

Monitoring polythionate bio-oxidation by conductivity measurement



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ABSTRACT

Polythionates are formed by the incomplete oxidation of sulphide minerals in the grinding and flotation circuits, and particularly of those containing pyrite. Polythionate levels in the recycling water must be adjusted; otherwise, it can affect metal recoveries. The presence of different species, such as thiosulphate, trithionate, and tetrathionate in certain effluents can affect the environment. In this paper, an indirect method based on conductivity measurement for monitoring polythionate bio-oxidation is proposed. Firstly, the conductivity of acidic solutions containing polythionates is verified as the sum of the conductivities corresponding to acid and tetrathionate and, therefore, in synthetic solutions, polythionate concentrations can be estimated by simply measuring conductivity. In process water and cultures with background conductivity, polythionate concentrations are predicted from the linear relationship between polythionate concentration and the total conductivity of the system. Once the slope of the linear relationship is known, polythionate concentrations can be estimated, and therefore it is necessary to perform only chemical analysis at the beginning and at an intermediate point. The degradation of polythionates can be continuously recorded, and hence the kinetic study of a culture can be more easily and accurately performed.

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1. Introduction

Polythionates are incompletely oxidized compounds, with general formula $S_nO_6^{2-}$. Polythionates appear in strongly acidic lakes near to volcanoes and in the runoff from excavated sites containing sulphur and sulphur-metabolizing bacteria (Takano et al., 1994). They are formed by the incomplete oxidation of sulphide minerals in the grinding and flotation circuits, and particularly of those containing pyrite, the most common sulphide mineral on earth. Polythionate levels in the recycling water must be adjusted; otherwise, it can affect metal recoveries (Silver, 1985).

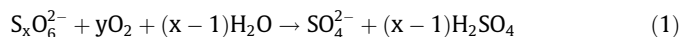
These compounds are not considered toxic and their release into receiving waters is not regulated. However, the presence of different species, such as thiosulphate, trithionate, and tetrathionate in certain effluents can affect the environment. The polythionates are discharged into rivers and lakes where they are oxidized into sulphuric acid by the presence of bacteria. This acid causes a decrease of pH in water, thereby affecting fish and other living

organisms (Miranda-Trevino et al., 2013). The severity of this effect depends on the concentration and flow rate.

In addition to the pH, other effects of polythionates on the receiving water include the reduction of dissolved oxygen concentration, the decrease in the buffering capacity, and the dissolution of metals from soil.

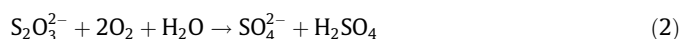
There are many routes of decomposition, depending on the pH, temperature and presence of oxidizing agents. The pH and temperature conditions in which polythionates are unstable are summarized in Vongporm (2008).

In the literature, several possible mechanisms are laid out for the oxidation of polythionates and thiosulphate (Suzuki, 1999). All polythionates are metastable species that finally oxidize to sulphuric acid by complex reactions in series. The overall reaction is the same for all mechanisms:



$$y = 5 \text{ if } x = 5 \quad y = (x-1) \text{ if } x = 3$$

$$y = (x-1/2) \text{ if } x = 4 \text{ or } 6 \quad y = (x-3/2) \text{ if } x = 2$$



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Extremophile microorganisms often catalyse these reactions. The presence of microorganisms improves tetrathionate oxidation, the most stable polythionate in acidic solutions (Druschel et al., 2003). The oxidation depends on the type of bacteria present in the medium, temperature and dissolved oxygen conditions. *Acidithiobacillus ferroxidans* and *Acidithiobacillus thiooxidans* oxidized various sulphur compounds over a broad pH range.

Currently, the best option for the treatment of effluents containing polythionates is to place them in ponds where natural oxidation takes place. This inexpensive, simple method introduces no chemicals. Finally, generated acidity is neutralized by adding alkali in the effluent discharge. However, this passive treatment is a very slow method, which leads to long residence times (months) to achieve the desired effect. The literature contains a wide variety of proposals for oxidation based on direct and indirect photolytic methods, ultrasonic irradiation, adsorption on iron hydroxides, and use of oxidizing agents such as ozone, oxygen, hydrogen peroxide, mix of SO₂-air, Fe(III)-O₂ (Kuyucak and Yaschyshyn, 2007; Lu et al., 2010). Although rapid, these methods are more expensive than passive treatment since they must bear the cost of reagents.

Bio-oxidation is postulated as an attractive option from a technical, economic and environmental point of view. According to Carranza et al. (2014), the continuous bio-oxidation of thiosalts in flooded packed-bed reactors, constitutes a major advance in the treatment of these effluents. Regarding the treatment in ponds, the operation time is reduced from weeks to hours. In addition, the reagent cost is reduced in comparison with active methods of treatment. Both in the design phase and during operation, it is necessary to ascertain the evolution of the determination of polythionates.

There are numerous methods of analysis for polythionate speciation, such as chromatography, electrophoresis, gravimetry, and thermal analysis or electro-analytical techniques (Miranda-Trevino et al., 2013). Although these methods are of relevance, the complexity between polythionates renders them inconclusive. The polythionate concentration is usually determined by the mercuric chloride acidimetric titration method (Makhija and Hitchen, 1978). This method involves quantifying the total amount of acid produced by polythionates, expressed as tetrathionate. However, this method is time-consuming, tedious, and requires the preparation of a series of solutions and the consumption of reagents that make it overly expensive. In addition, it involves disturbing and manipulating the culture for a complete kinetic characterization. Furthermore, the method fails to enable monitoring of the evolution of polythionates in a culture. These drawbacks lead to the search for an alternative method for the indirect but rapid and continuous measurement of the polythionate concentration.

In this paper, the measurement of conductivity is proposed as an indirect method for the monitoring of the evolution of the polythionate concentration in a culture in order to follow the kinetics of the degradation of polythionates. According to reactions (1) and (2), the polythionate oxidation increases the conductivity of the medium mainly due to the generation of acid, whereby a decrease in the concentration of polythionates involves an increase in the conductivity of the solution.

The conductivity of a solution, K , is defined as the reciprocal of the specific resistivity, ρ , or as the conductance of an electrolyte solution cube of 1 cm³. It is an additive magnitude, which means that in an electrolytic solution, both the solute and the solvent contribute, and it can be stated that:

$$K_{\text{solution}} = K_{\text{solute}} + K_{\text{solvent}}$$

Conductivity is a measure of the number of free-moving ions in a solution. For a given electrolyte, the conductivity of its solutions is a function of the solution concentration and the temperature. It

depends on the number of ions per unit of volume (concentration) and also on the nature of ion (electrolyte). Since conductivity depends on the ion movements and these movements, in turn, depend on temperature, then the conductivity measurements must be performed at constant temperature.

In this paper, the specific bio-oxidation rate and polythionate degradation rate is determined by continuous conductivity measurement. The Paired Student *t*-test validates the proposed method.

2. Materials and methods

2.1. Strain

All the cultures performed in the present work are originally 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 Lundgreen, 1959). Phylogenetic analysis shows three major phylotypes: *Acidithiobacillus*, *Leptospirillum*, and *Ferrimicrobium*. The dominant microbial species is *Acidithiobacillus ferrooxidans* _ATCC23270 (Mazuelos et al., 2012).

For the development of the sulphur oxidation metabolic pathway of bacteria, a liquid portion of inoculum was adapted to polythionates as the only source of energy. The inoculum was centrifuged at 900–1000 g in a Du Pont Instruments Sorvall SS 3 Automatic Centrifuge in order to remove solid particles. The supernatant was centrifuged again at 16,000 g for 5 min. The decanted cells were washed and suspended in the tetrathionate medium whose composition is shown in Table 1.

2.2. Process water

The process water of a flotation plant located in Huelva (Spain) is studied. This plant treats cupriferous and polymetallic sulphide ores, which are characteristic of Iberian Pyritic belt. The average composition of process water is shown in Table 2.

2.3. Synthetic liquors

Solutions of anhydrous sodium tetrathionate (Sigma Aldrich) in ultra-pure water acidified with sulphuric acid were prepared as synthetic liquors. The concentration of solutions ranges between 0 and 6 g/L of tetrathionate and the pH between 1.3 and 1.8. All laboratory material was carefully sterilized. In this same manner, solutions of anhydrous sodium tetrathionate without added acid were also prepared.

2.4. Analysis

The total concentration of polythionates was determined by the acidimetric method with mercury chloride (Makhija and Hitchen, 1978). Thiosulphate and sulphite ions were analysed through iodometry; discrimination between the two ions was achieved by masking the sulphite ion with formaldehyde (Kurtenacker and Bittner, 1924; KoH, 1990).

Table 1
Chemical composition of the tetrathionate medium.

Salt	(g/L)
(NH ₄) ₂ SO ₄	3.0
K ₂ HPO ₄	3.0
MgSO ₄ ·7H ₂ O	0.5
CaCl ₂	0.2
Na ₂ S ₄ O ₆ ·2H ₂ O	4.0
H ₂ O (mL)	1000

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