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Recovery of nickel and zinc using biogenerated sulphuric acid

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Abstract. Sludge generated in automotive and related industries often contains heavy metals. Bioleaching is an attractive alternative for the treatment of metal containing solids. Bacteria of the genus *Acidithiobacillus* are the most important microorganisms applied to metal solubilisation. These microorganisms are able to produce sulphuric acid from the aerobic oxidation of elemental sulphur. The biogenerated sulphuric acid can be applied to the solubilisation of metals from a solid matrix. In this paper we present the results of our experiments aimed at the removal of nickel and zinc from sludge generated in the water treatment plant of an automotive industry. *Acidithiobacillus thiooxidans* cells were immobilised on sulphur pearls in a column reactor. The effects of sulphur pulp density and the dilution rate on the production of sulphuric acid were studied. In a second stage, sulphuric acid was used to solubilise the nickel and zinc from the sludge. The effects of different sludge pulp densities and initial acid pH were studied. High recoveries of zinc and nickel were obtained when the pH value of the sulphuric acid solution was lower than 2.0 for 1 and 2 % of pulp density.

Introduction

Sludge generated in automotive and related industries generally contains heavy metals. The disposal of heavily contaminated sediments may pose a potential hazard to human health and to the environment. Therefore, it is necessary to remove the heavy metals from the sediments before being disposed [1].

Bioleaching has serious potential for remediation of heavy metal contaminated materials [2, 3]. Bioleaching processes are based on the ability of microorganisms (bacteria, fungi) to transform solid compounds, resulting in soluble and extractable elements which can be recovered [4]. Probably, the most important microorganism able to participate in this process are the sulphur-oxidising bacteria. These bacteria generate sulphuric acid from the aerobic oxidation of elemental sulphur. This acidification allows the solubilisation of metals from solids. As other biotechnological techniques, bioleaching is economically and environmentally advantageous [2].

The aim of this work was to recover nickel and zinc contained in a solid sludge, generated in the treatment plant water of an automotive plant using sulphuric acid generated by sulphur-oxidising bacteria, immobilised on elemental sulphur pearls.

Material and methods

Microorganisms. The strain used throughout this work was *Acidithiobacillus thiooxidans* (DSM 11478). Cells were maintained in iron-free 9K culture medium [5] with 1% (w/v) sulphur as energy source.

Sludge. Sludge used in this work came from the wastewater treatment plant of automotive factory. Prior to experiments, sludge was dried, ground and sieved. Particles retained size between 100 and 200 mesh were used for the experiments. pH= 8.00 was measured mixing 1:2.5

(sludge:water, p/v). The chemical analysis of the sludge indicated that the main toxic components of the sludge are zinc (59.2 mg Zn/ g dried sludge) and nickel (14.6 mg Ni/ g dried sludge).

Sulphuric acid production by *Acithiobacillus thiooxidans* in a packed-bed bioreactor. Three glass columns (17.0 cm length and 4.0 cm internal diameter) with inlets for medium and air at the bottom and an outlet for effluent at the top of the column and a lateral port for sampling, were used as bioreactors. The columns were filled with 50 g (Column A), 100 g (Column B) and 150 g (Column C) pearls of elemental sulphur (particle size: 2- 4 mm). Columns were filled with culture medium at pH 5 and inoculated at 10% (v/v). Pulp densities in each column were 24, 54 and 94 % respectively. Columns were incubated at 30ºC.

The immobilisation was achieved by recirculating the culture medium in the columns until the pH was around 1.0. Then, the exhausted medium was replaced by fresh medium (without inoculation). The procedure was repeated until a constant rate of proton production was obtained. It was assumed that a biofilm had been formed on the sulphur particles. At that moment, the system started to work in continuous operation mode, with the influent (fresh culture medium) flow supplied by a peristaltic pump at variable rates (dilution rates between 0.03 and 0.37 h^{-1}). Samples were withdrawn at regular intervals to analyse the pH and proton production (by titration with 0.1 N NaOH)

Bioleaching of heavy metals in column reactor. Different amounts of sludge (pulp densities: 1.0; 2.0 and 4.0 %) were placed in a glass column (18 cm length and 2.25 cm internal diameter). Sulphuric acid solutions of different pH (1.0; 1.5 or 2.0) generated in the previous stage were added at the bottom of the column with the aid of a peristaltic pump at 15 mL h^{-1}, (dilution rate 0.21h^{-1}). The system was magnetically stirred. Assays were run in duplicate. Samples were withdrawn at regular intervals to measure the pH and soluble metal concentration (by atomic absorption spectroscopy, (AA6500 Shimadzu)).

Results and discussion

Sulphuric acid production by *Acithiobacillus thiooxidans.* Fig. 1 shows the behaviour of pH and the concentration of H^+ for each column during the immobilization stage, which lasted *c.a* 18 days. The sharp increase in pH and decrease of H^+ concentration occurs when the exhausted medium is changed by fresh medium. As a general rule, the time needed for the decrease of pH was shorter in each cycle. Comparing the three columns it is possible to see that the higher the pulp density, the longer the cycle.

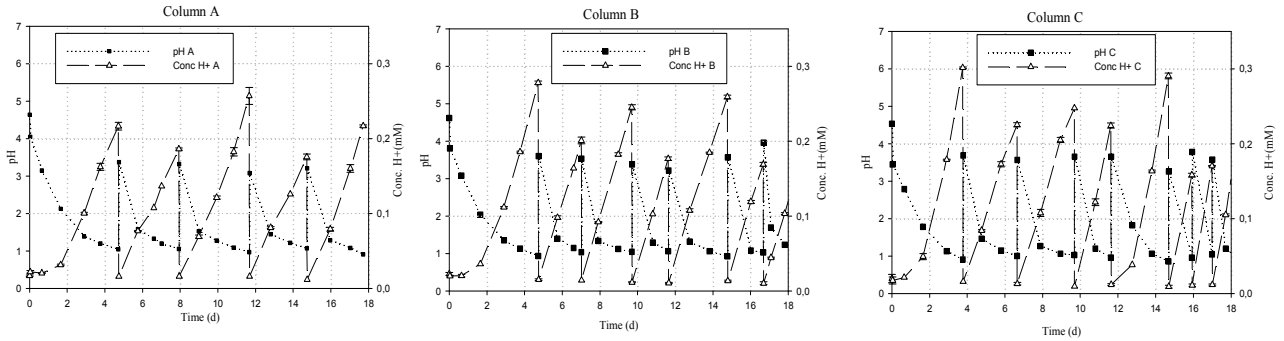

Figure 1. Evolution of pH and H^+ concentration during the attachment of *A. thiooxidans* on sulphur for three different columns: A (24% w/v sulphur), B (54%) and C (94 %).

When the attachment stage was finished, the systems started to produce sulphuric acid in a continuous way. To compare the acid productivity of *A. thiooxidans* as a function of the dilution rate when growing on elemental sulphur in the three columns, the amount of proton produced was calculated by integrating the amount of protons produced while the pH of the systems remains between 1 and 2 during 70 h. Fig. 2 shows the calculated production of protons in the three columns

as a function of the dilution rate. It can be seen in the figure that the highest acid production was obtained in column B at 0.22 h^{-1}. This dilution rate was chosen for the metal leaching stage.

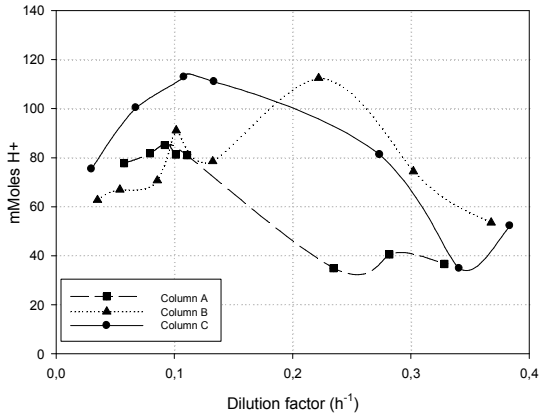

Figure 2. Proton production by *A.thiooxidans* growing on elemental sulphur as a function of the dilution rate, for three different columns: A (24% w/v sulphur), B (54%) and C (94 %).

Recovery of nickel and zinc from the solid sludge. 360 ml of biogenerated acid sulphuric (with different pH values) were used the leaching experiments. In all the cases, at the end of the experiment the leachate had the same pH of the inlet solution, except when sulphuric acid of pH 2 was applied to columns with 2 % and 4 % sludge. In these cases the final pH values were 3.0 and 4.5 respectively. The percentages of metal recoveries were very high (between 80 and 100 % in most cases). The increase in the pulp density produced a decrease in the recovery of metals, especially for the sulphuric acid solution of pH= 2. Fig. 3 shows the percentage of nickel and zinc recovered. Two-way analysis of variance applied to analyse the effect of initial pH and pulp density on the recovery of zinc and nickel showed that both factors and the interactions between then are significant (F>Fcritical; α= 0.05). When each factor was compared with the interaction, no significant difference between the interaction of factors with respect to either of the individual factors, and, therefore, the interaction of both factors is important indicating that the combination of pH and pulp density could play an important role in the final recovery. That is why, further and deeper investigation about such interaction should be done.

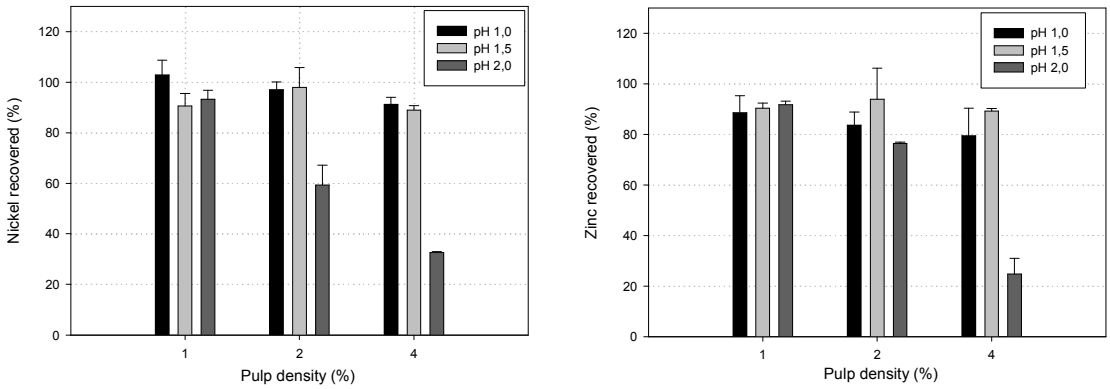

Figure 3. Percentage of nickel and zinc recovered using biogenerated sulphuric acid of different pH.

Conclusions

The results presented in this work shows that the sulphuric acid generated by *Acidithiobacillus thiooxidans* growing on sulphur is able to removed the nickel and zinc present in a sludge generated at a water treatment plant of an automotive factory. The highest acid production was obtained in a column with 50% (w/v) of sulphur. In this condition a high dilution rate can be applied. Percentages of metal recoveries near 100% were obtained when the pH of biogenerated sulphuric acid solution

were 1.0 or 1.5. Using sulphuric acid solution of pH= 2.0 the recoveries of nickel and zinc were remarkable lower. Applying this two-stage process based on the ability of *A. thiooxidans* to produce sulphuric acid, the remediation of a solid sludge with a high level of nickel and zinc was achieved.

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