spent petroleum catalyst. Leaching studies of spent petroleum catalyst were carried out in single and two-stage methods using sulfur oxidizing bacteria. The leaching efficiency was observed to be more in case of two-stage process [17,18]. Zeng and Cheng [19] recently reviewed application of bioleaching process to recover metal values from spent petroleum catalyst.

Although a number of acidophiles have been used to recover valuable metals from spent petroleum catalysts, no systematic studies have been conducted to compare the efficiencies of bioleaching. Therefore, the present study was conducted to illustrate the bioleaching kinetics of two different acidophiles using multivariate technique.

2. Experimental

2.1. Pretreatment and characterization of spent petroleum catalyst

The spent catalyst was collected from SK Petroleum Corporation in South Korea. The organic content of the spent catalyst was removed in a soxhlet using acetone as the solvent. The de-oiled mass was then dried, ground and sieved to obtain the required fraction. The metal contents of the waste were analyzed by ICP and the following values were obtained (wt%): Al – 19.5, S – 11.5, Ni – 2.0, V – 9.0, Mo – 1.4 and Fe – 0.3. This material was used as the base material throughout the leaching process.

2.2. Microorganisms

The iron oxidizing bacteria culture (hereafter denoted as IOB), *A. ferrooxidans*, were isolated from local mining effluent by enrichment in 9K medium [20]. The sulfur oxidizing bacteria culture (hereafter denoted as SOB), *Acidithiobacilus thiooxidans*, were obtained from Parker CRC, Australia. The microorganism was grown in sulfur media as described earlier [17]. The growth rate of both iron and sulfur oxidizing bacteria culture were measured in terms of iron oxidation and acid production rate, respectively.

2.3. Bioleaching studies

Bioleaching experiments were conducted in shake flasks where the speed of shaking incubator was fixed at 180 rpm. Both bacteria were inoculated into the leaching media followed by addition of the required amount of the pretreated spent petroleum catalyst. Inoculum volume was fixed at 10% (v/v) for both the bacteria. For the IOB, the active bacteria cultures were added to the leaching media in a single step [21], whereas the two-step process was used to inoculate the leaching media with SOB [18]. Specifically, the sulfur bacteria cultures were initially grown in sulfur media for 5 days, after which the cell suspension was filtered to remove the undissolved elemental sulfur and the culture filtrate along with the bacterial cell was used for leaching. During the leaching studies, samples were periodically collected and used to determine the pH, Eh and metal ion concentration. The metal ion concentrations were analyzed by ICP-AES (YOBIN make). A pH meter (Orion-720+) with glass membrane electrode was used to measure pH, which was calibrated using pH 4.00 and 7.00 buffers. Redox potential (Eh) was measured by using Ag/AgCl as reference electrode.

For IOB culture, the following bioleaching conditions were maintained unless otherwise specified: temperature, 35 °C; pulp density (PD), 10%; particle size (PS), -106μ m; pH, 2.0; inoculum volume, 10% (v/v); Fe(II), 2 g/L [instead of 9 g/L of Fe(II) in 9K medium]. Lower concentration of Fe(II) was used here to avoid iron precipitation during the experimental course. Similarly, the following leaching conditions were maintained for the SOB culture unless otherwise specified: temperature, 35 °C; pulp density, 10%; particle size, -106μ m; pH, 2.5; elemental sulfur, 10 g/L. For the SOB leaching experiments, 5-day-old culture filtrate grown in 10 g/L of elemental sulfur was used.

All the experiments were carried out in duplicates and the average deviation among the replicates was observed to be within \pm 5%.

2.4. Multivariate statistical analyses

The leaching data were subjected to multivariate statistical analysis to evaluate the inference of various leaching parameters on the leaching rates. Multivariate statistical approaches such as principle component analysis (PCA) and multi linear regression analyses (MLRA) have previously been utilized [22] to determine the significance of specific parameters among datasets. In PCA, eigen values were used to determine the percentage of variance as well as the cumulative percentage of variances. A varimax rotation of different varifactors with factor loading was calculated using eigen values greater than 1 and sorted by the results having values greater than 0.6 to have p < 0.01 (99% confidence level). Multiple linear regression analysis was conducted using the step-wise forward integration method. Both PCA and MLRA were carried out using SPSS-10.

3. Results and discussion

3.1. Effect of contact time

Bioleaching studies were conducted using two different microorganisms, IOB and SOB. In both cases, the leaching kinetics slowed beyond 40 h, therefore, all further leaching studies were conducted for 40 h (Fig. 1). It was further observed that, immediately after inoculation, the extent of leaching was significant for Ni and V (~40% at 10% pulp density (PD)), indicating the environmental leachate problem associated with the stability of the spent catalyst. Within 40 h of leaching period, both Ni and V accounted nearly 90% of leaching in both the cases. Whereas the control flasks, containing no inoculums, have oxidative metal dissolution through atmospheric oxygen. Amount of Ni and V leached in control flasks limited to nearly 40%, respectively, during the whole leaching period in case of both bacteria.

For both the bacteria culture, the leaching rate of Mo was slow compared to V and Ni. To find out the reason for the slow Mo leaching, the original and leached residue samples were subjected to physico-chemical characterization by XRD and SEM. XRD analyses revealed that Mo and S were present as sulfide and elemental form respectively as reported previously [18]. The SEM analyses also revealed the formation of a sulfur layer over the molybdenum matrix. This layer of elemental sulfur that forms over the Mo species may act as an impervious or porous layer. If the layer is impervious, then leaching would be controlled by diffusion and the dissolution reaction can be written as shown in Eq. (1) [23],

$$k_{\rm p}t = 1 - \frac{2}{3}x - (1 - x)^{(2/3)} \tag{1}$$



Fig. 1. Effect of contact time on bioleaching with the acidophiles (a – IOB, b – SOB). Conditions: pulp density = 10 g/L, Fe(II) = 2 g/L for IOB, S^o = 10 g/L for SOB.

where k_p is the parabolic rate constant, t is the time, h, x is the fraction of metal reacted.

Alternatively, if the 'S' layer is porous, then the dissolution reaction would follow shrinking core particle model rate equation, as shown in Eq. (2) [23]

$$K_{\rm c}t = 1 - (1 - x)^{(1/3)} \tag{2}$$

where k_c is the rate constant.

Both equations were used and the generated R^2 (\cong 0.90) value revealed that the process occurred via a diffusion controlled reaction (Fig. 2); therefore, the sulfur layer was assumed to be impervious. Similar linearity was also observed in the case of SOB. Taken together, these findings indicate that the dissolution of Mo requires an oxidant for oxidation of both MoS₂ and elemental sulfur. The oxidation of the elemental sulfur is required to remove the layer so that attacking species can react with the MoS₂ matrix.



Fig. 2. Diffusion control model of Mo at different pulp densities.



Fig. 3. Effect of pulp density on bioleaching (solid line – IOB, dotted line – SOB). Conditions: reaction time = 40 h, temperature = $35 \circ C$, Fe(II) = 2 g/L for IOB, elemental sulfur = 10 g/L for SOB.

3.2. Effect of pulp density

Leaching studies were conducted by varying the pulp density from 5% to 25%. The leaching rates of three metals, Mo, V and Ni, are shown in Fig. 3. When IOB were used, the leaching rate decreased as the pulp density increased. Conversely, when SOB were used, the leaching rate increased as the pulp density increased, except for Mo, which decreased after the pulp density increased beyond 10%. The decrease in the leaching rate in response to the increased pulp density that occurred when IOB were used may be for several reasons. As previously reported [18], Mo and part of the Ni in the waste were present as sulfides; therefore, the dissolution of V and Ni required only acid. IOB can generate acid via the oxidation of elemental sulfur or the precipitation of iron. In the present study, because there was only a marginal precipitation of iron, the sole source of acid must have been the oxidation of sulfur. Therefore, the decrease in leaching rate may have been due to the slow depletion of acid with the increase of pulp density. On the other hand in case of SOB, the lixiviant contained sufficient amounts of acid that supported the high dissolution rate at high pulp densities.

In both cases, the Mo leaching rate was lower than that of Ni and V. The dissolution kinetics of MoS₂ is rather complicated [24]. However, the chemical dissolution reaction can be shown as:

$$Mo^{4+} + 5H_2O + S^{2-} + 3/2O_2 \rightarrow MoO_4^{2-} + 10H^+ + SO_4^{2-} + 4e^-(3)$$

The Eh–pH diagram of the Mo–S–Fe–H₂O system [25] shows Fe(III) and $HMOQ_4^{-1}$ to be stable under oxidizing conditions (Eh > 800 mV and pH <1.3) when there is a Mo/Fe ratio of 1/100. There were high Eh values (>600 mV) in both cases, which maintained the oxidative conditions that enabled dissolution of the Mo matrix. The low recovery of Mo may have been due to precipitation of the HCl-soluble Fe₂(MoO₄)₃. However, in the present case, the extent of precipitation was marginal. Therefore, the low leaching kinetics of Mo occurred due to the refractory nature of MoS₂ as well as the sulfur diffusion barrier.

3.3. Effect of initial pH

The initial pH of the lixiviant ranged from 1.5 to 3 using the two different types of microorganisms (Fig. 4). In both cases, the reaction rate increased as the initial pH of the leaching increased up to 2.5, after which a reverse trend was observed. Furthermore, the iron oxidation rate (IOR) for IOB increased as the initial pH increased (data not shown). Specifically, the maximum IOR was achieved around pH 2.5, above which a downward trend occurred. Similarly, when SOB were evaluated, the sulfur oxidation rate reached its peak around pH 2. In addition, at higher pH and Eh values the chance of



Fig. 4. Effect of initial pH on metal recovery during bioleaching (solid line – IOB, dotted line – SOB). Conditions: reaction time = 40 h, temperature = $35 \degree C$, Fe(II) = 2 g/L for IOB, elemental sulfur = 10 g/L for SOB.

iron precipitation is more [26], thereby producing an additional product layer over the reactant. Taken together, these results indicate that the downward leaching trend at higher pH was due to lower bacterial activity as well as the formation of a product layer.

3.4. Effect of particle size

Bacterial leaching studies were conducted using three different particle sizes based on sieve fraction, -45, -106 and $-212 \,\mu$ m. For both the acidophiles, the leaching rate increased as the particle size decreased (Fig. 5). This may have occurred due to the increased surface area, which ultimately led to an increase in the depth of penetration of the lixiviant species into the particle and enhancement of the leaching rate.

3.5. Effect of nutrient concentration

The effects of Fe(II) and elemental sulfur on the reactivity of IOB and SOB, respectively, were evaluated. In the case of IOB, Fe(III) helped oxidize MoS_2 , whereas the acid production rate increased as the sulfur concentration increased for SOB. For IOB and SOB, the initial iron and sulfur concentrations ranged from 0 to 9 g/L and 10 to 20 g/L, respectively (Fig. 6). For IOB, the leaching rate increased as the initial Fe(II) concentration increased up to 2 g/L, above which it had a negative effect. The negative effect at higher initial iron concentrations may have been due to decreased bacterial activity, an increased iron precipitation rate (IPR) or both. The bacterial activity



Fig. 5. Effect of particle size based on sieve faction on metal recovery during bioleaching (solid line – IOB, dotted line – SOB). Conditions: reaction time = 40 h, temperature = $35 \circ C$, Fe(II) = 2 g/L for IOB, elemental sulfur = 10 g/L for SOB.



Fig. 6. Effect of nutrient concentration on bioleaching (a – IOB, b – SOB). Conditions: pulp density = 10 g/L, reaction time = 40 h, temperature = $35 \degree$ C.

in the present case was evaluated indirectly through iron oxidation rate (IOR), which increased as the Fe(II) concentration increased, indicating good bacterial activity [27]. However, at initial iron concentrations greater than 2 g/L, the IPR increased, thereby creating an additional diffusion barrier and leading to a decreased leaching rate. In the case of SOB, the leaching rate increased as the nutrient concentration increased. The positive leaching rate was due to the increase in acid concentration as well as the enhanced bacterial activity.

3.6. Effect of temperature

To study the effect of temperature on leaching kinetics, the same process was evaluated at temperatures ranging from 10 to 35 °C. In both cases, the leaching rate of the three metal ions increased as the temperature increased. Since bacteria were mesophilic in nature, the higher temperature study was detrimental for bacterial growth and reduced the metal extraction efficiency. The activation energy was calculated from Arrhenius equation by plotting ln (reaction rate) versus 1/temperature [23]. In case of IOB, the activation energy for Ni, V and Mo was calculated to be 29.1, 36.7 and 45.1 kJ/mol, respectively. Whereas, using SOB, the activation energy for Ni, V and Mo was found to be 10.7, 8.9 and 6.9 kJ/mol, respectively. Based on these activation energies it can be concluded that the dissolution process followed a mixed kinetic reaction when both bacteria were used [23].

3.7. Multiple linear regression analysis (MLRA)

Multiple linear regression analysis is a statistical technique in which a single correlation is established between a dependent vari-

Table 1

Coefficient values and other statistical data obtained through MLRA.

Parameter	Coefficient values								
	IOB			SOB					
	Mo%	V%	Ni%	Mo%	V%	Ni%			
Eh	0.132	0.197	0.21	0.034	0.04	0.06			
рН	5.516	14.07	14	3.3	-2.5	-			
PD	-1.194	-1.27	-1.35	-0.15	_	-			
Time	0.137	0.19		0.4	1.1	1			
Temperature	0.439	0.47	0.47	-0.93		-0.42			
Fe(II)	-1.055								
Fe(III)	-1.095								
S		0.28	0.28						
PS				-0.08	-0.04	-0.07			
	Statistical values			Statistical values					
$SD(\sigma)$	6.2	8.55	9.97	3.59	3.67	5.2			
R ²	0.78	0.78	0.85	0.82	0.96	0.96			



Fig. 7. Comparison between calculated values based on MLRA versus observed value for all leaching parameters for IOB.

able and several independent variables. In the present study, the percentage of leaching was considered as dependent variable and leaching parameters such as pH, Eh, temperature, particle size, nutrient concentration and pulp density were the independent variables. The primary objective of this analysis was to use independent variables with values known to be capable of predicting the dependent variable to estimate the percentage of leaching. The reliability of this method can be evaluated based on various statistical parameters such as the correlation coefficient (R^2) and standard deviation (σ). The R^2 values and the σ values for the individual independent variables of three different metal concentrations are shown in Table 1. The B values were then considered to be the theoretical leaching (%). These B values were compared to the actual leaching (%) for IOB and SOB, as shown in Figs. 7 and 8, respectively. In both cases there was very good matching between the theoretical and observed percentages of leaching.

3.8. Principal component analysis (PCA)

3.8.1. Iron oxidizing bacteria

PCA is a standard data reduction technique in which variables are separated based on their correlation with specific factors. Factor-1 accounted for 40.6% of the total variance and was associated with a strong positive loading of time (reaction time), Eh, Fe(III), Fe(II) /Fe(II) ratio, % of metal ions leached and a negative correlation with Fe(II) (Table 2). The positive correlation of oxidizing indicators such as Fe(III), Fe(III)/Fe(II) ratio and Eh indicated the requirements of the oxidant for the dissolution of Ni and Mo. The negative correlation between Fe(II) and the percentage of metal ions leached indicated a decrease in leaching efficiency

with increased Fe(II) concentration. Since Factor-1 related to the leaching efficiency, it can be defined as efficiency factor. Factor-2 explained 58.8% of the total variance with strong positive loading of pH and IOR and moderate negative loading of time, Eh, Fe(III)/Fe(II) ratio and acidity. In addition, moderate positive loading was observed in the case of acid consumption. The correlation between pH and IOR indicated that the bacterial iron oxidation activity increased as the pH increased. The correlation between time and Eh and the Fe(III)/Fe(II) ratio indicated a progressive increase in bacterial activity. The negative correlation between acid consumption and acidity indicated that acid was consumed during the dissolution process. Therefore, Factor-2 can be defined as bacterial oxidation activity. Factor-3 explained 66.9% of the total variance. This factor showed a strong positive correlation with pH and acid consumption, a strong negative correlation with temperature and acidity, and a moderate correlation with Fe(II). Basically, Factor-3 showed intra-correlationship of different leaching parameters. Therefore, it can be defined as leaching parameter correlation. Factor-4 explained 73.9% of the total variance and included only two variables, Fe(III) and IPR. Both variables had a strong positive correlation. During the leaching process, bacteria oxidize Fe(II) to Fe(III) and their activity can be measured indirectly in terms of their metabolite concentration (Fe(III)). The positive correlation between these two variables implies that IPR increased as Fe(III) increased. Because Factor-4 consists exclusively of metabolites, the factor can be taken to define metabolite concentration. Factor-5 and Factor-6 explained 80.4% and 86.3% of total variance, respectively. Factor-5 and Factor-6 included variables such as pulp density and particle size, respectively; therefore, they can



Fig. 8. Comparison between calculated values based on MLRA versus observed value for all leaching parameters for SOB.

Table 2

Factor analyses for IOB (Acidithiobacillus ferrooxidans).

Parameter	Factor					
	1	2	3	4	5	6
Time	0.826					
рН		0.921				
Eh	0.924					
PD					0.91	
Fe(II)	-0.642					
Fe(III)				0.634		
Fe(III)/Fe(II)	0.857					
IOR		0.52	0.405			
IPR				0.861		
PS						0.988
Temperature			0.863			
Al%	0.911					
Mo%	0.904					
V%	0.925					
Ni%	0.954					
Acidity		-0.931				
Acid consumption		0.95				
Eigen values	6.9	3.1	1.4	1.2	1.1	1
Cumulative % variance	40.6	58.8	66.9	73.9	80.4	86.3

Table 3

Factor analyses for SOB (Acidithiobacillus thiooxidans).

	Factor				
	1	2	3	4	5
Time	0.968				
рН	-0.706		0.579		
Eh	0.94				
PD		0.898			
PS				-0.801	
S				0.596	
Temperature					0.916
Al%	0.853				
Mo%	0.824				
V%	0.973				
Ni%	0.969				
Fe%	0.956				
Al rate		0.764			
Mo rate		0.849			
V rate		0.91			
Ni rate		0.935			
Fe rate		0.855			
Acidity	0.523		-0.766		
Acid consumption			0.844		
Eigen values	7.2	5.1	1.3	1.2	1
Cumulative % variance	37.8	64.3	71.3	77.7	83.2

be termed solid concentration and solid characterization, respectively.

3.8.2. Sulfur oxidizing bacteria

In the case of SOB, Factor-1 explained 37.8% of the total variance (Table 3). Specifically, Factor-1 contained strong positive loading of time, Eh, acidity and percentage of metal ions leached and a strong negative loading of pH. The negative loading of pH indicated that leaching efficiency increased as pH decreased. The positive correlation between Eh, time and acidity indicated a progressive increase in bacterial activity. Therefore, Factor-1 can be classified as leaching efficiency. Factor-2 explained 64.3% of the total variance. Specifically, Factor-2 showed strong positive loading of pulp density and leaching rates of various metals ions. Therefore, Factor-2 can be taken as the leaching parametric effect. Factor-3 explained 71.3% of the total variance and included bacterial metabolites and acid concentration; therefore, this factor was defined as bacterial metabolites. Factor-4 and Factor-5 explained 77.7% and 83.2% of the total variance, respectively. Factor-4 included particle size and oxidants (sulfur). The negative correlation of particle size suggested

a higher acid consumption when there were finer particle sizes, indicating a higher leaching rate. Factor-5 included only temperature.

4. Conclusions

Both acidophiles, *A. ferrooxidans* and *A. thiooxidans*, showed high Ni and V leaching. However, the leaching rate of Mo was low due to the refractory nature of MOS_2 as well as the diffusion barrier provided by elemental sulfur. Different leaching rates were observed for both the acidophiles while varying the leaching parameters. Higher pulp densities showed decreased trend in leaching rate for IOB whereas application of SOB revealed increased leaching rate with increase of pulp density. The amount of acid present in the lixiviant in case of SOB supported high metal dissolution (except Mo) at higher amount of spent petroleum catalyst. Similarly, while varying initial pH of the leaching, IOB showed maximum leaching rate at pH of 2.5 whereas the same for SOB was obtained at pH 2.0. For both acidophiles the nutrient content in the lixiviant was different. For IOB, the major oxidants were Fe(III) and SO_4^{-2} in the lixiviant and thus variation of initial Fe(II) concentration affected the leaching rate. Increasing initial Fe(II) concentration up to 3 g/L could depict appreciable leaching rate and beyond this concentration there was negative effect on leaching. The negative effect was due to increase in iron precipitation rate as well as decrease in bacterial activity. While in case of SOB the nutrient concentration increased with increase of elemental sulfur in the growth medium and thus leaching rate increased. However, the leaching parameters like particle size and reaction temperature could show similar leaching rate for both the acidophiles. Based on the activation energy, the dissolution process followed a mixed kinetics model. The MLRA showed good matching between theoretical and observed leaching percentages for metal ions such as Mo, V and Ni. Finally, PCA for IOB and SOB revealed 6 and 5 factors, respectively, which described more than 80% of the total variance.

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