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Scrutiny of the Acidithiobacillus Thiooxidan in leaching metals from the effete catalysts

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Abstract: This study aims at determining some physical and chemical behaviors of the effete catalysts and surveying the field of the application of microorganisms in the extraction of heavy metals from these effete catalysts .In the present study, the sampled bioleaching of the effete catalyst in the Unit of gasoline filtration is surveyed. The main constituent elements of this catalyst include Co and Mo with Alumina basis; and, the major constituent elements include Ni, Fe, S, Ni, Ar, and Pb to a small extent. To calculate the optimum levels, using the Surface Response Method, several different variables were used synchronously. Also, the bacterium of Acidithiobacillus Thiooxidan was employed to bestir the metals of Al, Co, Mo and Ni in the dangerous effete catalysts. The metallic ions of the bacterial species were determined by using an inductive coupled light-plasma emitting spectrometer. The produced acids were assayed using high-leveled liquid chromatography. Also, the efficiency of the bioleaching process considering conditions, such as Palp density, particle size, PH value, the temperature, the speed rotation of the stirrer and the Inoculation percentage was optimized by using the Surface Response Method. The recovery efficiency values of these metals using the bioleaching with the help of Acidithiobacillus Thiooxidan were measured to be4.2%, 83%, 95%, and 16 %, respectively. The results from the present study indicate that in the bioleaching of the effete refinery catalyst of type Co- Mo-Alumina, it is better to use Acidithiobacillus Thiooxidan, due to the fact that the process happens in a higher PH value; also, this is a better option for the metals that are surrounded by substrate Alumina. Although, further studier are required to survey the toxic levels of the metals against the bacteria enabled to bear the higher Palp densities in the effete catalysts.

Key words: Acidithiobacillus Thiooxidan, Leaching; Metals; The effete catalysts

1. Introduction

The Bioleaching can be defined as the reactions between the metals and microorganisms whereby the metals are dissolved; while, it depends on the capability of the microorganisms to transform into solid compounds that results in the production of soluble and extractable elements which are recoverable (Bredberg et al., 2004).

There are 3 types of microorganisms which are used in the bioleaching processes: Autotroph bacteria, Heterotroph bacteria and the fungi. Acidithiobacillus Autotroph is employed because of the fact that no total organic carbon is needed for the growth of the bacterium. In the other hand, heterotroph bacterium and the fungi are capable of being used in higher PH values, eg.in alkaline materials and Ascidia consumers (Wang et al., 2009).

Catalytic processes are among the most important and crucial operations in the industries of gas, Petrochemicals, and chemicals in the developed or developing countries which use “catalysts” to produce different fuels and a large range of middle or final products necessary for the modern societies with an increasing daily importance. The catalysts direct and increase the speed of the chemical reactions to produce the desired products. It has been more than a century that catalysts have attracted the center of the attraction of researchers and industry owners (Mishra et al., 2007). In most of the chemical industries the use of large quantities of the solid catalysts is popular. These catalysts need to be replaced after 2 or 3 years from exploiting. For example, in the fluid catalytic cracking (FCC), which is the main secondary transform in the petroleum refinement, nearly an amount of 4* 10^{8} Kgs of the effete catalysts are produced worldwide (Gadd, 1993). In 1993, the worldwide production of the effete catalysts from hydro processing was estimated to be about 5*10^{7}Kg annually (Mohapatra et al., 2009).

While hydro processing operation of the raw material, the catalysts are enriched with S, Van, and coke; while, at the same time Ni, Co, and Mo are transformed into their homologous sulfides. So, the porosity and activity of the catalysts is reduced such that we will be obliged to replace the catalyst in the reactor (Zhao et al., 2008).

Also, the effete catalysts are subjected to metal extraction by the different leaching processes. In these processes, the leached and recovered metals are capable of retrieving the cycle; and, they can be re used as raw material in the metal composing industries; while, the residuals can be safely stored

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or used in other composing materials (Zhao et al., 2008).

The application of bioleaching in the refinement of waste solid materials is more economical and more pro-ecological than the current technologies of the recovery of elements. The applicability of microorganisms has also been reported in the bioleaching of different metals from the residual and settled materials of ores, and in the refinement waste materials. This study aims at determining some physical and chemical behaviors of the effete catalysts in the hydrogen refinement of naphtha, and, also it aims at evaluating the effect of the application of heterotrophic fungi, such as Aspergillus Niger, Penicillium simplicissimum, and Cumulitotroph or Acidithiobacillus ferroxidans, and Acidithio bacillus thiooxidans in the leaching of heavy metals from the effete catalysts, and in making a comparison between the leaching efficiency of these four micro- organisms. Further, the optimized conditions of the extraction of some metals including Al, Co, Mo, and Ni are surveyed.

2. The study procedure

The Cumulito Autotroph bacterium or Acidithiobacillus thiooxidans was employed in this study. The case of the bacterium was chosen a pure Acidithiobacillus thioxidan, isolated from the copper mine sites of Sarcheshmeh and Pb and Zn mine sites of Koushk in Bafgh, Yazd. This bacterium was presented by research center of the Bioechological and Biochemistry studies of Sharif University. The fresh and effete catalysts used in this project are gifts provided by the petroleum refinery of Abadan, Iran. The catalyst bases involve Alumina, and usually used in the unit of hydrogen refinement of naphtha in the processes of petroleum refinement; and, since the rate of Co, and Mo available in the catalyst is high, it is also called "Co Mo". In the early step of the whole-staged bioleaching process, the operation was performed in a 500 ml Erlen Mire flask containing 100 ml of the implant bed together with the effete catalyst with 1% proportion of palp density of the weight to the volume. The body – the body of the bacterium with the population of x1071 cells per 1 milliliter inoculation up to 10% was carried out in every Erlen mire flask; and, the bacteria were implanted inside the stirrer with the temperature of 30°c, and the stirrer with 150 rpm. The compatibility operation of the bacteria against metals including Al, Co, Ni, and Mo in the concentrations from 100 to 800 mgs was performed with the adage of 100 mgs/l in every step in order that the bacterium adopt to the effete catalyst environment.

3. Analytical methods

The sample analysis with respect to the concentration of available metals before and after the bioleaching process was performed by Iran Institute of Advanced Researches on the Production of Minerals.

3.1. Metal analyses

Metal analyses were performed with the inductive coupled light – plasma emitting spectrometer (ICP-OES) (type ICP-OES, Perkin-Elmer, optima 3000V) with the following nanometer wavelengths:

Al (308/215), Ni (231/604), Mo (202/03), Zn (213/856), Cu (324/754). Also, Merek's IV standard multiplied element ICP was performed in 1000mg/l, for the preparation of calibrated standards after dilution with1 molar Nitric acid. The resulted samples from bioleaching before analysis were infiltrated by using a filter with 0.45 micrometer porosity (Whatman Autovials®).

To measure the concentrations of the cell body, in this study, the direct method of counting the cells by using the special counting chamber (Thoma Chamber) was employed. In this regard, some infiltrated sample was chosen by pipet and then it was put on Thoma chamber (Newbar).

4. The statistical procedure

Using the statistical software model (Design-Expert 7.1.4 State-Ease Inc., Minneapolis, MN), a central composite design with 5 levels was employed to evaluate the importance of the experimental results obtained from the microorganisms.

5. The method of measuring the concentration of the cell body

In the studies on this bacterium, different methods are adopted to measure the bacteria population. These methods are:

- The direct counting by using the special counting chamber
- The measurement of the protein concentrations
- The spectrophotometry method and the calculation of light density in the wave lengths of 50 nanometers
- The measurement of total organic carbon (TOC)

In the present study, the direct cell counting method by using Thoma chamber (with 0.1 mm in-depth and the surface area of 0.00025 mm²) with 1000 zooming magnification.

6. The findings

6.1. The study of bioleaching by using the microorganism of Thiobacillus Thiooxidans

Before implementing the bioleaching process, a serene implant bedroom of Thiobacillus Thiooxidans was provided until it reached the equilibrium phase. In another phase, this implant bedroom was separately adopted to the available effete catalysts which contained heavy metals such that, in every phase, with the gradual adage 100 mg/l of Palp density the microorganism adopted to an environment containing 800mg/l of the catalysts.

Then, this adopted implant bedroom was used in the future tests. With the help of this optimized bioleaching process by using these microorganisms, 32 tests were run by benefitting from the software of the surface response method, mentioned earlier, and by considering the operative limitations of each one of the determined parameters. The obtained results are discussed further on. Then, a series of confirming tests were run to evaluate the optimizing tests which results are shown at the end. Not only this study aims to survey the reciprocal effects of the study parameters, but also it aims at finding the best model that is indicative of the utmost efficiency of bioleaching the assumed metals by making use of this microorganism.

The obtained results from these 32 phases of tests on the mentioned microorganisms were statistically analyzed so that the effect of each parameter could be studied.

6.2. The bioleaching model of the effete catalyst Acidithiobacillus Thiooxidans

In the bioleaching of the effete catalyst by Acidithiobacillus Thiooxidans, it can be observed from the models of the Al, and Mo efficiency that there is a negative curve in the linear of the temperature. The negative curve is also observable in the linear Palp densities. The direct effect of PH values, and S rates were significant in none of the cases. The negative linear or nonlinear contrast of PH values, together with S rate or the catalyst quantity, or temperature is observable for Al. this negative contrast, also, was present for Co with Palp density and temperature. The negative contrast between PH values and Palp density and between PH values and the catalyst size is obtained from the model of Mo efficiency.

Table 1: The proper models obtained from the bioleaching of the effete catalysts by using Acidithiobacillus Thiooxidans in accordance with the optimizations of the process by using the software of the Surface Response Method

The bioleaching of the effete catalysts by Acidithiobacillus Thiooxidans
Al Efficiency (%)= $0/65 - 0/11B + 0/93C - 0/28D - 0/12AE + 0/39C^2 - 0/98A^2C + 0/24A^2E - 0/25AB^2$
Co Efficiency (%) = $47/80 + 5/35C - 5/47D - 6/31AD - 7/72CD - 5/34CE + 10/56DE + 3/57C^2 - 6/48A^2B + 6/20A^2E - 4/57AB^2$
Mo Efficiency (%) = $45/74 - 6/85B + 13/77C - 7/35D - 9/57AD - 7/01BC - 5/48CD + 9/04DE + 4/80C^2 - 12/09A^2C + 6/47B^2E$
Ni Efficiency (%)= $6/66 - 0/72A + 1/96C - 3/52D - 1/24AB - 1/73AD - 1/54BC - 1/19CD + 1/35CE + 0/92D^2 - 2/15A^2C + 2/53A^2D + 1/70B^2E$

A: PH, B: temperature, C: size of the particles, D: Palp Density, and E: S

7. The variation analysis

The fitness of the adopted model was determined by the calculation of the coefficients of R^2 and the variation analysis. The results of variation analysis of the decreased 3rd staged models for each microorganism are also represented in table 4-4. The model degree of freedom equals to the number of model terms in the crossing sections minus one. The residual degree of freedom is the adjusted total degree of freedom minus the degree of freedom of the model.

Table 2: The variation analysis of the 3rd staged decreased model in the bioleaching process by Acidithiobacillus Thiooxidans

		Sum of squares	d.f.	Mean square	F-value	p-value	Lack of fit
Al recovery	Model Residuals	16/02 0/92	8 23	2 0/04	50/27	<0/0001	0/5125
Co recovery	Model Residuals	7243/44 1343/16	10 21	724/34 63/96	11/32	<0/0001	0/1877
Mo recovery	Model Residuals	9385/81 1163/76	10 21	938/58 55/42	16/94	<0/0001	0/4091
Ni recovery	Model Residuals	391/77 28/20	12 19	32/65 1/48	21/99	<0/0001	0/1668

In the control tests lacking the bacterium observation of a trend of PH value similar to the leaching test indicated the oxidation of the available metallic sulfides via the dissolved oxygen from the air. In this control system, the efficiency of leaching metals under optimized bioleaching conditions after 30 days was lesser (Al 1.37%, Co 39.17%, Mo 53.13%, and Ni 7.19%). In general, the extraction of Mo, and Co were in good accordance with the bacterium development whereby Sulfuric Acid was a by- product of the process. The toxic order of the metals against Acidithiobacillus thiooxidans in a mixture of these metals in the effete catalyst is like Al>Ni>Co>Mo.

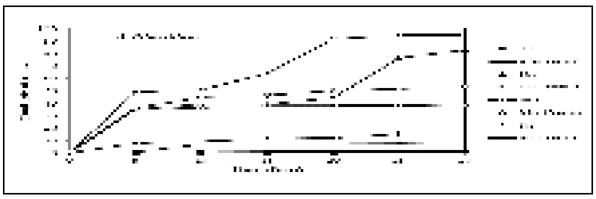

Fig. 1: The efficiency of the extracted metals from the effete catalysts by using Acidithobacillus thooxidans under optimized conditions during 30 days.

8. The comparison of bioleaching efficiencies between Acidihiobacillus Ferro-oxidants and Acidithiobacillus thiooxidans

In each of these microorganisms, shooting heavy metals from the effete catalysts is different. Acidithiobacillus thiooxidans is only capable of oxidizing element S into Sulfuric Acid; so the extraction of metals is carried out by aside leaching. Meanwhile, according to the previous studies, Acidithiobacillus Ferro-oxidants, oxidizing the Ferro ions, is capable of the metals extraction via direct and indirect mechanisms. Acidithiobacillus Thiooxidans does not much influence the leaching of Ni, and Al; while as, Acidithiobacillus Ferro-oxidants is much more capable of influencing the bio extraction of Ni, and Al. the capability of leaching Co, and Mo was almost the same for these two bacetria.so, generally the Acidithiobaciluss Ferro-oxidants showed greater efficiency in the metal leaching in comparison to Acidithiobacillus Thiooxidans in the bioleaching of the effete catalysts. Of course, the metals efficiencies in both cases did not show a similar trend. During the first 5 days, Co and Ni were rapidly extracted by Acidithiobacillus Ferro-oxidants and in the final 20 days of the process they were remained almost stable; while as, by Acidithiobacillus Thiooxidans the metals leaching was slowly progressing, which Acidy leaching, the main factor was the metal dissolve ability; but, as time passed by, the bacterium adopted to the higher concentrations of the metals, resulting in the sulfur oxidization and every other surface metallic sulfide. Also, it was obvious that the metal efficiency in the presence of each of the organisms was significantly higher than the leaching lacking the bacterium (control group).

9. Discussion and the results

9.1. The total results of bioleaching by the bacteria

The stain sediments of metals such as Al, Co, Mo and Ni on the catalysts lead to the decreased activity of the catalysts. Our findings showed that in the case of Acidithiobacillus thiooxidans it could be notified that the whole staged bioleaching could be influential in the extraction of the mentioned heavy metals from the refinery effete catalysts. In practice, this process could be run as a pretreatment of the effete catalyst before its burial under the soil.

The surveys in the present study showed that the bacterium in the presence of the effete catalyst under optimized conditions well continued its development. Also, the bioleaching tests showed higher efficiencies of extraction in comparison to the tests (lacking the bacterium). Under optimized conditions, the highest efficiency of metals from the effete catalysts by using ACithiobacillus thiooxidans with the adage of S, the extracted amounts of Al, Co, Mo and Ni during 30 days in the PH of 3.9-4.4 were 2% , 83%, 95%, 16%, respectively. The results of the present study showed that in the bioleaching of the refinery effete catalyst it is better to use the type of Co-Mo Alumina rather than Acidithiobacillus thiooxidans; because, the process is run in a higher PH, and because it could be a better choice for the metals surrounding the substrate Alumina. Of course, further studied are required to survey the toxicity of the metals against the bacterium to bear the higher Palp densities of the effete catalysts.

The bioleaching tests in higher Palp densities are to be surveyed and scrutinized so that the effect of Palp densities on the efficiencies of metals extraction is determined. Tests are necessary by using the effete implant bedroom; because of the fact the effete implant bedroom is more prominent due to easier access and the shortened time of the process. Furthermore, because of the reason that a development less chemical process is bio-Cu, it shows more adaptation of optimality in comparison to a bioleaching process.

It is also required to scrutinize the synchronous whole staged, 2 staged and chemical bioleaching to obtain the proper efficiency by comparing these methods.

Also, the synchronous adoption of 2 or more microorganisms in surveying the usability of bioleaching can be effective. Surveying the efficiency of eliminating low metals, the effective parameters of bioleaching such as the substrate size, the feed type, the temperature, PH value, etc. are adjusted; also, the development of more effective microorganisms are determined.

Even more, the proper adaptation of microorganisms to the environment in the case of using higher Palp densities in the system is a requirement. In the case of the studied bacterium with respect to bearing the higher Aside environment it is suggested to use adjacent bio-reactors of the bacterium in the industrial applications.

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