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Treatment of tetrathionate effluents by continuous oxidation in a flooded packed-bed bioreactor

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ABSTRACT

Thiosalts are compounds commonly present in process plant liquor for the concentration of metal sulphide ores by milling and flotation. Since thiosalts are metastable species that are oxidized to sulphuric acid as an end product, they cannot be discharged nor recycled into the process. Therefore, the development of a cost-effective process for the treatment of these effluents is necessary. In this paper, the continuous bio-oxidation of tetrathionate is carried out in a flooded packed-bed reactor by an immobilized microbial consortium. Batch tests show that the initial tetrathionate concentration and pH slightly affect the tetrathionate bio-oxidation process in the ranges 3 to 5 g/L and 1.5 to 2, respectively. The specific bio-oxidation rate is 0.08 h^{-1}. Only sulphate ions and protons have been detected as end products. For the starting up of the bioreactor, a new method of biofilm formation for tetrathionate bio-oxidation is implemented. The maximum bio-oxidation rate in continuous operation is 0.415 gh^{-1} (0.830 kg h^{-1} m^{-3}). The biofilm was stable for the whole period studied, i.e. 35 days. These results indicate that a flooded packed-bed reactor is an interesting option from an economic point of view for the treatment of waters contaminated by thiosalts.

1. Introduction

Thiosalts are chemicals commonly present in process plant liquor for the concentration of metal sulphide ores by milling and flotation. Alkalinity conditions and the additives employed in these plants favour the partial conversion of sulphides into thiosalts. A common practice in this kind of facility is to recycle the liquors in process. However, the accumulation of thiosalts in liquors negatively affects the efficiency of flotation; this effect renders it necessary to continuously purge the generated thiosalts from the circuit. In these effluents, tetrathionate ion is usually the most abundant thiosalt, since it remains stable in solution at temperatures below 30 °C (Druschel et al., 2003).

Thiosalts are not considered toxic in themselves; however, their solutions can have an indirect impact on the environment. The incorporation of thiosalts into a receptor aquatic body can be the cause of a decrease in pH and in the dissolved oxygen concentration, and can severely affect its chemical-biological equilibrium. This is due to a natural oxidation process whose end product is sulphuric acid. This process is catalysed by metal ions in solution (Chanda et al., 1984; González-Lara et al., 2009; Senanayake, 2005a,b) and by the metabolic action of sulphur-oxidizing microorganisms (Eccleston and Kelly, 1978; Friedrich et al., 2001; Kelly and Tuovinen, 1975; Shiers et al., 2011), commonly present in these mining environments (Dopson and Johnson, 2012; Ghosh and Dam, 2009; Hedrich et al., 2011). These are frequently *Acidithiobacillus* genus bacteria, of which the most abundant species is usually *Acidithiobacillus ferrooxidans*.

Currently, the purification of effluents containing thiosalts consists of their oxidation in ponds (Kuyucak and Yaschyshyn, 2007). This is a simple and economic but very slow method, which leads to designs characterized by very large areas. One of the main inconveniences of these ponds is their low activity in cold seasons. Alternatively, several active treatments have been developed that consist of adding oxidants, such as Caro's acid (H_2SO_5), Fenton reagent, ozone, and hypochlorite (Kuyucak and Yaschyshyn, 2007; Lu et al., 2010).These methods are faster and more controllable but involve very high reagent costs, potentially dangerous operation, and include the incorporation of undesirable substances into the environment.

The controlled biological oxidation of thiosalts is postulated as an attractive future option. This option will be developed in bioreactors designed to hold high concentrations of cells and to operate continuously. Very few reactors have been described in the literature for this purpose (Miranda-Trevino et al., 2013). Liljeqvist et al., 2011 tested a bioreactor design that included a biogenerator and a main reactor containing *A. ferrivorans* attached to a structured plastic bed. Despite containing a biofilm carrier, this reactor needs to be assisted by an external supply of cells throughout its operation.

A bioreactor for the continuous bio-oxidation of thiosalts should meet the needs of treatment, with a size that enables the control of

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the variables (mainly temperature) and the stability of operation. In addition, its construction should be economical and simple.

Flooded packed-bed bioreactors have been developed for the oxidation of ferrous ion. In flooded packed-bed bioreactors, if the energetic substrate is Fe (II), then it is possible to reach steady states and very high oxidation rates without any supply of cells (Mazuelos et al., 1999 and 2000). In these bioreactors, biomass is immobilized in a biofilm that consists of an inorganic matrix, formed by precipitated ferric compounds (mainly oxyhydroxides and jarosites), in the pores of which cells are attached. This biofilm covers the surface of particles that form the bed (Karamanev, 1991; Mazuelos et al., 2012). In these bioreactors, biofilm is very robust against changes in composition and dynamic fluid conditions.

The present work aims to study the oxidation of tetrathionate in a flooded packed-bed reactor with the following objectives:

1) To achieve tetrathionate oxidation in a stable operation over time.
2) To establish a simple and quick methodology for the commissioning of bioreactors, consistent with the above objective.
3) To lay the foundation for optimization and piloting studies for the implementation of this technology.

2. Materials and methods

2.1. Batch tetrathionate bio-oxidation

All cultures performed in the present work originate from a mixed culture obtained from the effluents from the Rio Tinto Mines (Huelva, Spain). This culture has been maintained for decades by successive inoculations in 9K medium (Silverman and Lundgren, 1959). The composition of 9K medium, in which the energetic substrate is Fe (II), is shown in Table 1.

Phylogenetic analysis of the culture shows the three major phylotypes to be *Acidithiobacillus*, *Leptospirillum*, and *Ferrimicrobium*. The dominant microbial species is *Acidithiobacillusferrooxidans* _ATCC23270 (Mazuelos et al., 2012).

The culture was pelletized in order to remove the iron. Pellets of cells were prepared by centrifugation at 12,000*g* for 15 min in a Sorvall SS 3 Automatic Centrifuge Du Pont Instruments. The decanted cells were washed and resuspended in tetrathionate medium, whose composition is shown in Table 1.

In order to ascertain the species originated during bio-oxidation and to study the influence of pH and of tetrathionate concentration, batch assays were performed in sterilized 250 mL Erlenmeyer flasks, placed in an orbital shaker at 180 rpm and at a temperature of 31 °C. Into these flasks, 96 mL of tetrathionate culture medium, modified in terms of pH and in the concentration of $Na_2S_4O_6 \cdot 2H_2O$ (see Table 1), was added.

Four initial concentrations of tetrathionate (2, 3, 3.5 and 5 g/L) and three initial pH values (1.5, 2 and 3), adjusted with dilute sulphuric acid, were studied.

Table 1
Chemical composition of culture media used in this study.

Salt (g)	9 K	Tetrathionate
$(NH_4)_2SO_4$	3.0	3.0
KCl	0.1	-
K_2HPO_4	0.5	3.0
$MgSO_4 \cdot 7H_2O$	0.5	0.5
$Ca(NO_3)_2$	0.01	-
$CaCl_2$	-	0.2
$Na_2S_4O_6 \cdot 2H_2O$	-	4.0
$FeSO_4 \cdot 7H_2O$	300 mL (14.7%)	-
H_2O (mL)	700	1000

To follow the evolution of cultures, pH, and concentrations of tetrathionate, the thiosulphate and sulphite were measured over time. To detect intermediate species, Ionic Chromatography was used.

2.2. Continuous tetrathionate bio-oxidation

The continuous bio-oxidation of tetrathionate was performed in a flooded packed-bed reactor (Mazuelos et al., 1999) by immobilized cells. This reactor is a column of 15 cm in height and 8.4 cm in diameter. It consists of a lower chamber, (hollow cylindrical, 5 cm in height), and an upper chamber (the bed) of 10 cm in height (Fig. 1).

In the lower chamber, two nozzles are placed for air and liquid medium inlet. The liquid rises through the bed and leaves the reactor via the overflow. The bed consists of siliceous sand particles between 6 and 8 mm in size. The bed porosity is 0.45.

The liquid is fed by a peristaltic pump and the air by a small compressor controlled by a rotameter. Unless specified otherwise, the liquid and air flows tested were 150 mL/h and 750 mL/min, respectively. The reactor operated in a chamber with the thermostat set at 31 °C.

For the starting of the bioreactor, a new method of biofilm formation for tetrathionate bio-oxidation was implemented. The method was developed in the following stages:

a. Biofilm formation for the Fe(II) bio-oxidation by the Mazuelos et al. (2000) method. The medium used was 9K and the inoculum was the RT culture.
b. Continuous operation feeding of 9K medium modified in pH. The pH was adjusted to 1.7 with sulphuric acid to prevent an excessive iron precipitation.
c. Change of feed from 9K medium to modified tetrathionate medium. The tetrathionate medium was modified in its concentration of $Na_2S_4O_6 \cdot 2H_2O$ to 2.5 g/L and its pH to 1.7.
d. Batch bio-oxidation. In this stage, the feeding pump is stopped while the reactor is maintained aerated. This serves as a test of whether attached cells accept tetrathionate as energetic substrate.
e. Recirculating bio-oxidation. The reactor was fed from an external reservoir of 2.5 L containing modified tetrathionate medium. In this tank, the initial concentration of $Na_2S_4O_62H_2O$ was 2.5 g/L. The effluent from the bioreactor was returned to the reservoir. The initial pH in the tank was set to 2.8 to prevent an excessive fall in pH of the bioreactor, which could mean substantial dissolution of the precipitated iron that formed the matrix of the biofilm.

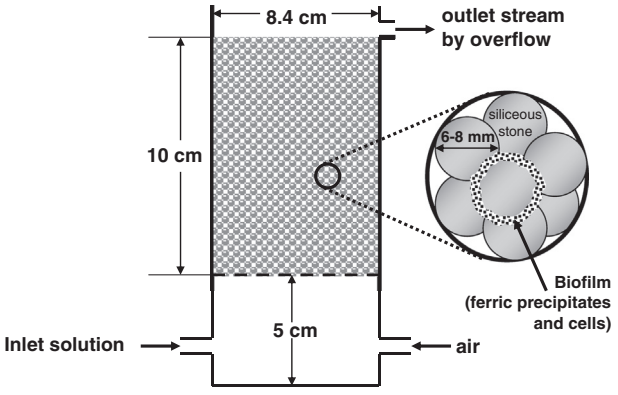

Fig. 1. Flooded packed-bed bioreactor used in this study. On the right, a portion of the packed bed is schematically shown; the siliceous stone particles bear the biofilm consisting of bacteria and a matrix of ferric precipitates.