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Bio-separation of heavy metals from spent catalysts using *Acidithiobacillus thiooxidans*

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Abstract: This study attempts to determine some physical and chemical properties of spent catalysts and study the application of microorganisms in heavy metals extraction through spent catalysts utilization. The study focuses on bioleaching of a spent refinery catalyst (Naphtha Hydrotreating Unit). Bioleaching in this study was accomplished using *Acidithiobacillus thiooxidans* in the presence of some spent catalyst and under optimized conditions in which temperature was at 32°C, pH = 2.5, catalyst size was 60 µm, pulp density 20 g.L and sulfur content was 10 g.L, assuming it was possible to measure the highest concentrations of metals extracted using spent catalysts. The output of bioleaching process was calculated for Ni and V using *Acidithiobacillus thiooxidans* in a given time under different conditions such as pulp density, particle size, mixer spinning rate, pH, temperature, and metal inoculation percent ,using *A. thiooxidans* the highest values of metals extracted were Al (2.4%); Co (83%), Mo (95%) and Ni (16%) under optimized conditions of pH=2/5, T=32°C, particle size=150µm, pulp density=20 g/L and sulfur content=10 g/L.

Key words: Bioleaching; Heavy metals; Spent catalysts; Bacteria

1. Introduction

Catalyzing processes are an integral part of petroleum, gas, chemical and petrochemical operations in developing and developed countries as well. Catalysts accelerate and direct chemical reaction in a way to obtain desired output and thus have attracted massive interest from researchers and industrial operatives (Gholami et al., 2011).

2. Materials and methodology

Spent catalysts used in this study were acquired thanks to Abadan refinery with Alumina as their base. Spent catalyst is in grey and powdered form with an Extrudite form 2mm in diameter. Its surface area is 210 ± 10/34 (m2/g). an old catalyst in Estrudite form containing substantial amount of coke was heated in a furnace for 4 hours at 700c for pretreatment, Then crushed and graded. Ball mills were used for crushing phase. Particles were graded at 35, 60,120 and 230.

This study has used acid-friendly chomolitotrophic acidithiobacillus thiooxidans. The potential of the bacteria in oxidizing sulfur has resulted in its extensive application in ferrous sulfides bioleaching. Research show that microbial oxidization of sulfur follows the direct contact of the bacteria and the sulfur. The bacteria can turn sulfur into oxide sulfate to gain energy. It was cultured in 9k environment through inoculation of 10% of pure bacteria genus (Mishra et al., 2007).

3. Instruments

The composition of fresh, spent and old catalysts are determined using various methods: Chemical analysis, scanning electron microscope analysis, x-ray energy scatterer, x-ray diffraction spectrometry, metal analysis using optical emission spectroscopy of inductively coupled plasma (ICP-OES, Perkin-Elmer, Optima 3000V) based on following wavelength on nm scale: nickel (231/604), vanadium (292/402).Fresh, spent and bioleached catalysts were quantitatively analyzed using scanning electron microscopes, SEM-EDX x-ray energy scatterer (JEOL JSM-5600LV). Ph was measured using a pH meter (Metrohm, model: 827 pH Lab, Switzerland). The accuracy of pH and Eh measurements were ±0/003 and ±10 mV respectively. Sulfate was measured to determine sulfur consumption rate by the bacterium.

3. Bacteria-mediated Bioleaching

Bioleaching was conducted in a 500 ml Erlain mayer flask containing 200 ml culture batches and in the presence of a spent catalyst. Inoculation of bacteria (1×10^{7} in every ml) was done for every flask and culturing was conducted at 30°C and at a spinning rate of 150× min. bacteria were adapted to nickel and vanadium through addition of 20 mg/l in every stage. To compensate water lost due to

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evaporation, deionized water was used. Effective parameters on microorganisms' growth such as pH, temperature, catalyst size, pulp density, mixer spinning and sulfuric content were optimized. Samples were taken at known intervals. Sulfate density, cellular mass density, bioleached metal and bacteria- mediated metal outputs were measured in the end.

Table 1: The specialized culture of acidithiobacillus thiooxidans (Beolchini et al., 2011)

Material	mg/1000ml
$(NH_4)_2SO_4$	3
$MgSO_4.7H_2O$	0.5
K_2HPO_4	0.5
KCl	0.1
S	10

4. Results and Discussion

4.1. Properties of Refinery Spent Catalysts

The composition of fresh, spent and old catalysts are determined using various methods: Chemical analysis, scanning electron microscope analysis, x-ray energy scatterer, x-ray diffraction spectrometry (Amiri et al., 2011).

Table 2 shows the results of XRF analysis. Catalysts possess oxidizing properties and contain elements such as aluminum, silicone, iron and molybdenum. These elements were analyzed using ICPOES. As the table shows, the results clearly indicate that catalysts contain aluminum, cobalt, nickel and molybdenum. Figure 1 displays the micro image of the spent catalyst being bioleached by acidithiobacillus thiooxidans taken by a scanning electron microscope (1000 times magnified). Some fine broken particles may be observed in the image, presumably due to bioleaching.

4.2. Data Analysis

Data were studied to help biological extraction of Nickel and Vanadium. Figures 2.4 and 3.4 show pH and Eh changes of acidithiobacillus thiooxidans in the presence of the spent catalyst. After 5 days, Ph rose to 3.04 from 2.5, while Eh reached as high as 380 Mv. The rise of Eh shows the high rate of sulfur consumption by bacteria and is thus considered a acidithiobacillus thiooxidans' response.

Table 2: Composition of spent catalyst as shown in XRF analysis

Element	Weight percent
Al_2O_3	54.9
SiO_2	31.41
Fe_2O_3	2.18
MoO_3	9.49
Nio	0.26
V_2O_5	1.15
As_2O_3	0.10

Table 3: Analysis of chemical elements of the spent catalyst by ICP-OES

Element	Unit	ICP-OES
Al	%	39/40
As	g/t	37/19
Ca	%	0/02
Co	%	2/4
Cr	g/t	145/15
Cu	g/t	79/80
Fe	%	0/48
Hf	g/t	117/94
K	%	< 0/1
V	%	0/3
P	%	< 0/1
S	%	0/50
Si	%	0/15
Ti	%	< 0/1
Mg	%	< 0/1
Ni	%	0/1
Mo	%	8
Na	%	< 0/2
Nb	g/t	361/97
Zn	g/t	99/79
Zr	g/t	37/19

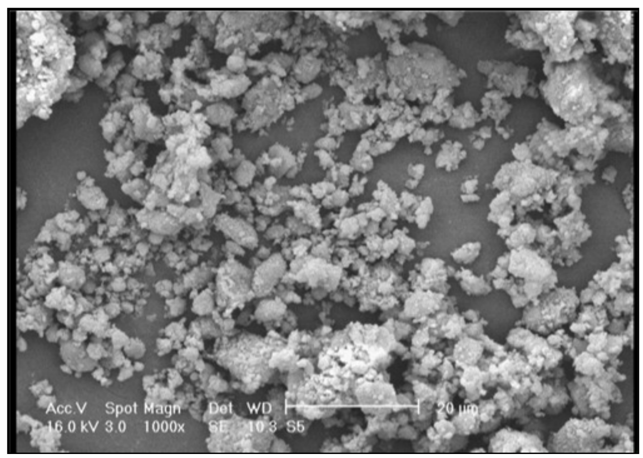

Fig. 1: The micro image of the spent catalyst bioleached by acidithiobacillus thiooxidans, taken by a scanning electron microscope (1000 times magnified)

As Fig. 4 shows, extraction output for nickel and vanadium in bacteria-mediated bioleaching (acidithiobacillus thiooxidans) was an average of 91% and 63% respectively. Production of sulfuric acid due to the bacterial oxidization is expected to rise as the surface area of sulfur expands. The results indicate that bioleached vanadium was to some extent less than untapped vanadium. This might be due to slow consumption of bacterial-produced acid by alumina substarate which triggers the sedimentation of aluminum and nickel as non-soluble oxidizing phases (Shahrabi Farahani, 2011). The toxicity of metals versus acidithiobacillus thiooxidans in spent catalyst is Ni>V.

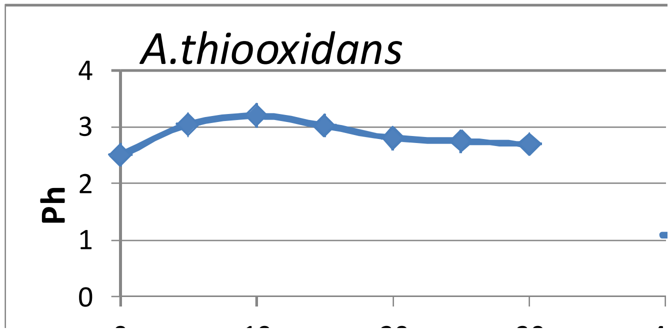

Fig. 2: pH changes during bacteria-mediated bioleaching of spent catalyst under optimal conditions

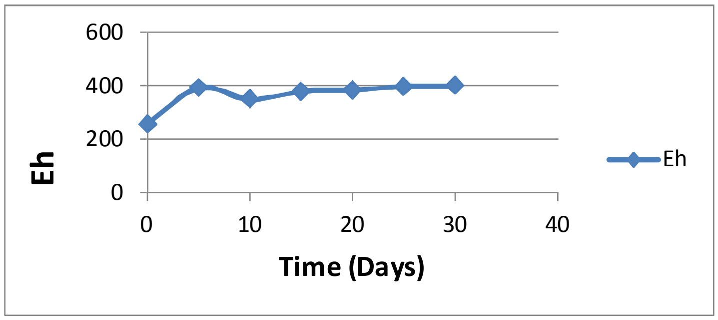

Fig. 3: Eh changes during bacteria-mediated bioleaching of spent catalyst under optimal conditions

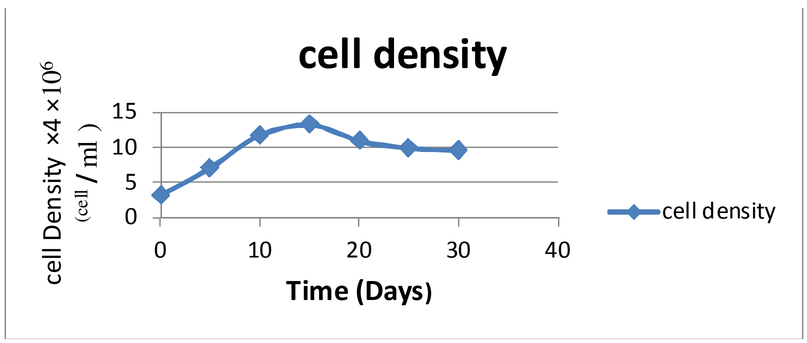

Fig. 4: changes in bacterial population during bacteria-mediated bioleaching of spent catalyst under optimal conditions

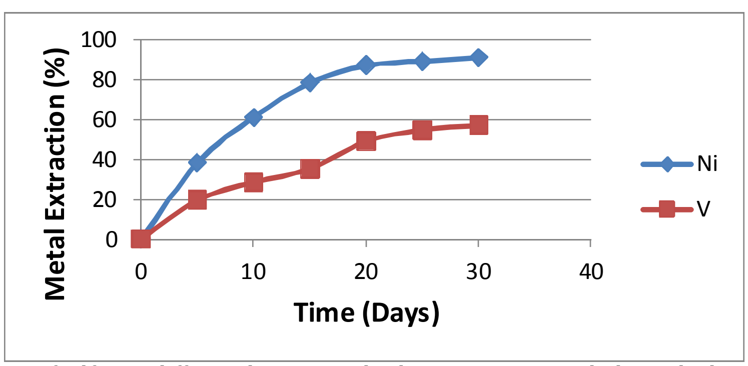

Fig. 5: The changes in ions of sulfate in different densities and in known time intervals during bioleaching. Microbial activity can be proved through comparison of densities of sulfate ions

Conclusion

Sedimentation of metal pollutants such as nickel and vanadium on catalysts results to a drop in their activities. Our findings show that a single-phase bacterial-mediated (acidithiobacillus thiooxidans) bioleaching might be helpful in bioleaching of heavy metals from refinery spent catalysts (type $Al_2o_3/Si0_2$). Moreover, recent bioleaching processes are confirmatory tests of the promising technology of biological detoxication of spent catalysts. Therefore, it can be considered as a viable option for pretreatment of spent catalysts ahead of landfilling. This study found out that in the presence of the spent catalyst and under optimized conditions, bacteria faced no major challenge for its growth. Under optimized conditions, the highest extraction rates from spent catalysts (using acidithiobacillus thiooxidans) in 30 days at a pH of 2.5 to 3.5 were 89% and 63%. The results showed that for bioleaching of the Al_20_3 /Sio_2 refinery spent catalyst, acidithiobacillus thiooxidans utilization is useful and appropriate as the process is done at a higher pH and also a more suitable option for metals with a alumina substrate basis. The higher the density of the local acid, the faster the solution of sedimentated metals on the surface of catalysts. More research are recommended on toxicity of metals for these bacteria to find out whether they are able to stand higher pulp densities of other spent catalysts.

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