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# Improvement in Metal Dissolution from Spent Catalyst by Adapted *Acidithiobacillus ferrooxidans*

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**Abstract:** The improvement in the leaching rate of Ni, V, Mo, and Al present in a spent catalyst sample was evaluated by the bacterial adaptation technique. For this purpose, leaching of the metals from the spent catalyst sample was conducted using both adapted and unadapted bacteria cultures. The evaluation was done on the basis of the variation of different leaching parameters such as pH, temperature, particle size, pulp density, and initial Fe(II) concentration. The adaptation technique was found to be fruitful as the leaching equilibrium reduced from 240 to 40hr. Further, the leaching rate of Ni and V was improved by 10%(w/w) due to bacterial adaptation. The leaching rate of Mo was lower due to combining the action of different factors like the presence of impervious elemental sulfur, refractory nature, and low solubility. The lower leaching rate of Al observed due to the refractoriness of the alumina matrix present in the spent catalyst sample. The pseudo rate order with respect to all leaching parameters was determined and found to be significant for the adaptation process.

**Keywords:** Bioleaching; Adaptation; Spent catalyst; Leaching parameter; Iron oxidizing bacteria.



## 1. Introduction

Oxides of Mo, Ni, and Co are used as catalysts in the petroleum refinery process for the purpose of the purification of different petroleum distillates and residues. They develop some deficiency in their physical properties after several usage cycles, which do not allow them for the purpose and are discarded as solid waste [1,2]. This solid waste is named as a spent catalyst (SC). The worldwide generation of SC is estimated to be 700,000-900,000metric ton/year [3]. The SC contains different metallic and nonmetallic elements like Al, V, Mo, Co, Ni, Fe, S, and C. Further, their high concentration in the SC sample does not allow it for a free landfill purpose as there are some obligations to dispose of the hazardous substance set by the environmental protection agencies of different countries [4]. Management of such a huge amount of SC become a headache for the petroleum refineries establishments. In order to utilize the SC values, a different group of researchers is working in their research horizons [5-8]. One of them is the dissolution of different valuable metals from the SC through hydrometallurgical technique, followed by their recovery for the development of usable products [9-14].

In the hydrometallurgical technique, the SC is generally roasted, followed by the metal dissolution using different suitable leaching reagents [7-10,14-20]. It can be leached directly at the high pressure [13,21]. However, these hydrometallurgical techniques are intensive in terms of chemicals and energy. In order to overcome the issues related to the conventional leaching process, bioleaching has emerged in the biotechnology era. Indeed, different naturally occurring microorganisms have shown the tremendous ability of metal dissolutions from different solid resources [22-26].

The microorganism genera like *Acidithiobacilli* spp., *Pseudomonas* spp., *Aspergillus* spp., and *Penicillium* spp has been examined by different bioleaching groups for the dissolution of different metals from a range of solid resources [27-35]. *Acidithiobacillus ferrooxidans* is one of them, which has proved its significance in the bioleaching of different metals by using its inborn quality of oxidation of ferrous and sulfur to ferric iron and sulfuric acid, respectively. During its metabolism, it helps the metal dissolution either by the direct cellular activity or indirect reactions compensated by the metabolic products [36].

However, in some cases, bacteria are not compatible with the leaching medium containing solid resources. There are different reasons for it. There may be some unwanted metals present in the solid samples which impede the growth of bacteria. Secondly, there may be a trace amount of toxic elements present in the solid samples. They create physiological stress in the life cycle of bacteria. As a result, either their population decreases or, in the worse case, they may die. In this case, the bacterial adaptation cumulates the leaching properties [37-39]. The bacterial adaptation process is a field type mutation process that does not require any molecular cloning of the bacterial gene. In this process, the bacteria resume the metabolic properties slowly by adopting the adverse environment and overcome the physiological stress. Further, the toxicity developed by different trace elements present in the solid samples during the bioleaching process can be suppressed by the adaptation [40]. Furthermore, the adapted bacteria can improve the leaching rate [38].

Although adaptation is a known process for the leaching improvement, its application in the SC bioleaching is not adequate. Therefore, bioleaching of a SC sample using the adapted bacteria and evaluation of its improvement is the main purpose of this article.

## 2. Materials and Methods

### *2.1. Chemicals.*

Only analytical grade chemicals and de-ionized water were used whenever required.

### *2.2. Pretreatment of SC sample.*

The petrochemical SC sample coated with waste oil, which was removed in the boiled acetone with the help of a soxhlet. The de-oiled SC sample was then dried and followed by ground with the help of a mortar and pestle. Then the SC powder sample was sieved to get different particle size fractions. The SC powder sample was then undergone an acid digestion process, and the digested liquor was analyzed using ICP-AES (JOBIN-YVON JY 38). The concentration of Al,S,Ni,V,Mo, and C in the SC powder sample was found to be 19.5,11.5,2.0,9.0,1.4, and 2.5%, respectively.

### *2.3. Microorganisms.*

The bacterium used in the bioleaching experiments was *A. ferrooxidans*, which was isolated from a water sample collected from the Dalsung copper project of South Korea[41]. The bacterium was sub-cultured in freshly prepared 9K medium at pH 1.8 and 35$^{o}$C. Further, the bacterium was sub-cultured repeatedly in the media with the same condition in order to achieve the highest iron oxidation rate[41]. This active culture was used in the leaching process was called unadapted bacteria culture (UBC).

*2.4. Adaptation.*

For the purpose of adaptation, the bacteria was repeatedly sub-cultured with the mimic version of 9K media+SC sample. Since the SC sample has metals like Ni, V, and Mo, the fresh media was prepared with the addition of the above metals. In the initial sub-culture, the concentration was less. However, the concentration of the metals was increased gradually with the number of sub-culturing[42]. The concentration of Ni, V, and Mo were increased up to 10.0,5.0 and 0.03g/L, respectively, on the basis of tolerance ability of the bacteria. Then the bacterium was further sub-cultured in the 9K media with the addition of SC sample. The adaptation process was done until the SC concentration increased up to 20 g/L. After the repeated sub-culturing in the presence of SC sample, the iron oxidation rate became the same as that in the case of UBC. This adapted bacteria culture was named as ABC.

*2.5. Bioleaching.*

The leaching experiments were conducted in the 250mL shake flasks, which contained 100mL(90mL of media and 10 mL of inoculums, i.e., UBC or ABC) of the lixiviant. The shaking of the lixiviant was done with the help of an orbital shaker-cum-incubator at an average speed of 180rpm. The time of each leaching run was counted after adding the SC powder sample based on the pulp density. The pH and Eh of the lixiviant were monitored in fixed time intervals using a pH-Eh meter(THERMO, ORION-720$^+$). Also, samples were collected in regular time intervals for the evaluation of metal dissolution. The metal ion concentration in the leach liquor was analyzed using ICP-AES(JOBIN-YVON JY 38). The leaching studies were conducted at pH-2.0, pulp density(PD)-10%(w/v), temperature-35$^o$C, Fe(II)-10g/L, and particle size(PS)-106μm, unless otherwise specified. The effect of different parameters on the leaching rate was examined and discussed in each sub-section. All experiments were triplicated, and the experimental errors were within ±3%.

## 3. Results and Discussion

*3.1. Equilibrium time.*

In order to evaluate the equilibrium time of the leaching of four metals (e.g., Al, Ni, Mo, and V) from the SC sample using the UBC, the experiments were conducted for 300hr. The leaching rate of the metals is shown in Fig.1. It can be observed that the leaching rate changed hardly after 240hr. Therefore, the equilibrium time of leaching using UBC was 240hr, and further, all leaching experiments using the UBC were conducted for 240hr. When the equilibrium time of the leaching using the ABC was evaluated, there was hardly any change in the metal leaching observed after 40hr (Fig.1). Therefore, the equilibrium time of the metal leaching using the ABC was set for 40hr, and all further leaching experiments were limited to the equilibrium time. The leaching rate of Ni and V was found to be about 85% in the case of UBC; however, those were about 95% in the case of ABC. This showed that bacterial adaptation not only improved the leaching rate by 10%; it also decreased the equilibrium time significantly. However, the leaching rate of Al and Mo were not encouraging for both the cultures. Al leaching was not affected by the adaptation process (Fig.1). It means the bacterial dissolution of Al was not occurred due to the refractoriness of the $Al_2O_3$ matrix[43]. The leaching rate of Mo increased due to adaptation; however, it was not similar to Ni and V. The lower Mo leaching observed due to the mutual effect of the refractoriness of $MoS_2$ matrix, lower solubility of Mo in the mild acidic medium, and the impervious sulfur layer over the Mo-matrix [44].

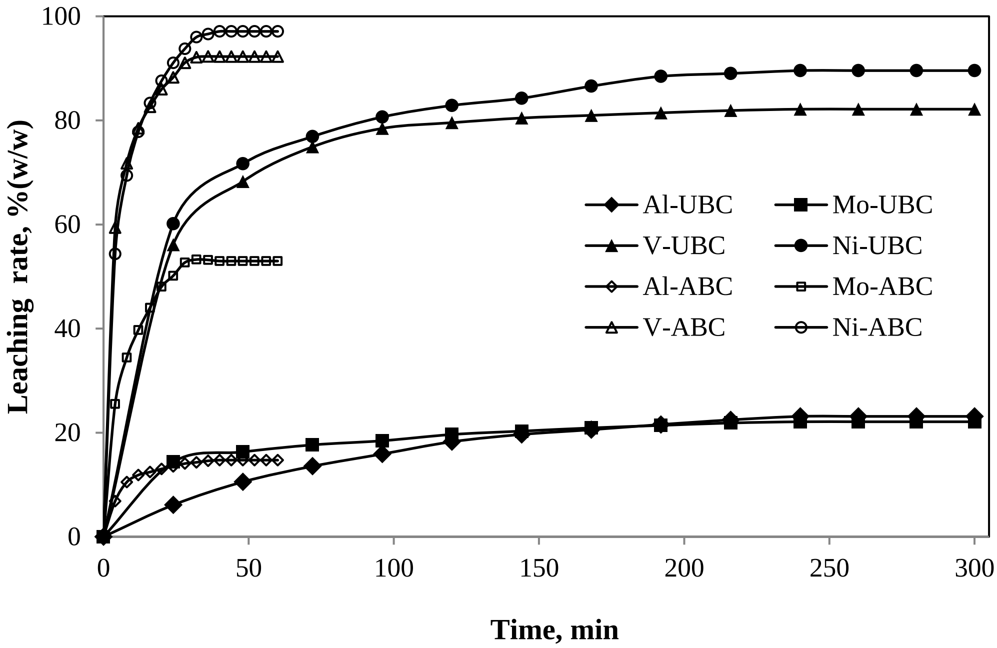


**Figure 1.** Effects of contact time on the dissolution of Ni,V,Mo, and Al by both UBC and ABC. Conditions:Fe(II)-10g/L,pulp density-10%(w/v),pH-2.0,particle size -106+45µm,temperature-35°C and 180rpm.

*3.2. Effect of pH.*

The initial pH of the lixiviant was varied as 1.5, 1.75, 2.0, 2.25, 2.5, 2.75, and 3.0, while other parameters kept constant, as mentioned in the experimental section. The pH of the lixiviant was adjusted by adding dilute $H_2SO_4$(10%) in the leaching medium. Figure 2 shows the leaching rate of metals from the SC sample by varying pH of the medium using both ABC and UBC. The leaching rate increased from pH1.5 to 2.0; however, it decreased with a further increase in the pH. This leaching pattern was due to the bacterial activity increased when the pH of the medium increased from pH1.5 to 2.0, and it decreased at a higher pH [45]. Further, the formation of jarosite in the leaching medium at a higher pH may be another reason for the falling leaching rate at the higher pH range[46]. However, the adaptation process showed beneficial at the optimum pH of 2.0. Since the bacterial activity was at the peak at pH2.0, the ABC efficiently dissolved the metals over UBC at the optimum pH.

*3.3. Effect of initial Fe(II).*

The initial Fe(II) concentration was varied as 0, 5, 10, 15, 20, 25, and 30g/L while other parameters kept constant as mentioned and the result of metal leaching from the SC sample using both ABC and UBC is shown in Fig.3. The leaching rate increased with the increase of Fe(II) concentration from 0 to 10g/L, and it decreased upon further increase of Fe(II) concentration. However, the ABC showed better results over the UBC in all range of the Fe(II) concentration for three metals such as Ni, V, and Mo.

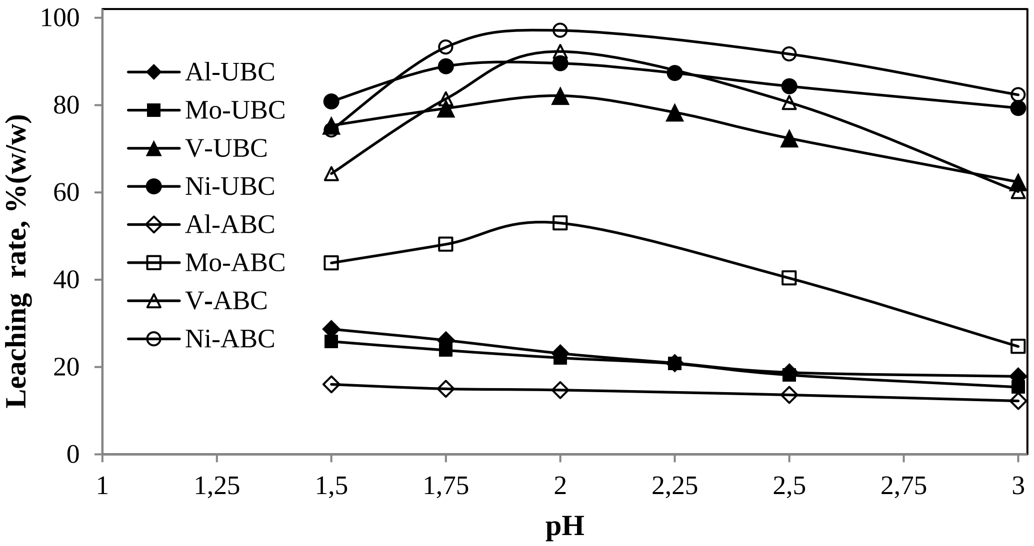


**Figure 2.** Effects of pH on the leaching of SC sample by both UBC and ABC. Conditions:Fe(II)-10g/L,pulp density-10%(w/v),particle size-106+45µm,temperature-35ºC and 180rpm.

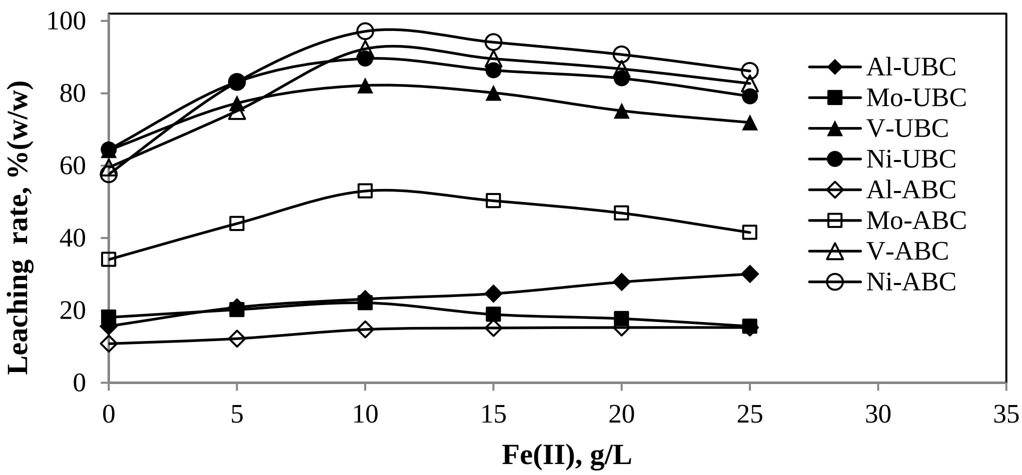


**Figure 3.** Effects of Fe(II) concentration on the dissolution of Ni,V,Mo, and Al from the SC sample using both UBC and ABC. Conditions:pulp density-10%(w/v),pH-2.0,particle size-106+45µm,temperature-35ºC and 180rpm.

*3.4. Effect of pulp density.*

The pulp density was varied from 5 to 30%(w/v) while other parameters kept constant as mentioned and the result of metal leaching from the SC sample using both ABC and UBC is shown in Fig.4. The leaching rate constantly decreased with the increase of pulp density for both ABC and UBC. At the lower pulp density, the solid sample gets adequate chemical reaction environment; however, at the higher pulp density, the solid sample was much more for the reaction environment. Further, when the number of solid particles increased, the competitive solid particles for the attacking reagent hindered the chemical reactions[44]. If the pulp density of 5%(w/v) is considered, the leaching rate of Ni and V increased by more than 10% with the application of the bacterial adaptation process.

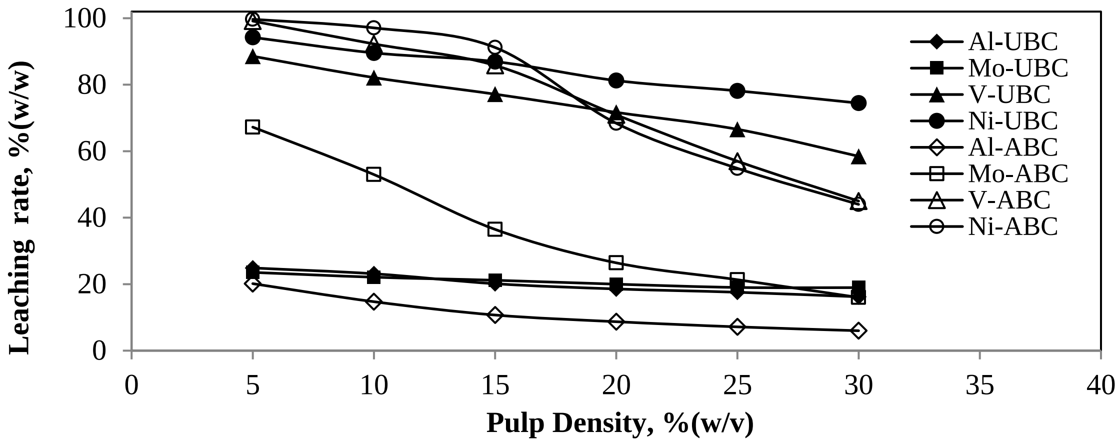


**Figure 4.** The effects of pulp density on the dissolution of Ni, V, Mo, and Al from the SC sample using both UBC and ABC. Conditions:Fe(II)-10g/L,pH-2.0,particle size -106+45μm, temperature-35°C and 180rpm.

*3.5. Effect of particle size.*

The particle size range of the SC sample was -45, -106+45, and -212+106μm while other parameters kept constant, and the result of metal leaching from the SC sample using both ABC and UBC is shown in Fig 5. The leaching rate of all four metals decreased with the increase of particle size for both the bacterial culture; however, the decrease rate was observed to be insignificant. Since our main aim to evaluate the improvement of the leaching rate due to bacterial adaptation, it was found to be beneficial for the wide range of particle size used in the leaching experiments.

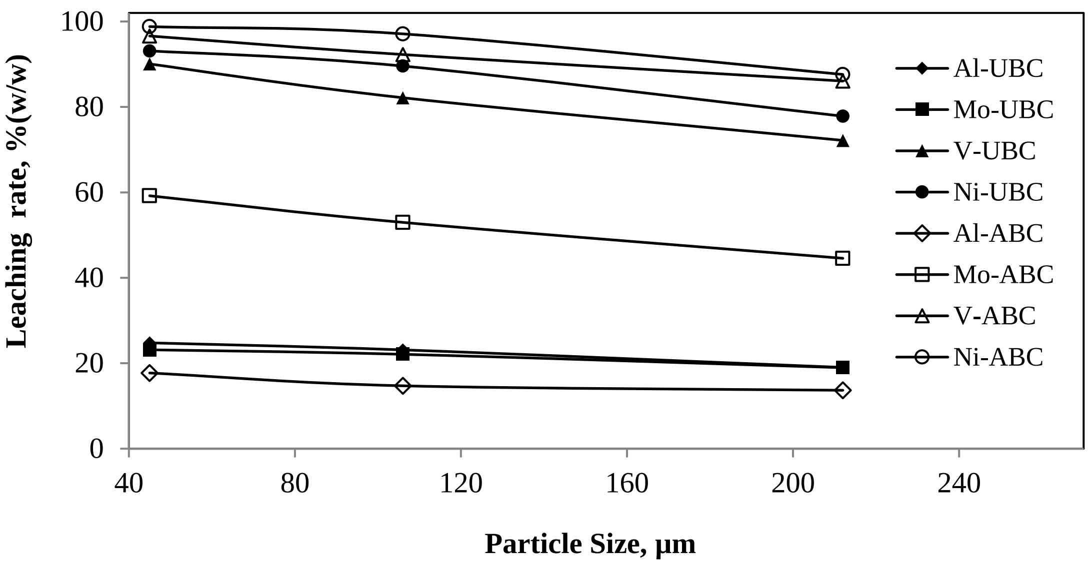


**Figure 5.** The effects of particle size on the dissolution of Ni,V,Mo, and Al from the SC sample using both UBC and ABC. Conditions:Fe(II)-10g/L,pulp density-10%(w/v),pH-2.0,temperature-35°C and 180rpm.

*3.6. Effect of temperature.*

The temperature was varied from 10 to 35°C while other parameters kept constant for both ABC and UBC. The result of the leaching rate of metals from the SC sample using both ABC and UBC is shown in Fig.6. The leaching rate increased with the increase of temperature from 10 to 35°C, and thereafter it decreased. At temperature 35°C, it can be observed that the ABC leached Ni, V, and Mo efficiently in comparison to the UBC due to the higher activity of the adapted bacteria culture. From the temperature variation study, it can be observed that the leaching reactions were endothermic in nature.

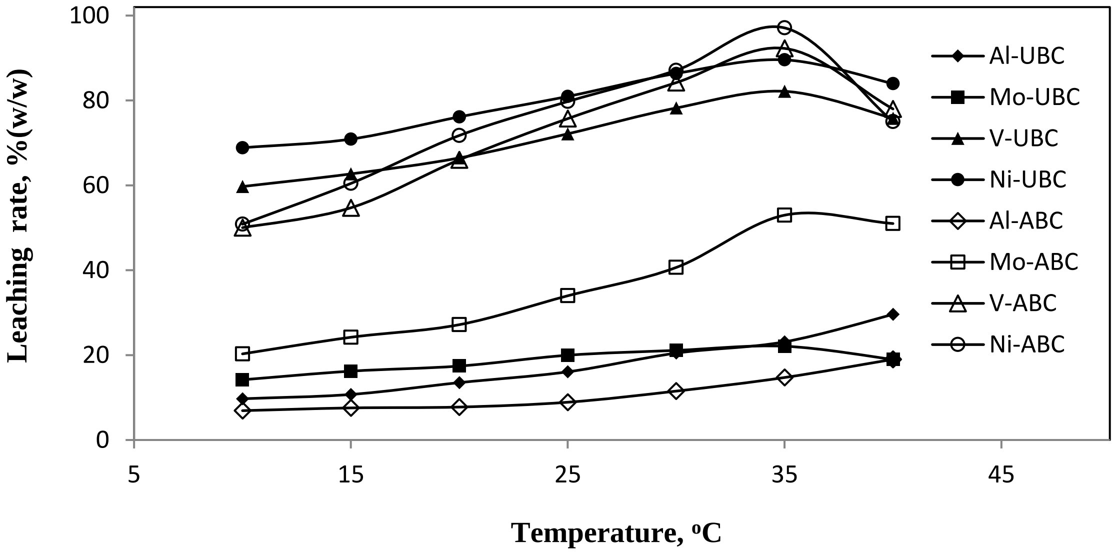


**Figure 6.** The effects of temperature on the dissolution of Ni, V, Mo, and Al from the SC sample using both UBC and ABC. Conditions:Fe(II)-10g/L,pulp density-10%(w/v),pH-2.0, particle size-106+45µm and 180rpm.

*3.7. Pseudo rate order.*

The leaching reactions were observed to be dependent on different leaching parameters. So the rate equation with respect to the parameter can be written as the equation given in Eq.1.

$$\text{Rate} \propto \text{Parameter}^{\text{n}} \qquad (1)$$

where n=dependence factor of the parameter or the order of the leaching reaction with respect to the parameter. The Eq.1 can be written as the equation given in Eq.2 by using a proportionality constant.

$$\text{Rate} = \text{k} \times \text{Parameter}^{\text{n}} \qquad (2)$$

where k=proportionality constant. If all parameters are used in the Eq.2, it can be written as the equation given in Eq.3.

$$Rate = k \times [pH]^{n_1} \times [PD]^{n_2} \times [Fe(II)]^{n_3} \times [PS]^{n_4} \times [Temp]^{n_5} \qquad (3)$$

where, $n_1$, $n_2$, $n_3$, $n_4$, and $n_5$ are the pseudo order of the leaching reactions with respect to the parameters such as pH, PD (pulp density), Fe(II) concentration, PS (particle size), and temperature, respectively. The logarithm form of the Eq.3 can be expressed as the equation given in Eq.4.

$$\log\,[\text{Rate}] = \log[\text{k}] + \text{n}_1 \log[\text{pH}] + \text{n}_2 \log[\text{PD}] + \text{n}_2 \log[\text{Fe(II)}] + \text{n}_4 \log[\text{PS}] + \text{n}_5 \log\,[\text{Temp}] \qquad (4)$$

Since the leaching rate of Ni and V were observed to be significant, the pseudo rate order of five parameters for them was evaluated from the slopes of the logarithmic graph of log(Rate) plotted versus log(parameters) for both ABC and UBC. For a particular parameter other parameters were kept constant in order to evaluate the pseudo rate order with respect to that parameter (e.g., for the determination pseudo rate order with respect to pH, the other parameter, such as PD, Fe(II), PS and temperature were kept constant). The values of the pseudo rate order of Ni and V for different parameters and bacterial cultures are given in Table 1. From the pseudo rate order values, it can be concluded that the ABC categorically improved the leaching rate of Ni and V for all parameters over the UBC.

**Table 1.** Values of pseudo rate order of Ni and V for both ABC and UBC.

| Pseudo rate order | Ni | | V | |
|---|---|---|---|---|
| | UBC | ABC | UBC | ABC |
| $n_1$ | -0.3 | -0.4 | -0.7 | -1.0 |
| $n_2$ | -0.218 | -1.041 | -0.384 | -0.921 |
| $n_3$ | -0.126 | -0.126 | -0.147 | -0.114 |
| $n_4$ | -0.113 | -0.075 | -0.141 | -0.073 |
| $n_5$ | 0.221 | 0.513 | 0.261 | 0.511 |

## 4. Conclusions

The isolated iron-oxidizing bacteria showed the ability of Ni, V, Mo, and Al dissolution capacity from the SC sample. The leaching rate of Ni, V, and Mo was further increased by 10% due to the bacterial adaptation process. However the leaching rate of Mo and Al was found to be very slow compared to that of Ni and V. The slow Mo leaching was due to the mutual effect of the refractoriness of $MoS_2$, lower solubility of Mo in the mild acidic medium, and the impervious sulfur layer over the Mo-matrix. The lower leaching rate of Al was due to the refractoriness of the $Al_2O_3$ matrix present in the SC sample. The equilibrium time of the leaching reaction was reduced from 240 to the only 40hr due to the bacterial adaptation process. Since the equilibrium time of bioleaching is its major drawback, this adaptation process was found to be fruitful for the higher scale implementation of the bioleaching process in order to extract the metal values from the SC sample. The improvement of leaching was confirmed by variation of five leaching parameters such as pH, pulp density, initial Fe(II) concentration, the particle size of the SC sample, and temperature. The pseudo rate orders of all parameters were found to be significant for the adaptation process. In the final conclusion, the SC sample can be utilized by the bioleaching process in order to recover different metal values present in it; however, a simple adaptation process is required for the development of an efficient bioleaching process.

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## Conflicts of Interest

The authors declare no conflict of interest.

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