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Removal Of Iron Impurities Of Clay Materials Using Aspergillus Niger

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Abstract:

The use of microorganisms for bio-leaching operations for the extraction of specific metals from their ores is known for very long time and is found to be economical and environmental friendly. Literature survey revealed that a variety metals which, includes copper, cobalt, gold, etc., were attempted to extract from their ores using various strains of microorganisms. The micro-organisms which, produces variety of organic acids, which are likely to act as a chelating agent, for removal of metal from respected ores. This technique facilitates in efficient extraction of metals by lowering operational cost and energy requirement. The present study evaluates, how to help the mineral processeser in eliminating the undesirable metal ion impurities. This paper presents a preliminary study of removal of iron through Bio-leaching treatments of clay material using organic acids derived from A.niger.

In this study we optimized the leaching ability of organic acids at particular concentration and also evaluated the various parameters that influence the A.niger in the production of organic acid, which includes citric acid and oxalic acids.

1. INTRODUCTION

Bio leaching of clay materials containing iron metal sulfides or oxides can be accomplished by using microorganisms. Earlier reports revealed that more than 11 species [1] of prokaryotic microorganisms found to be performing the solubilization of metal sulfides or oxides for effective removal of metal from clay materials. It is understood that the dissolution (bio)chemistry of metal sulfides or oxides follows only two pathways, which are determined by the acid-solubility of the sulfides: the thiosulfate and the polysulfide pathway, where as the oxides follows sulfate pathway. The prokaryotics can affect this sulfide dissolution by "contact" and "non-contact" mechanisms. The non-contact mechanism assumes that the prokayotes oxidize only dissolved iron(II) ions to iron(III) ions. The latter can then attack metal sulfides or oxides and be reduced to iron(II) ions. The contact mechanism requires attachment of Mo’s to the sulfide or oxide surface of the metal. The primary mechanism for attachment to pyrite is electrostatic in nature. The resulting positive charge allows attachment to the negatively charged pyrite. Thus, the first function of complexed iron(III) ions in the contact mechanism is mediation of cell attachment, while their second function is oxidative dissolution of the metal sulfide or oxide, similar to the role of free iron(III) ions in the non-contact mechanism. In both cases, the electrons extracted from the metal sulfide or oxide reduce molecular oxygen via a complex redox chain located below the outer membrane, the periplasmic space, and the cytoplasmic membrane of leaching prokaryote. The dominance of either MO’s in mesophilic leaching habitats is highly likely to result from differences in their biochemical iron (II) oxidation pathways, especially the involvement of rusticyanin. In view of this an attempt has been made to evaluate the ability of a eukaryotic microorganism *Aspergillus niger* in bioleaching of iron from clay materials.

The term bioleaching is used for efficient and effective extraction of metal from a low-grade ores, thereby improves the quality of ore in accomplishing the ore beneficiation process. In this study kaolin is used for near-white clay deposits which are dominantly comprised of kaolinite mineral, or for products refined from such deposits. For most modern industrial applications clay must be extensively refined and processed to enhance some important commercial characteristics. In the case of ceramic and paper industry, the main consumer, one of the most important specifications for clay is the brightness. In general, a brightness of 79 - 83.5% is required for filler and 83.5-85.5% for coating purposes.[2,3]

The presence of iron oxides in most of the clays has detrimental effect on the color of the product, which declines in brightness with increasing iron content. The process employed for improving the brightness of the mineral product can be classified as physical and chemical ones, or both. These methods are usually suitable for achieving a higher extent of iron removal but, at the same time, they are more expensive, the operating conditions are very complicated, and the processes are environmentally dangerous.

Earlier reports revealed that the heterotrophic microbial leaching have been demonstrated that iron could be removed from quartz sand. The ability of heterotrophic microorganisms to leach iron from oxide minerals can be used for the removal of this element from clays for improvement of filler and coating properties via the action of metabolic products.[4]. The solubilization of iron occurs through the action of organic acids and other excreted metabolites, acting as complexing agents, as well as enzymatic and non-enzymatic iron reduction. Microbiologically produced organic acids of particular effectiveness are citric and oxalic acids, produced by many fungi in their metabolism of carbohydrate substrates. For low-grade hematitic laterites, [5] were found that citric acid was the most effective organic acid for nickel extraction while oxalic acid displayed remarkable selectivity on iron extraction.

The aim of the present study was to investigate the possibility of using fungal fermented medium for the removal of iron, and consequently to improve the brightness, of for a clay sample derived from the clay mines at Dwaraka Tirumala of East Godavari District of Andhra Pradesh. Also, a chemical leaching experiment was conducted with citric and oxalic commercial acids for the same purpose.

2. EXPERIMENTAL

2.1 Clay Sample

Sample of clay from Dwaraka Tirumala of East Godavari District of Andhra Pradesh was used in this study. Initially the sample is grounded to a pulp after dispersion and de-sanding operation and is not subjected for magnetic separation.

The mineralogical and chemical analyses are presented in Tables 1, respectively.

Table 1 - Mineralogical and Chemical Analysis of Clay Sample [Qualitative Fraction: - 44 mm (% wt)]

Sample of the mineral is composed of kaolinite, quartz, magnetite/hematite

Component	Composition	Percentage
Kaolinite	Al_2O_3	39.30
Quartz	SiO_2	46.50
Dolamite	CaO, MgO	00.16
Hemetite	Fe2O3	01.60
Alkali Oxides	Na_2O, K_2O	01.30

2.2 Microorganism and Media

The microorganism used in this work was a strain of *Aspergillus niger* isolated from a talc ore. The strain was maintained in potato-gelose in order to produce spores. For fermentation, it was used the medium with the following composition (g/L):

Table 2

Compound	Quantity (g/L)
Sucrose	80.00
$(NH_4)_2SO_4$	03.00
KH_2PO_4	02.00
$MgSO_4$. 7 H_2O	00.20
$ZnSO_4$	00.10

The pH of the medium was adjusted to 7.0 with NaOH solution 0.1 M.

The surface process was used for conducting the fermentation at 23^oC in Erlenmeyer flasks. At the end of the process, indicated by constant acidity, the fermented medium was filtered and the content of citric and oxalic acids were determined. A reported standard method was used for citric acid and oxalic acid determination.

2.3 Bioleaching Experiments

The bioleaching tests were carried out at 60^oC in 250 ml flasks containing 50 ml of clay pulp and 50 ml of bleaching solution. As bioleaching solutions citric and oxalic commercial acids, as well as fermented medium, were used. The final pulp densities at the systems were around 10% for all the experiments. The systems were continuously agitated in rotatory shaker for 3 hours.

The ISO brightness was determined after filtration and drying the solid at 100^oC, in a colorimeter. The dissolved iron was determined in the filtrate by atomic absorption spectrophotometer.

All the experiments were repeated for reproducibilty.

3. RESULTS AND DISCUSSION

This study is part of an Industrial Consultancy assigned to the University College of Technology, Osmania University, Hyderabad by SV Minerals of Dwaraka Tirumala of East Godavari District of Andhra Pradesh. The clay sample is subjected for leaching with organic acids and its susceptibility towards microorganisms for bioleaching ability. It was observed a greater effectiveness of oxalic and citric acids on clay sample bleaching, when compared with microorganisms bioleaching. This could effectively modified by using certain mineral ions, which affects the release of oxalic acid by the microorganism. Another important observation was the influence of the temperature on the bioleaching process. The use of high temperatures instead of raising the concentration was more effective in order to enhance the bioleaching process of clay sample when oxalic commercial acid was used. These previous results indicated that these two acids, citric and oxalic, would be more promising to investigate than other organic acids microbiologically produced.

The use of bioleaching as a bleaching process requires, in this case, a two-stage process. These two stages (fermentation and bleaching) were required due to the mineral granulometric characteristics (very small particles), which rendered difficult the further separation, besides the necessity of adapting the mineral processing at a low iron concentration.

Table 3 summarizes the characterization of the filtered fermented medium used for the experiments of bleaching, after 4 days of fermentation, in terms of citric acid, oxalic acid, pH and final acidity.

Table 3 - Characterization of the filtered fermented medium from *A. niger*

pH	***Final Acidity (H+ eq/L***	***Citric Acid***	***Oxalic Acid***
1.62	***1.16***	***0.28***	***60***

Tables 4, 5, and 6 show the results of the bleaching tests carried out with citric acid, oxalic acid and fermented medium, respectively.

Table 4 - Bleaching of samples kaolin with citric acid. Final concentration at the bleaching system: 0.25M

Sample Initial Brightness	**Final Brightness**	**Brightness Increase**
79.20	**80.30**	**1.10**

Table 5 - Bleaching of samples kaolin with oxalic acid. Final concentration at the bleaching system: 0.25M

Sample Initial Brightness	**Final Brightness**	**Brightness Increase**
79.20	**80.40**	**1.20**

Table 6 - Bleaching of clay sample with filtered fermented medium. Final concentrations at the bleaching system: Citric acid 0.14M, Oxalic acid 30 mM.

Sample Initial Brightness	**Final Brightness**	**Brightness Increase**
79.20	**80.80**	**1.60**

For better evaluation of the action of organic acids and fermented medium, it was interesting to compare the increase of the sample brightness. These values were obtained by the difference between the final and initial brightness of each sample.

The results obtained with filtered fermented medium should be emphasized, considering the final concentrations of citric and oxalic acids on the bleaching system (0.14 M and 30 mM, respectively), that were inferior to those employed when synthetic solutions were used (0.2 5 M). The increases of brightness were similar to that of oxalic acid one (0.25 M), that provided the best results. This behavior could be explained due to the possible action of others metabolites present in the fermented medium as well as an enzymatic action. By now, it is not still possible to attribute enzymatic activity of the fermented medium, as no tests were conducted to evaluate this mechanism on the removal of contaminants from the mineral. However, a possible enzymatic involvement can not be neglected as the fermented medium was not subject to harmful conditions that could inactive possible excreted enzymes. These results recommends additional studies about the mechanisms involved in the bleaching process by using organic acids and fermented medium as well as its relation to the iron form occurring in the mineral sample, providing the best evaluation of the method. Due to its great application in the food industry, the majority of the studies found in the literature showed information about the citric acid production. However, for removal of iron from minerals, the best results are provided by oxalic acid, which is an undesirable by-product of commercial citric acid fermentation.

According to reported literature the citric acid and oxalic acid act on the oxidized mineral through an initial acid-base reaction, carried on by chelation and complexation of metal ions. In the case of iron, a reduction from Fe+3 to Fe+2 could occur by the action of oxalic acid. This could explain the best results reached with oxalic acid when compared to citric acid.

4. CONCLUSIONS

The results obtained in the leaching experiments with fermented medium, citric and oxalic acids showed the possibility of using these solutions as bleaching agents.

The use of microorganism in leaching operations is an efficient and economic process without any deleterious effects on the environment.

Bioleaching is a robust and cost-effective technology and a leader in this rapidly developing field and aims at the sustaining of human life through cleaner environment. This study helps for further evaluation and commercial implementation of microbial leaching processes. This includes fungal and bacterial cultures, bench scale and piloting test work, and the design and commissioning of turn key projects on ore beneficiation.

Further it can establish the capabilities for development, optimisation, piloting and plant design in the fields of separation, purification and concentration and metal recovery.

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