

Bioleaching of spent hydro-processing catalyst using acidophilic bacteria and its kinetics aspect

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Abstract

Bioleaching of metals from hazardous spent hydro-processing catalysts was attempted in the second stage after growing the bacteria with sulfur in the first stage. The first stage involved transformation of elemental sulfur particles to sulfuric acid through an oxidation process by acidophilic bacteria. In the second stage, the acidic medium was utilized for the leaching process. Nickel, vanadium and molybdenum contained within spent catalyst were leached from the solid materials to liquid medium by the action of sulfuric acid that was produced by acidophilic leaching bacteria. Experiments were conducted varying the reaction time, amount of spent catalysts, amount of elemental sulfur and temperature. At 50 g/L spent catalyst concentration and 20 g/L elemental sulfur, 88.3% Ni, 46.3% Mo, and 94.8% V were recovered after 7 days. Chemical leaching with commercial sulfuric acid of the similar amount that produced by bacteria was compared. Thermodynamic parameters were calculated and the nature of reaction was found to be exothermic. Leaching kinetics of the metals was represented by different reaction kinetic equations, however, only diffusion controlled model showed the best correlation here. During the whole process Mo showed low dissolution because of substantiate precipitation with leach residues as MoO₃. Bioleach residues were characterized by EDX and XRD.

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1. Introduction

Spent hydro-processing catalysts, the major solid wastes of petro-chemical industries, contain various hazardous components, such as Al, Ni, Co, V, Mo and some organic contaminants. During the use of the catalysts, metal sulphides and oxides and metallorganic compounds are deposited on the catalyst surface, causing loss of activity and specificity [1,2]. Spent catalysts were traditionally deposited in landfills, but due to strict environmental regulations and economical conditions, proper recovery of the valuable metals from the catalysts has become essential [3,4]. To avoid pollution in land disposal as well as minimise landfill space, the spent catalysts are subjected to metal extraction by var-

ious solubilization process and reused in a variety of applications [5].

Compared to conventional techniques, biotechnological leaching processes offer attractive features for metal extraction from solid materials. Such processes are more cost efficient, simpler and more environmentally friendly than their chemical counterparts. A review of literature reveals that the role of micro-organisms in bioleaching of various metals from ore deposits and mine tailings has been studied extensively [6,7]. Also, the bioleaching process has been applied in various solid waste treatments for recovery of valuable metals. These include biodissolution of metals from fly ash [8–10], spent batteries [11,12] and electronic scraps [13]. Bioleaching studies have also been carried out on different types of spent catalysts. For example, Blaustein et al. [14] used a bioleaching technique for Mo extraction from coal liquefaction catalyst residues using *Acidithiobacillus ferrooxidans*. Valuable metals like Al, Ni, Mo,

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V, Sb are reported to be mobilized by *Aspergillus niger* from the metal-contaminated fluid cracking catalysts. The production of primary metabolites such as citric, gluconic and oxalic acids do play the major role to leach out metals from such wastes [15–17]. Vanadium has also been recovered from spent vanadium-phosphorus catalysts using *Acidithiobacillus thiooxidans* [18].

Comparative studies of one step and two-step leaching processes were reported by different researchers, and the feasibility of the latter was demonstrated [13,19,20]. For industrial application, a two-step process is believed to be appropriate to increase leaching efficiency. In general, the advantages of two stage processes are that independent lixiviant generation removes the link between the bioprocess and the chemical process and thus makes it possible to optimize each process independently to maximize productivity. This strategy can be used when the ore/waste does not contain the necessary mineral components in sufficient quantities to sustain a viable bacterial population. Furthermore, higher waste concentrations can be treated compared to the one-step process, which results in increased metal yields [21].

The most effective and common bacteria for metal solubilization are the chemolithoautotrophs *A. ferrooxidans* and *A. thiooxidans*. These bacteria utilize elemental sulfur (S^0) and Fe^{2+} ions for growth and produce sulfuric acid as a key metabolite. When grown on elemental sulfur, *Acidithiobacilli* produce several intermediate sulfur species with high reducing power including thiosulfate and sulfite [22,23]. The sulfite so formed can be oxidized by oxygen action catalyzed by bacteria. Such bacteria can thrive on low pH and tolerate harsh conditions that exist in concentrated metal solutions. In addition, *A. thiooxidans* and *A. ferrooxidans* have been previously reported to reduce vanadium (V) to vanadium (IV) in the presence of elemental sulphur [13,23].

The current investigation reports bioleaching of spent hydro-processing catalysts using *Acidithiobacilli* type of bacteria. Exploring the potential for organisms using sulfur metabolism to aid in the dissolution process is a major aim of this project. Metal recovery was performed using a two-step process where lixiviants contain the bacterially produced acidic solution or the spent medium as the leaching agent for pre-treated spent catalysts. There was no direct contact of the metals in spent catalysts with the biomass in this step. The effect of time, spent catalyst concentration, amount of elemental sulfur and reaction temperature were studied in detail for the two-step process. Chemical leaching with sulfuric acid was compared with bacterially produced acid solution, and the suitability of sulfur oxidizing *Acidithiobacilli* for spent catalyst bioleaching was demonstrated.

2. Experimental

2.1. Chemicals

All chemicals were analytical grade reagents (AR) unless otherwise stated and all aqueous solutions were prepared using de-ionized water.

2.2. Spent catalyst

The hydro-processing spent catalyst was obtained from SK Petroleum Corp., South Korea, and this material was the basis of all samples used in the experiments. The spent catalyst material was a granular solid with black, waxy covering and a film of surface oil that drained on standing. Particle size ranged from 2 mm to 5 mm. The spent catalyst was pre-treated in a soxhlet apparatus using acetone as the solvent. The catalyst was then dried in a 50 °C oven overnight. The black particles were then ball milled and sieved to ~106 μm (sieve no. # 140) size and stored in a vacuum desiccator. This material is the pre-treated spent catalyst.

2.3. Growth of micro-organisms

A mixed sulfur oxidizing bacteria was collected from Parker CRC (Murdoch University, Australia). The culture was mainly constituted by *A. thiooxidans* species. Initial growth was conducted using 10 g/L of elemental sulfur (S^0). The growth medium consisted of macronutrients or mineral salts: 5 g/L $(NH_4)_2SO_4$, 2.5 g/L K_2HPO_4 , 2.5 g/L $MgSO_4 \cdot 7H_2O$, 0.2 g/L $CaCl_2 \cdot 1/2H_2O$ [24]. The 1 L stock medium was prepared, and the pH of the solution was adjusted to 2.5 with concentrated H_2SO_4 . The inoculum was incubated in a rotary shaker (SI-600R) at 180 rpm and 32 ± 1 °C. Bacterial growth was monitored by cell counts (Neubauer counting chamber) and pH change in the medium.

2.4. Bioleaching process

All experiments were performed in shake-flasks in an orbital shaking incubator at 32 ± 1 °C and 180 rpm except where specified. A pH meter (Orion-720+) with glass membrane electrode was calibrated using pH 1.68 and 3.65 buffers and used to measure pH. The bioleaching experiments were carried out in two-stage method. First, the bacteria were grown with elemental sulfur in 300 mL Erlenmeyer flasks containing 100 mL of growth media. As the bacteria consumed substrate, they produced sulfuric acid in the growth culture (the first step). At the end of the batch culture (determined through cell count) the suspensions were filtered, and the filtrate that contained bacterially produced metabolites was used for the leaching of spent refinery catalyst (second step). The addition of spent catalysts to the filtrate in the second step usually occurred after 12 days of bacterial growth. Experiments were conducted by varying reaction time, spent catalyst concentration, amount of elemental sulfur and temperature during this process. To ascertain the reproducibility of results, a group of experiments were repeated a number of times and the results were found to vary within $\pm 5\%$.

2.5. Chemical analyses

Elements in liquid phases and digests of solid phases were determined by ICP-AES, Spectro Analytical Instruments (CIROS). After the desired leaching time, the solid and liquid phases were separated. The liquid phase was acidified and

Table 1
Metal analyses (wt% recover) during pre-treatment process

Sample	Al	Fe	Mo	Ni	S	V
Acetone washed	19.5	0.3	1.4	2.1	11.5	9.0
Calcined, 750 °C	17.4	2.1	1.4	2.0	3.1	10.3
Raw SC	14.2	1.5	1.2	1.7	10.6	7.7

diluted to known volume, while the solid phase was digested in boiling (at 60 °C) concentrated HCl before filtration, dilution and analysis. Data from these analyses were used to calculate the weight fraction of metal in the solution phase and are reported throughout as percentage recovered.

3. Results and discussion

3.1. Pre-treatment process

Prior to leaching, the oily spent refinery catalyst was pre-treated by various methods and the metal composition of the same was also examined by ICP-AES. Solvent extraction of replicate masses showed some variation in mass reduction due to the mobile oil film but losses of 15% were characteristic. Calcination of the oily spent catalyst (750 °C for 2 h) gave mass losses of 36%. However, the pre-treated (oil removed through acetone washing) material resulted in mass losses of 33%. We concluded that our raw spent catalyst sample was 64% non-volatile phase and 36% volatile carbonaceous phase with 15% of the original mass dissolved in solvent extraction. So, digestion of acetone washed pre-treated material gave good agreement on the weight fraction of metals present after correction for the mass reduction. The detail of the metal content of both the pre-treatment processes and raw spent catalyst is given in Table 1. The table clearly shows that amount of sulfur is more in case of acetone washed spent catalyst than the calcined one. From the XRD analysis (Fig. 1), it is evident that the spent catalysts contained nickel, molybdenum, vanadium and sulphur and alumina substrate in it. Considering the attachment of V and Mo with the

sulphide matrix, we have chosen the acetone washed sample for our bioleaching study.

3.2. Microbial growth

Growth of the mixed bacteria consortia was carried out using 10 g/L elemental sulphur as the substrate. The initial pH of the medium decreased with increase of incubation period as did cell number (data not shown). The cell number attained stationary state after 2 weeks of incubation. The oxidation of colloidal sulphur particles decreased the pH of the solution (pH = 0.9–1.0) due to formation of sulfate (SO_4^{2-}) ion. In due course, the sulphur was also observed to lose its hydrophobicity and found well dispersed in the solution.

3.3. Metal extraction

As a primary test, the acetone washed pre-treated spent catalyst (15 g/L) was exposed to three different solution sets: (i) sulfur oxidising culture media with cells and metabolites, (ii) the same media as (i) but with the cells removed by membrane filter (0.25 μm size, ADVANTEK, membrane filter paper), and (iii) mineral salt solution (pH 1.5) containing only elemental sulfur, but no cells. Multiple sample sets were used for each solution condition. Samples were taken from each set for analysis at regular intervals for a period of up to 7 days (Fig. 2). Metal extraction in the medium having only bacterially produced metabolites (cells filtered) is the same as that of the flask with both cells and metabolites. However, the flask where only elemental sulfur is added shows low dissolution for all the three metals and undissolved sulfur powder floats on the surface of the medium. In presence of cell plus metabolites, recovery of Ni, V and Mo is found to be 88.2%, 93.0% and 17.4%, respectively within the 7 days period. Similarly, the flasks where cells are absent and only cellular metabolites are used for leaching, recovery of Ni, V and Mo is found to be 89.3%, 95.1% and 24.0%, respectively, within the same time period. Both Ni and V show consistence leaching efficiency in presence of cells plus their metabolites as well as in presence of only cellular metabo-

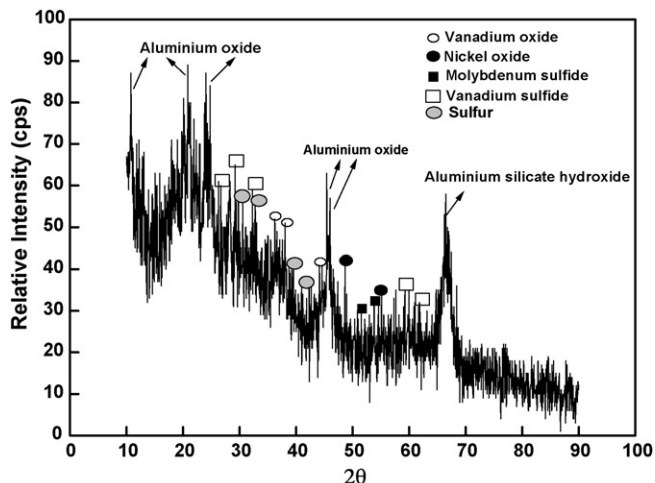


Fig. 1. X-ray diffractogram of acetone washed spent catalyst.

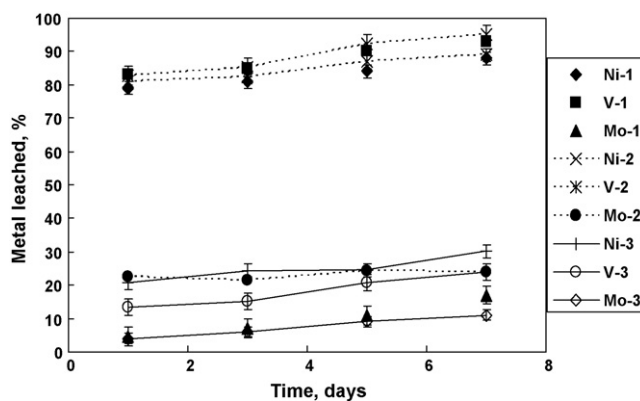


Fig. 2. Metal extraction at different experimental conditions. Symbols without line, media with cells and metabolites; symbols with dashed lines, media with only cellular metabolites; symbols with dark line media in absence of cells and metabolites.

lites. The cellular metabolites present in the lixiviant contains SO_4^{2-} ion as the major leaching agent. So, the major reaction mechanism here is the protonic action of sulfate ion on the spent catalyst to mobilize the metals. This ascertains that the cellular metabolites play the major role for the extraction of the metals into the solution.

3.4. Effect of reaction time

Representative results of batch leaching of the spent refinery catalyst are shown in Fig. 3, where the leaching percentages of Ni, Mo and V are plotted with respect to the reaction time at 15 g/L of spent catalyst concentration. From the figure, the percentage of Ni, V and Mo recovered after 1 day was 80.9%, 82.8% and 22.4%, respectively. When the reaction period was prolonged to 7 days, the amount of Ni, V and Mo was 89.3%, 95.7% and 24.2%, respectively. This inferred that the rate of reaction becomes slower after 2 days and a period of 7 days was chosen for an efficacious leaching. The figure also shows that Ni and V were equally released into the solution after 1 day, but Mo, on the other hand showed very slow and little solubilization.

The major reaction takes place in the second step through the protonic attack of SO_4^{2-} ion that produced earlier in the first step [18] by following mechanism:



The soluble H_2SO_3 is considered as the key intermediate of the oxidation. The bacteria attach onto sulfur particles and grow with the oxidation of sulfur. The sulfuric acid is released into the solution as the metabolic products. This highly acidic medium did help in leaching of the metals into the solution. However, here the result depicted the poor extraction of Mo into the solution compared to Ni and V. Referring to the potential Eh–pH diagram [25], it was noted that there was possibility for precipitation of Mo as molybdenum trioxide with the solid phase. The other reason of lower solubility of Mo is that the target mineral phases of Mo are either not co-located and/or that the pre-treatment process has exposed those phases to different extents [26].

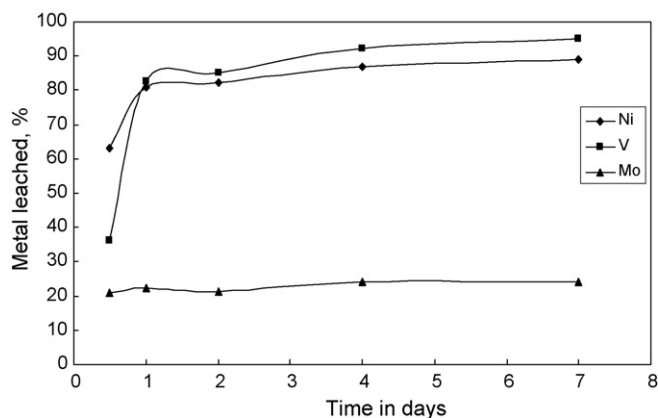


Fig. 3. Metal leaching with respect to time. Conditions: spent catalyst = 15 g/L, elemental sulfur = 10 g/L.

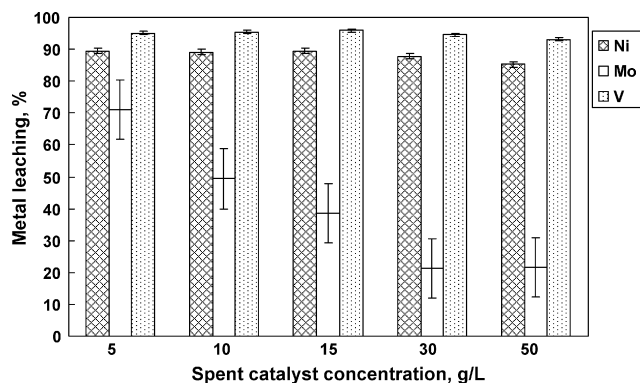


Fig. 4. Leaching of metals at different spent catalyst concentration. Conditions: time = 7 days, elemental sulfur = 15 g/L.

3.5. Effect of spent catalyst concentration on bioleaching of metals

Varying amounts of the spent catalysts, 5–50 g/L, were added to the 100 mL leaching solution with 15 g/L elemental sulfur. After 7 days, Ni (85–89%) and V (93–95%) were significantly recovered with increase of spent catalysts concentration in the solution (Fig. 4). On the other hand, Mo in the solution, decreased from 71.1% to 21.5% whilst increasing catalysts concentration from 5 g/L to 50 g/L.

While varying the spent catalyst concentration, the pH of the solution at all the solid loadings remain within pH 0.9–1.35 (data not shown), however, there is change in the redox potential of the lixiviant (Fig. 5). In the present investigation the electrode potential of the aqueous system observed to be within (+)250 mV to (+)470 mV. The speciation study of V and Ni reveals that within such pH-potential range V is stable in the aqueous phase as VO^{+2} and Ni as Ni^{3+} [27,28]. On the other hand, Mo, shows low dissolution due to its sparingly soluble nature at the acidic ambient and finally with increase of potential (at the same pH), Mo covers itself with a passivating layer of MoO_2 and MoO_3 [25]. This can be represented by following equations:

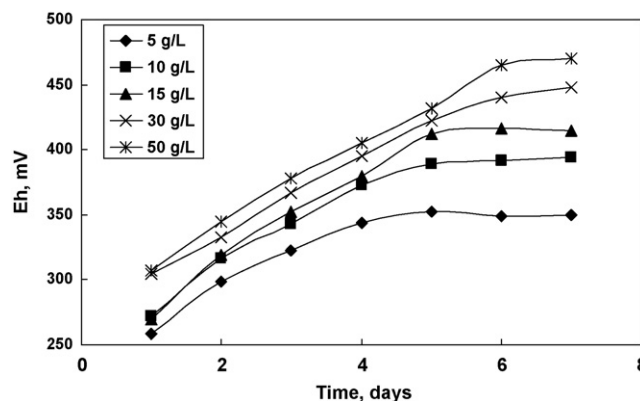
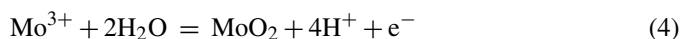
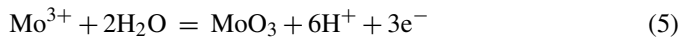


Fig. 5. Redox potential of the solution at different concentration of spent catalyst.



Mo dissolution is higher at lower amount of spent catalyst and it is obvious that the dissolution percentage depends on the concentration of metal ion available at the same time within the material (spent catalyst). The XRD diagram of the pre-treated spent catalyst depicted the occurrence of Mo in the solid as MoS₂. Considering the oxidation of MoS₂ by cellular metabolites, the major product of the reaction will be H₂MoO₄, which is soluble in the aqueous solution. The reaction can be presented as:



However, the formation of H₂MoO₄ in the aqueous system occurs at Eh > ~600 mV, pH 1–2, and, since the redox potential in the present bioleaching process remains <500 mV, therefore, sparingly soluble of molybdenum is observed [25].

It can also be speculated that the low electrode potential and strong acidic medium at low concentration of spent catalyst favours Mo³⁺ ion stability in the aqueous phase. However, at spent catalyst amount of 30 g/L or 50 g/L, the redox potential of the aqueous solution increased. As a result, Mo³⁺ transform into MoO₃ or MoO₂ and precipitates with the solid phase [29]. It has also been reported that in hydrometallurgical processes Mo is usually recovered by precipitating it at lower pH and higher redox potential as molybdenum trioxide [30,31].

The major part of Mo is found attached with solid phase of catalysts when we analyzed the digest of solid residues. Also, it seems that by increasing the catalyst amount, an appropriate synchronization between the rate of Mo extraction and that of Mo precipitation occurred, and this caused Mo species to be low in the solution.

3.6. Effect of amount of elemental sulfur

Since the metal dissolution is accompanied by protonic attack through SO₄²⁻ ion, therefore, variation of elemental sulfur amount was expected to increase the leaching efficiency of all the metals. Initially, bacteria were grown in presence of different concentration of elemental sulfur such as 10, 15 and 20 g/L. The cell number and sulfuric acid produced during the same process were monitored. In the second-step, the percent of Ni extracted ranged from 87.4% to 88.3% and V ranged from 89.2% to 94.8% when elemental sulfur varied from 10 g/L to 20 g/L (Fig. 6). The figure shows that Mo leaching was increased from 21.0% to 46.3% when elemental sulfur concentration varied from 10 g/L to 20 g/L at 50 g/L of spent catalyst concentration. Mo leaching was not effective, although the elemental sulfur increased to higher amount. It is believed that if the Mo phases are associated with the residual carbon then greater levels of occlusion to the leach solution would result in lesser recovery under the most favourable transport conditions [32]. The extent of Ni and V recovery relative to the amounts predicted to be present was uniformly high (80–90% for Ni and 90–95% for V) under all conditions tested but never beyond this indicating that the pre-treatment method leaves some amount of the Ni and V phases inaccessible to the leaching solution.

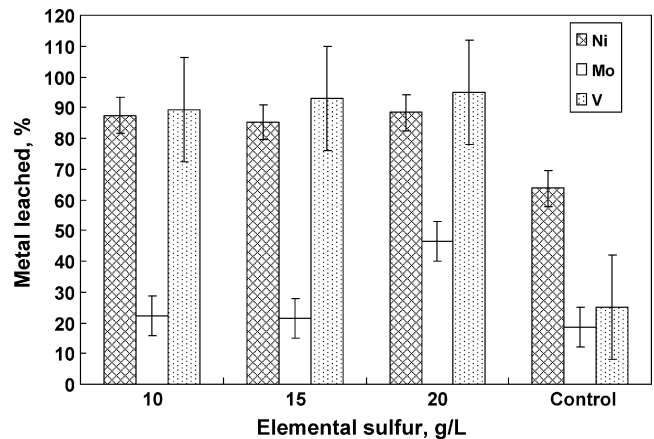


Fig. 6. Metal leaching at different amount of elemental sulfur. Conditions: spent catalyst concentration = 50 g/L, time = 7 days.

Control flasks containing no sulfur and no inocula but open to the atmosphere still had an oxidative solution with the Eh value set by the oxygen/water couple in sulfuric acid solution. Oxidation of the target metal phases is possible with dissolved oxygen from the atmosphere. This system recovered 63.7%, 18.6% and 24.9% of the Ni, Mo and V, respectively, after 7 days at 32 °C at a solid loading of 15 g/L (Fig. 6).

3.7. Effect of temperature

Varying the amount of elemental sulfur, we also studied the recovery of metal at three different temperatures, 25 °C, 32 °C and 40 °C. The extraction % of Ni, V and Mo is shown in Table 2. Ni and V released to solution did not show significant change; Ni recovery varied in the range of 80–90% while V from 89% to 97%. However, Mo dissolution into solution was observed to decrease with increase of temperature. At temperature of 25 °C and varying amount of elemental sulfur, the leaching % of Mo was varied from 50% to 60% (Table 2), but the same decreased sharply at the temperature regime of 32–40 °C. The low dissolution of Mo was also observed in this case. Huang et al. [29] have also noticed the reduction of Mo into the solid phase while increasing the reaction temperature from 20 °C to 80 °C. However, leaching of Ni and V during this process looks independent of temperature. As a whole, the leaching behavior of these metals can be resolved by studying the thermodynamic parameters. So, thermodynamic parameters such as ΔH and ΔS were obtained

Table 2
Leaching (%) of Ni, V and Mo at different temperature

Amount of sulfur (g/100 mL)	298 K			305 K			313 K		
	Ni	V	Mo	Ni	V	Mo	Ni	V	Mo
1.0	88.8	89.8	56.5	87.4	94.8	18.8	85.1	91.9	26.5
1.5	88.4	97.1	60.3	87.8	94.6	21.2	82.5	90.4	24.6
2.0	89.0	92.1	50.9	88.7	95.4	16.7	81.5	89.7	34.4

Condition: spent catalyst concentration = 30 g/L.

by using the following equation:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

where ' K ' is the reaction rate constant of the metals during leaching process derived from reaction temperature experiment at a constant time duration, ' T ' is the absolute temperature and ' R ' is the gas constant, i.e. $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. The plot of $\ln K$ versus $1/T$ was linear with the slope and the intercept giving values of ΔH and ΔS . The free energy of the reaction ' ΔG ' was calculated from the Gibbs relation, $\Delta G = \Delta H - T\Delta S$ at constant temperature.

The enthalpy, ΔH , was calculated to be -44.17 kJ/mol , -22.80 kJ/mol and -100.62 kJ/mol for nickel, vanadium and molybdenum, respectively. The highest enthalpy of Mo is due to its precipitation with the solid residues when reaction temperature increases. The negative value of ΔG indicates the feasibility of the leaching reaction process. All the calculated data for thermodynamic parameter is shown in Table 3.

3.8. Chemical leaching with sulfuric acid

Biorecovery experiments were initially compared with chemical leaching using similar amount of sulfuric acid that produced by the bacteria (200 mM). The experiments were conducted varying the spent catalyst concentration from 15 g/L to 50 g/L and Fig. 7A shows the result. As can be seen from the figure that Mo recovery at 15 g/L of catalysts concentration was 61.4%, but the solubility of the same decreased to 31.8% while catalysts concentration increased to 50 g/L due to its a . The chemical leaching of Ni by commercially available H_2SO_4 showed similar and consistent recovery that of biological process at all solid loadings. However, V recovery was found to be 8–18% less than biologically performed two-stage process. Percentage of V at 15 g/L spent catalyst concentration was 88.4% and it decreased to 77.8% when spent catalyst increased to 50 g/L. Aung and Ting [16] have also obtained similar higher metal recovery in biogenically produced acid medium than chemical leaching process while treating spent fluid catalytic cracking catalyst using *A. niger*. In another study, we diluted bacterially produced sulfuric acid ten-fold and conducted the leaching

Table 3
Calculation of thermodynamic parameters (ΔH , ΔS , ΔG)

Metal	Temperature (°C)	$-\Delta H$ (kJ/mol)	$-\Delta S$ (kJ/(K mol))	$-\Delta G$ (kJ/mol)
Ni	25	44.17	0.207	17.51
	32			18.96
	40			20.62
V	25	22.80	0.131	16.24
	32			17.15
	40			18.20
Mo	25	100.62	0.412	22.15
	32			25.03
	40			28.33

Conditions: spent catalyst = 30 g/L, elemental sulfur = 15 g/L.

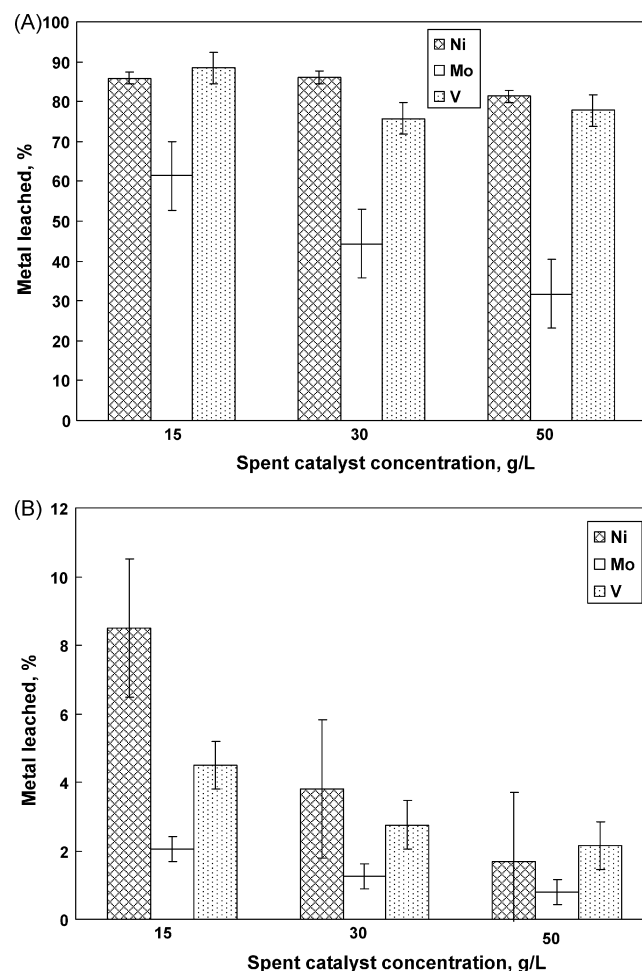
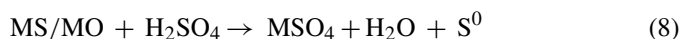


Fig. 7. (A) Comparison of direct acid leaching at different spent catalyst concentration. Conditions: time = 7 days, H_2SO_4 concentration = 200 mM. (B) Metal dissolution by bacterially produced sulfuric acid diluted 10 times.

study. The leaching efficiency was reduced to less than 10% for each element (Fig. 7B). From above results, it seems that the bacterially produced metabolites have pronounced effect on leaching efficiency. This has been also proved previously in our study (Fig. 2).

3.9. Reaction kinetics

In the present hydro-processing spent catalyst, Ni, V and Mo are expected to be present in oxide or sulphide form over the alumina matrix ($\alpha\text{-Al}_2\text{O}_3$) [33]. Bacterially produced sulfuric acid reacts with these metals according to following equation:



The matrix alumina is not reacted with the acid [34]. The reaction of these metals can proceed in a topochemical manner, in which the inner core of the unreacted particle decreases with time [35].

Leaching kinetics are controlled either by diffusional mass transfer of either reactant or product ions through a liquid boundary layer or a product metal deposit [36]. Liquid film diffusion control would be implied by linear first order kinetics, i.e. a plot of ' F ' the fraction of metal solubilised, versus time should be

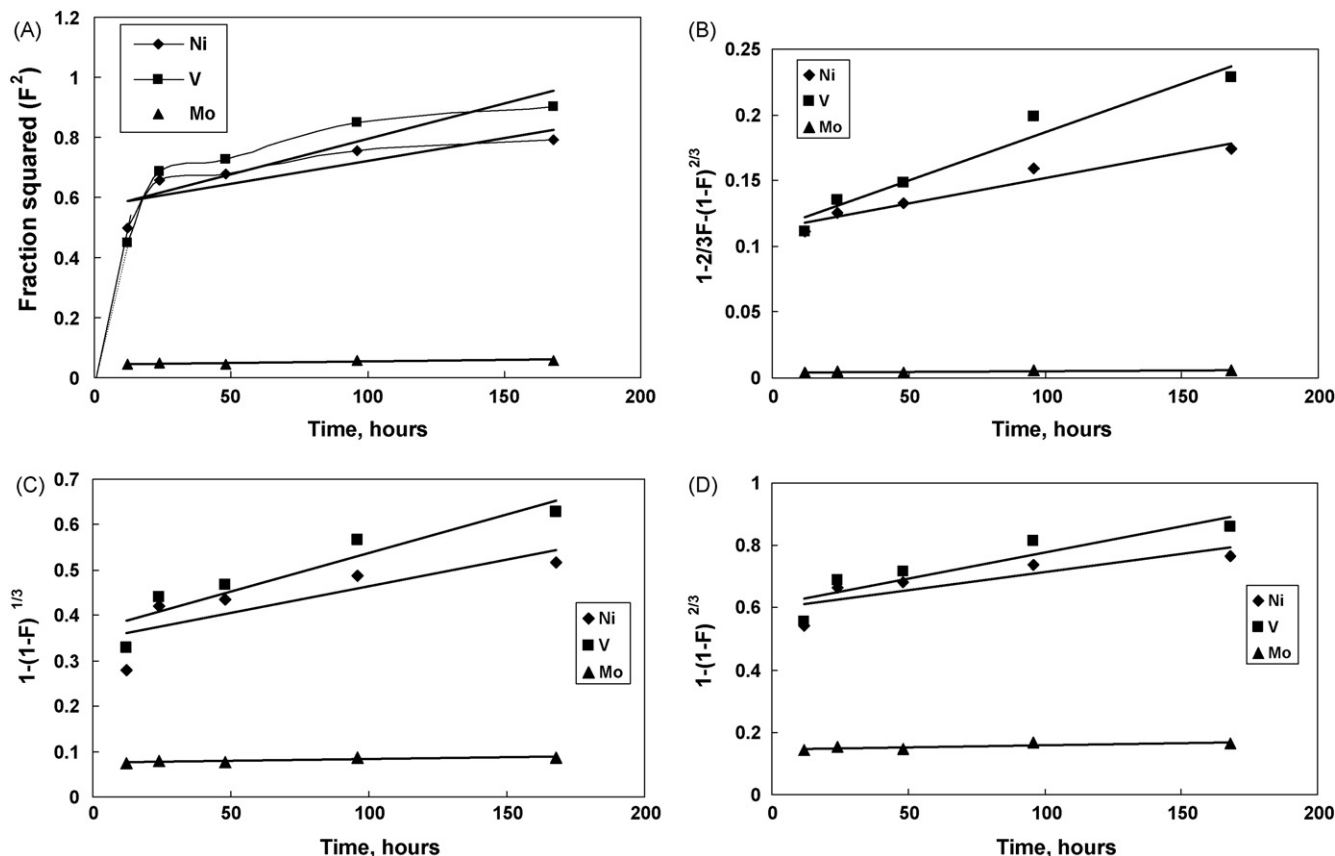


Fig. 8. (A) Parabolic product layer diffusion model of leaching kinetics of Ni, V and Mo. (B) Diffusion-controlled model of leaching kinetics for Ni, V and Mo. (C) Chemical-controlled model of leaching kinetics for Ni, V and Mo. (D) Shrinking sphere model, Stoke's regime for leaching kinetics for Ni, V and Mo.

linear. If product layer diffusion controls rate, then ' F ' versus $t^{1/2}$ or ' F^2 ' versus t should be linear. If the reaction is controlled by boundary layer, it can be described by application of shrinking core model theory,

$$kt = 1 - \frac{2}{3}F - (1 - F)^{2/3} \quad (9)$$

And, rate control by chemical reaction at particle surface gives,

$$kt = 1 - (1 - F)^{1/3} \quad (10)$$

as a linear plot of gradient k (the first-order rate constant for the surface reaction). Since the progress of the reaction would be unaffected by the presence of any product layer, the quantity of material reacting is proportional to the available surface of unreacted core. When no product layer forms, the reacting particle shrinks during the reaction, finally disappears. For small particle

this can be explained by a Stokes regime, for which,

$$kt = 1 - (1 - F)^{2/3} \quad (11)$$

The applicability of each kinetic model was derived using the metal leaching data from Fig. 3. Results for each model are plotted in Fig. 8(A–D). From the figures it can be seen that all the leaching kinetics attain linear trend after 48–50 h of reaction time for each model. None of the model has consistent data over the period of 0–150 h. It is due to the multi-elemental composition of the spent catalysts where different metal ions have dissimilar solubility and hence different leaching rate [37].

Equations for the lines of best fit are given in Table 4 for each model with the respective correlation coefficients. The table indicates that the diffusion-controlled reaction approaches the linearity more closely than the others, i.e. the resistance to diffusion through a product layer controls the rate of reaction of the

Table 4
Lines of best-fit equations and correlation factors for various kinetic leaching models

Kinetic model	Line of best-fit and correlation factor		
	Ni	V	Mo
Diffusion controlled	$Y=0.0004x+0.1134, R^2=0.9426$	$Y=0.0007x+0.1134, R^2=0.9532$	$Y=0.00001x+0.0042, R^2=0.6922$
Chemical reaction controlled	$Y=0.0012x+0.3467, R^2=0.6641$	$Y=0.0017x+0.3676, R^2=0.8712$	$Y=0.00007x+0.0759, R^2=0.6876$
Shrinking sphere, Stoke's regime	$Y=0.0012x+0.5982, R^2=0.7108$	$Y=0.0017x+0.609, R^2=0.8179$	$Y=0.0001x+0.1463, R^2=0.6872$
Product layer diffusion, parabolic	$Y=0.0015x+0.5693, R^2=0.722$	$Y=0.0024x+0.558, R^2=0.7302$	$Y=0.00009x+0.0452, R^2=0.6909$

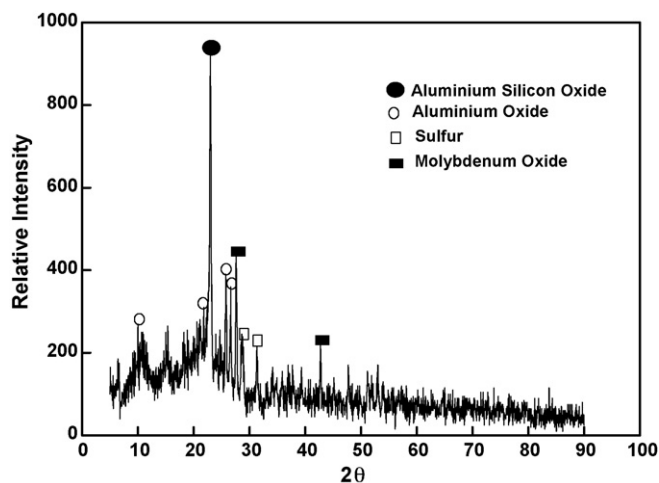


Fig. 9. X-ray diffractogram of bioleach residues.

bioleaching of spent catalyst. This may be attributed to the formation of a sulfur layer, as detected by XRD of bioleach residues. Due to lower solubility, Mo does not have good correlation factors at all the reaction kinetics.

3.10. Characterization of bioleach residue

The XRD of the leach residues (Fig. 9) depict the deposition of molybdenum, sulfur, alumina along with silica and aluminum oxide. These phases are undissolved phase during the bioleaching process. The major phase of Mo was found to be molybdenum trioxide. EDXA mapping corroborates the presence of those elements in the leach residues clearly (Fig. 10(A and B)). In the leach residues, we observed that the intensity of sulfur and molybdenum were greater than Ni and V. The results indicate that the lixiviant could easily dissolve Ni and V from the solid spent catalysts in the leaching process. The mapping

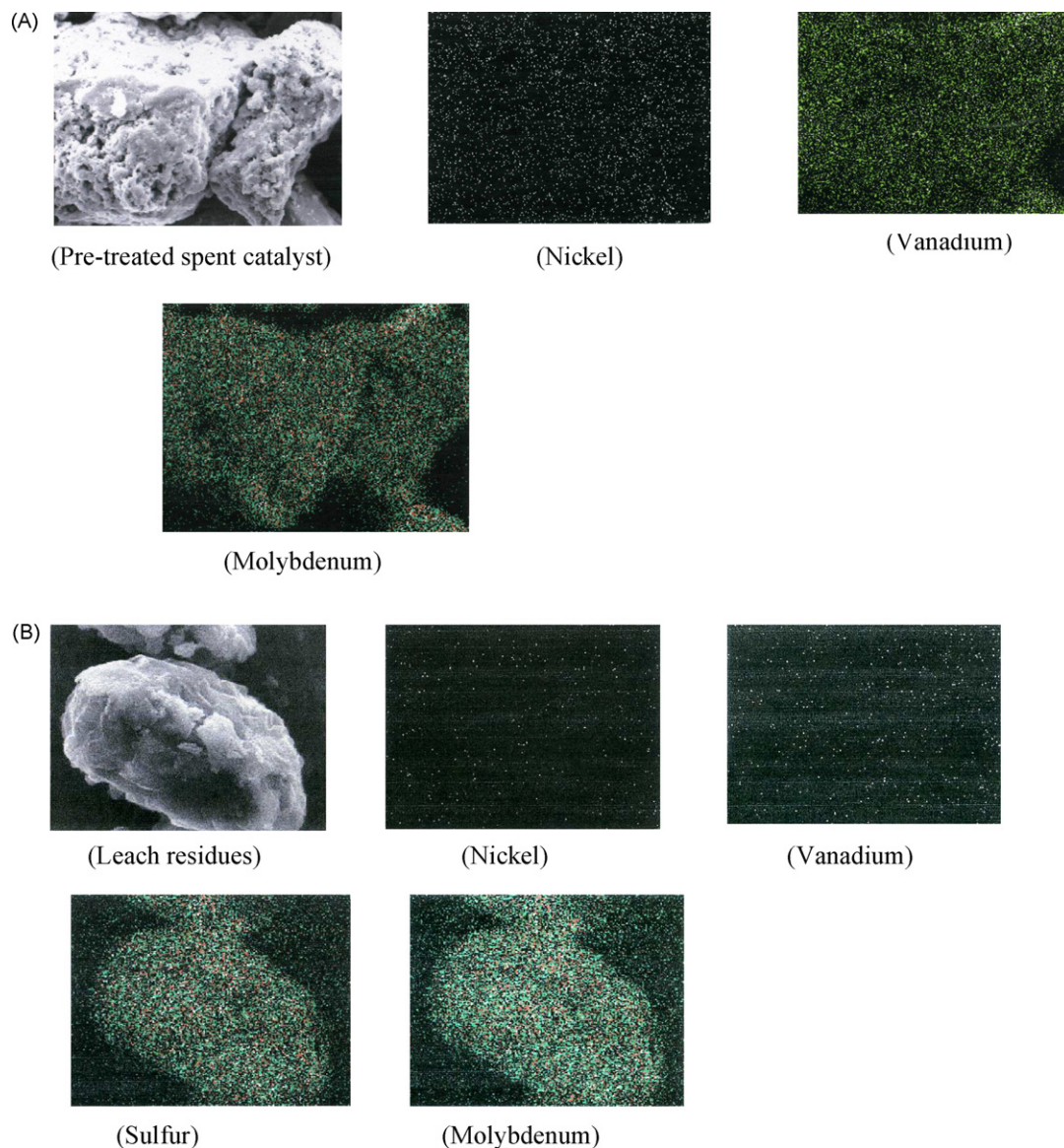


Fig. 10. . EDXA mapping. (A) Mapping of solid catalysts before leaching, (B) mapping of solid catalysts after leaching. Conditions: spent catalyst = 30 g/L, sulfur = 1.5 g/100 mL, temperature = 32 °C.

corroborates the slow dissolution rate of molybdenum as Mo covers the whole periphery of the residue. From Pourbaix [25] phase diagram it is believed that molybdenum can be precipitated as MoO_3 form at acidic pH with the solid matrix. This precipitates is believed to be attached with the elemental sulfur on the surface of the catalysts, forming complex compounds and exactly what type of complex forms in the residues is not clearly understood.

4. Conclusions

The release of nickel, vanadium and molybdenum from hazardous spent refinery catalysts using bacterially produced sulfuric acid has been well demonstrated. In the whole experimental set up Ni and V showed significant recovery during the reaction process while Mo was being precipitated. Increasing elemental sulfur in the growth media resulted in a solution richer in sulfuric acid, and hence, a leaching efficiency of Ni, V and Mo of 88.3%, 94.8%, and 46.3%, was obtained, respectively, at 5% (w/v) spent catalysts concentration. The reaction processes were demonstrated as diffusion-controlled. The lower solubility of Mo in the reaction process is due to its sparingly soluble nature in acidic regime and this is supported by Pourbaix equilibrium theory. Thermodynamic parameters such as ΔH , ΔS and ΔG are calculated from the data and the bioleaching process was found to be exothermic one and the free energy value showed the feasibility of the process. The leach residues were compared with original sample by EDXA mapping, and the distribution of molybdenum and sulfur was clearly visible. This substantiated the slow dissolution rate of molybdenum into solution and the deposition of insoluble sulfur on the surface of the solid catalysts. The XRD figure also depicted the deposit of the mineral phases in the leach residues. The leach residues mostly contain the alumina being associated with the silicate, insoluble elemental sulfur, and molybdenum trioxide.

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