Polyurethane foam as biomass support for removal of thiosalts from flotation process water.

Alfonso Mazuelos*; Nieves Iglesias-Gonzalez, Cristina Montes-Rosua, Aurora Romero-Garcia, Rafael Romero, Francisco Carranza.

Department of Chemical Engineering, Faculty of Chemistry, University of Seville, Spain

Corresponding author: Alfonso Mazuelos*

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Abstract.

Water recycling is a common practice in sulphide ore processing plants by flotation. Inherent thiosalts accumulation in process water often causes efficiency drop and environmental issues for wastewater discharging. Passive and active depuration methods have been applied for thiosalts removal and bio-oxidation in packed bed bioreactors can be considered the most promising option.

In this work, polyurethane foam is for first time used as biomass support material in continuous bio-oxidation of thiosalts. Two columns, 15 and 197 cm in height and 8.4 cm in diameter, packed with 1 cm in edge length cubic particles were trialled. A new and fast start-up procedure was performed allowing to effectively operate them in less than seven days. Complete removal of thiosalts in real liquors were achieved with bio-oxidation rates close to 0.45 kg/hm^3 and residence time lower than 7 hours. Stability, robustness and versatility showed by the bioreactors allows to affirm that polyurethane foam is a suitable material as biomass support in continuous packed bed bioreactors for thiosalts bio-oxidation.

Symbols:

TBR: thiosalts bio-oxidation rate ($kg \cdot h^{-1} \cdot m^{-3}$)

c_i: thiosalts concentration in inlet solution (g/L)

c_o: thiosalts concentration in outlet solution (g/L)

C(t): conductivity in outlet solution as function of time

E(t): residence time distribution function.

E(Θ): normalised residence time distribution function.

F1: real liquor collected from a thickener overflow.

F2: real liquor collected from a tailing pond.

F(t): cumulative residence time distribution function.

F(Θ): normalised cumulative residence time distribution function.

k: adjustable parameter for plug-flow reactor with a recycle loop model.

Me: mass flow rate of thiosalts.

RTD: residence time distribution

TC: culture used as inoculum.

v: liquid flow rate (L/h)

V: working volume of bioreactor (L)

τ: mean residence time (min)

σ^2: variance (min^2)

Θ: dimensionless function of time

1. Introduction.

Mineral processing industries count on limited freshwater availability and process water recycling is commonly implemented. This sustainable practice minimises both demand of this scarce natural resource and volume of effluents discharge to the environment, nevertheless its impact on industrial plant efficiency is a recurring issue. (Muzinda and Schreithofer, 2018).

Thiosalts are present in waters from processing of sulphide ores by grinding and flotation, mainly thiosulfate $S_2O_3^{2-}$, trithionate $S_3O_6^{2-}$ and tetrathionate $S_4O_6^{2-}$ although low concentrations of higher polythionates $S_nO_6^{2-}$ (n<10) can be found as well (Miranda-Treviño et al, 2013). These sulfoxy anions are generated by partial oxidation of the sulphides, largely pyrite and pyrrhotite, depending on alkalinity, residence time, aeration/mixing, temperature and chemicals used, especially sulphur dioxide SO_2 and metabisulphite $S_2O_5^{2-}$.

Thiosalts are metastable species which spontaneously react with O_2 (r1, r2, r4) to sulphate with acid generation or disproportionate (r3). These processes can be catalysed by metal ions and by sulphur-oxidising bacteria commonly present in these environments. (Chanda et al., 1984, Pronk et al, 1990, Susuki, 1999, Druschel et al., 2003, Dopson and Johnson, 2012).

$$S_4O_6^{2-} + {}^{7}\!/\!_{2}\, O_2 + 3H_2O \rightarrow 4SO_4^{2-} + 6H^+ \qquad \text{(r1)}$$

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \qquad \text{(r2)}$$

$$S_2O_3^{2-} + 2\ H^+ \rightarrow S + H_2SO_3 \qquad \text{(r3)}$$

$$H_2SO_3 + ½\ O_2 \rightarrow SO_4^{2-} + H^+ \qquad \text{(r4)}$$

Thiosalts must be continuously purged from process water since their accumulation can cause the following negative effects:

- A drop of the flotation efficiency. They interfere with the performance of the mineral collectors and act as a depressant (Rao and Finch, 2006, Liu et al, 2013, Bicak et al, 2018).

- Clogging in pipes. As lime is used to achieve the alkalinity conditions required by flotation, a high degradation of thiosalts result on an excessive sulphate content in waters which promotes precipitation of gypsum (Guerrero-Flores et al, 2018). Additionally, if thiosulfate is present elementary sulphur may also precipitate due to disproportionation of this thiosalt (r3).

- Uncontrolled acidification of process water.

Thiosalts not only cause technical issues but also environmental risks. Although they have relatively low toxicity, the environmental impact associated to them is related to its chemical instability (r1 to r4). Thus, a discharge of effluents containing them can progressively alter the chemical-biological equilibrium of receiving waters, decreasing pH and increasing chemical oxygen demand. Consequently, environmental codes related with mining industry state strict limits for the thiosalts content in wastewater from ore processing (Kuyucak and Yaschyshyn, 2007).

Either per fulfilment of environmental, legal or technical requirements, waters from processing of ore sulphides must be commonly treated for thiosalts removal. The simplest and more extensively applied technique for depuration of industrial effluents is lagooning. This method consists in the accumulation of the wastewater in ponds, where it is exposed to air, biological population, and sunlight, resulting on natural degradation of thiosalts

(Silver, 1985, Kuyucak and Yaschyshyn, 2007). This passive method is inexpensive, with very low reagents and energy costs. However, since slow kinetic of depuration, high residence times and thereby huge areas are required, which entails desolate visual impact and unproductive management of the territory. Because of temperature control is technically unfeasible, ponds efficiencies are very low in cold seasons (Montes-Rosua et al, 2018, (Liljeqvist et al, 2011).

Passive methods can be assisted or replaced by active treatments. Unlike the passive ones, active methods are based on adsorption, ion exchange and fast and controlled degradation of thiosalts with oxidizing agents, such as oxygen peroxide H_2O_2, Caro´s acid H_2SO_5, ozone O_3, or hypochlorite ClO^- (Kuyucak and Yaschyshyn, 2007; Lu et al., 2010, Range and Hawboldt, 2020, Gervais et al, 2020). Between them, chemical oxidation with oxygen peroxide is the most applied since no toxic substance is generated, but this oxidant is a very expensive reagent whose storage and handling are dangerous.

Controlled and complete oxidation of thiosalts by aeration is feasible when is catalysed by sulphur-oxidising bacteria. Stirred tanks and packed bed bioreactors holding Acidithiobacillus genus bacteria have been successfully tested for this purpose (Eccleston and Kelly, 1978, Silver and Dinardo, 1981, Pronk et al, 1990, Kupka et al, 2009, Liljeqvist et al, 2011, Shiers et al, 2011, Miranda-Trevino et al, 2013, Iglesias et al, 2016, Monte-Rosúa, 2018).

Continuous bio-oxidation of tetrathionate has been carried out in flooded packed-bed bioreactors inoculated with mixed cultures containing Acidithiobacillus genus bacteria (Iglesias et al 2016). This design consists of a column randomly packed with siliceous stone particles where bacteria were attached. Air and fresh solution, containing tetrathionate as unique thiosalt, are fed in at the bottom and go up through the bed flooding it. Tetrathionate bio-oxidation rates higher than 0.75 kg/hm^3 were obtained with

conversions higher than 70%. But when, besides tetrathionate, thiosulphate and sulphite were present, which is the most representative scenario in industrial flotation plants, thiosalts bio-oxidation rate dropped close to 80% (Mazuelos et al, 2019). This deceleration is attributed to inhibitory effects associated to cytotoxicity of SO_3^{2-} (Tuovinen and Kelly, 1974; Masau et al, 2001; Sääf et al, 2009), initially fed and spontaneously generated by disproportionation of thiosulphate in acidic medium (r3) (Johnston and McAmish, 1973).

This technical limitation has been recently overcome by applying a pre-treatment which consists of controlled disproportionation of thiosulfate to sulphite, by acidifying to pH lower than 2 with sulfuric acid (r3), and a subsequent oxidation of sulphite generated to sulphate (r4), by aeration in stirred tank reactors for at least 8 hours (Mazuelos et al, 2019). The sulphite oxidation (r4) is catalysed by adding cupric ions Cu^{2+} up to 20 mg/L. This pre-treatment prevents any inhibitory effect associated to the presence of sulphite or instability of thiosulphate and clogging in the packed-bed due to the generation-precipitation of elemental sulphur (r3).

This economical and simple design constitutes the major advance and the most promising option for the treatment of industrial effluents containing thiosalts. However, some improvements can be introduced regarding inert support for biomass. Siliceous stone is a suitable material for bacterial support in terms of stability, availability and price, but it has some disadvantages with respect to other manufactured materials such as polymeric ones:

- It is not a porous material and has a low specific surface area.

- High density (higher than 2 g/mL). Installation and maintenance operations of a heavy packed bed can be complex. Support particles should be periodically replaced because of

total or partial clogging of bed caused by gypsum accumulation, especially in well aerated zones with a fast sulphate generation (Guerrero-Flores et al, 2018).

- Regular particles in shape and size according to design specifications are not available.

Polyurethane foam has not these technical limitations and is an inexpensive material as well. This material has already been applied for biological depuration of other effluents by bio-trickling filters (Yang et al, 2011, Shamsi et al 2017, Dobslaw and Engesser, 2018, Dacewicz, 2019). It was successfully tested as inert support for *Acidithiobacillus ferrooxidans* for ferrous iron bio-oxidation (Armentia and Webb, 1992).

In this work polyurethane foam is tested for the first time as material support for sulphur-oxidising microorganisms for continuous thiosalts bio-oxidation in packed bed bioreactors. Stability, robustness and versatility of the operation are tested in long term using real liquors from a sulphide ores processing plant.

2. **Materials and methods.**

2.1. Process waters.

Recycled waters in ore processing plants can be commonly found in dams, ponds, dewatering and solid-liquid separation units (Bikac, 2018). In this work, two real liquors from a polymetallic sulphide flotation plant (Iberian Pyritic Belt), were used:

- F1: From a thickener overflow.
- F2: From a tailing pond.

F1 and F2 samples were periodically collected and stored in absence of air. Thiosalts content was variable over time and different from a sample to another, although some predictable aspects were observed:

- Thiosalts concentration was always higher in F1 (2.0-4.5 g/L) than in F2 (0.5-2.5 g/L).
- Unlike tetrathionate, thiosulphate and sulphite were not always detected. Thiosulphate concentration was lower than 1 g/L in F1 and 0.2 g/L in F2, and sulphite concentration was lower than 0.2 g/L in F1 and 0.02 g/L in F2.
- pH presented values close to 2.8.
- Sulphate and calcium concentrations were around 2 and 1 g/L respectively.

For thiosulphate and sulphite removal, F1 and F2 were aerated for 24 hours in a tank, after adjusting pH to 1.7 with sulphuric acid and adding copper sulphate up to reach 20 mg/L of copper ions. Detailed values of thiosalts concentration are given in results section.

2.2. TC culture.

TC culture was used as inoculum of the bioreactors. It is a mixed culture which consists of *Acidithiobacillus ferrooxidans* and *Acithiobacillus thiooxidans*. This culture is maintained by successive inoculations on an enriched medium containing 3.5 g/L of $S_4O_6^{2-}$, 3 g/L of $(NH_4)_2SO_4$, 3 g/L of K_2HPO_4, 0.5 g/L of $MgSO_4 \cdot 7H_2O$, and 0.2 g/L of $CaCl_2$.

2.3. Biomass support particles.

Cubic particles of polyurethane foam with edge length of 1 cm were used as biomass support. Polyurethane density was 25 kg/m^3 and internal porosity was 96%.

2.4. Bioreactors.

In this work, two flooded packed bed bioreactors, named B10 and B200, have been operated in continuous. These bioreactors consisted of polypropylene columns with inlets for fresh liquor and air at the bottom (figure 1).

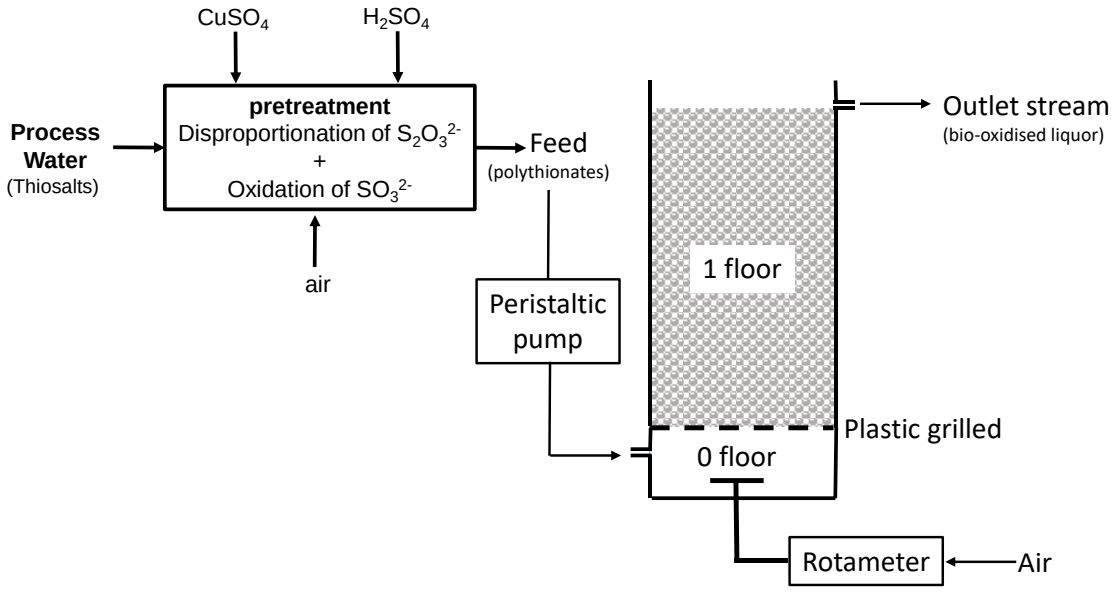

Figure 1: Scheme of bio-reactors operation.

At the top, bio-oxidised liquor went out by overflow. These bioreactors had two differentiated zones:

- 0 floor. In this hollow zone, placed at the bottom of the column, oxygen transfer is favoured since bubbles are generated with no obstacles, promoting turbulent flow and mixing (Mazuelos et al, 2002).

- 1 floor. Above 0 floor, this zone was randomly packed with the support particles and biomass attached to them was continuously flooded with oxygenated liquor from 0 floor.

0 and 1 floors were separated by a plastic grille where packed bed was supported.

These two bioreactors were different in size. In table 1, the main geometrical parameters are detailed. Working volume (V) is the volume of the column minus the volume occupied by the support particles.

	height (cm)	diameter (cm)	0 floor height (cm)	0 floor volume (mL)	1 floor height (cm)	1 floor volume (mL)	Working Volume (V) (mL)	Porosity
B10	15	8.4	5	277	10	488	765	0.88
B200	197	6.4	7	225	190	5348	5573	0.88

Table 1: Geometry of the bioreactors B10 and B200.

B10 and B200 bioreactors were operated at room temperature and fed with pre-treated F1 and F2 real liquors; thiosulphate and sulphite removal in feed was verified.

Thiosalts bio-oxidation rate (TBR) was calculated by the following equation:

$$TBR = \frac{(C_i - C_o) \cdot v}{V} \qquad (1)$$

where, c_i is thiosalts concentration in inlet solution, c_o is thiosalts concentration in outlet solution and v liquid flow rate.

Mass flow rate of thiosalts entering the bioreactor Me is calculated by the following equation:

$$Me = v \cdot c_i \qquad (2)$$

Since the utility of these bioreactors is to remove thiosalts in water recycling in flotation plants, it must be assumed bio-oxidation rates are restricted by substrate limitation.

2.5. Start-up procedure.

To start up these bioreactors, TC was used as inoculum and L1 was fed. This process was performed in two steps:

- Inoculation: the bioreactors were filled with 20% of TC and 80% of L1 and were aerated at 750 mL/min. Once thiosalts were completely oxidised (2 days) following step started.

- Recirculation: each bioreactor was connected to a tank filled with F1, whose volume was equal to bioreactor working volume, and both liquors recirculated up to thiosalts exhaustion. This operation was three times repeated (3 days) and after continuous operation was started.

2.6. Residence time distribution (RTD).

RTD was studied for B200 by pulse input experiment, using a 3M KCL solution as tracer. 40 g of tracer was suddenly injected in one shot into the feed stream and conductivity measured in outlet solution as a function of time (C(t) curve) (Levenspiel, 2004, Fogler, 2006). Data are continuously collected online using -Labview- software. Liquid and air flow rate were 820 mL/h and 1000 mL/min respectively.

Residence time distribution function E(t) was calculated as follow:

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} \qquad (3)$$

Mean residence time τ and variance σ^2 were calculated by the following equations:

$$\tau = \int_0^\infty t \cdot E(t)dt \qquad (4)$$

$$\sigma^2 = \int_0^\infty (t-\bar{t})^2 E(t)dt \qquad (5)$$

The cumulative RTD function F(t) and E(t) are related:

$$F(t) = \int_0^t E(t)dt \quad \text{or} \quad 1\text{-}F(t) = \int_t^\infty E(t)dt \qquad (6)$$

E(t) and F(t) can be normalised referring them to the dimensionless function of time Θ.

$$\theta = \frac{t}{\tau} \qquad (7)$$

$$F(\theta) = \int_0^\theta E(\theta)d\theta \quad \text{or} \quad 1\text{-}F(\theta) = \int_\theta^\infty E(\theta)d\theta \qquad (8)$$

E(Θ) and F(Θ) allows to compare directly flow performance inside reactors of different sizes, thereby they are used for defining the most of models in literature.

2.7. Analysis and control.

Total thiosalts concentration was analysed by acidimetric method with $HgCl_2$ (Makhija and Hitchen, 1978). $S_2O_3^{2-}$ and SO_3^{2-} concentrations were measured by iodometry (Kurtenacker and Bittner, 1924; KoH, 1990); to discriminate $S_2O_3^{2-}$ and SO_3^{2-} concentrations, CH_2O (formaldehyde 38%) was used to mask SO_3^{2-}.

The concentration of dissolved oxygen was measured with an Orion 3 Star dissolved oxygen meter equipped with a semi-permeable to gas membrane electrode, with Thermo Scientific 081010MD temperature compensation.

Radiometer CDM 210 conductivity meter was used to conductivity control.

Calcium ion concentration was determined by atomic absorption spectroscopy.

3. Results and discussion.

3.1. Continuous bio-oxidation with polyurethane foam as biomass support material.

B10 bioreactor was operated to study continuous thiosalts bio-oxidation with sulphur-oxidising bacteria supported on polyurethane foam particles. The main challenge was to get thiosalts removal in F1 and F2 in steady state.

For this purpose, the bioreactor was started-up by the procedure previously presented. This method postulates inoculating with the TC culture, which is routinely maintained in a medium containing 3.5 g/L of tetrathionate and thereby is already adapted to metabolise thiosalts at that concentration. This start-up protocol is noticeably shorter (around two weeks) than that hitherto found in literature (Iglesias et al 2016), consisting of the adaption -in situ- to thiosalts of an iron-oxidising biofilm formed in a continuous bioreactor for ferrous iron bio-oxidation.

Once biofilm was formed, the B10 bioreactor was fed with F1; after 350 h, inlet solution was changed, and the bioreactor was fed with F2. In these two campaigns, liquid and air flow rates were 130 mL/h and 750 mL/min, respectively. In figure 2 inlet and outlet thiosalts concentrations are shown.

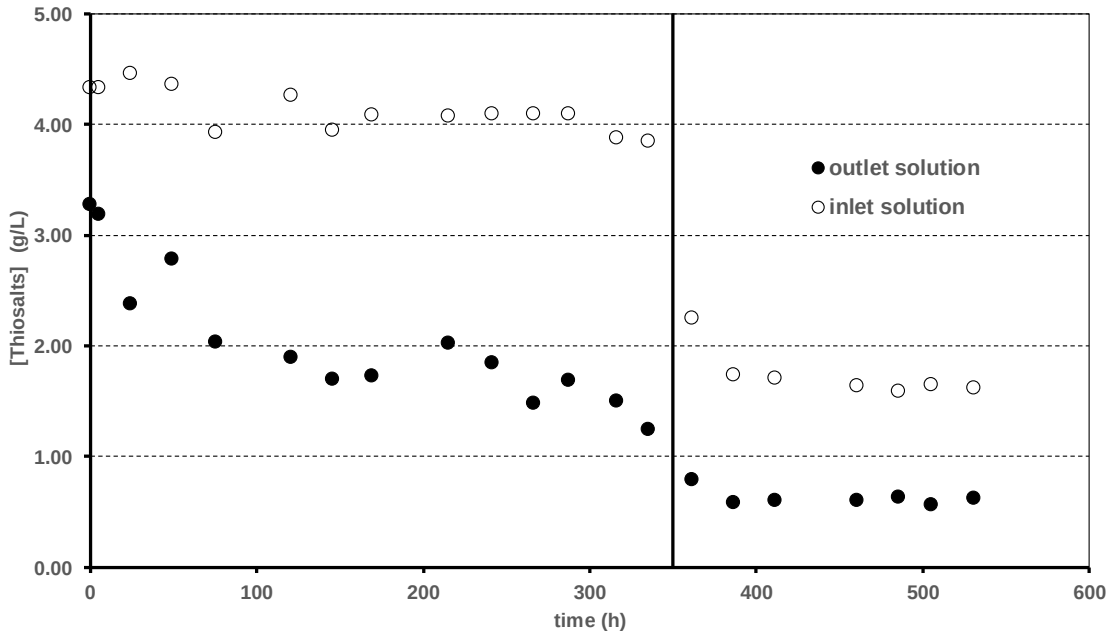

Figure 2: Thiosalts concentration in inlet and outlet solutions. Bioreactor B10. Feed: F1 and F2. Feed change from F1 to F2 at 350 h. Air flow rate:750 mL/min. Liquid flow rate: 130 mL/h. Room temperature.

Thiosalts bio-oxidation rates TBR were calculated by the equation (1) for each campaign (figure 3).

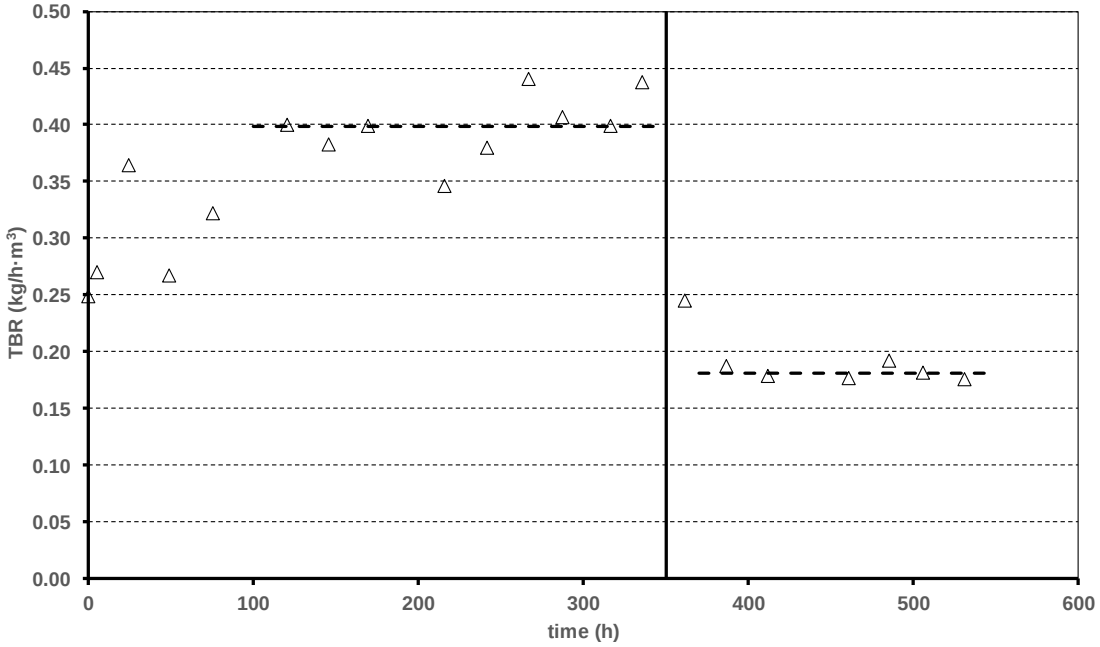

Figure 3: Thiosalts bio-oxidation rate. Bioreactor B10. Feed: F1 and F2. Feed change from F1 to F2 at 350 h. Air flow rate:750 mL/min. Liquid flow rate: 130 mL/h. Room temperature.

In figures 1 and 2, it can be seen it was feasible to achieve a stable continuous operation. In both campaigns TBR varied less than 10% for periods of time 35 times higher than the mean residence time of this bioreactor (5.9 h); in figure 3, these steady states are marked by dashed lines. In both campaign pH in outlet solution was close to 1.7.

Although thiosalts were not completely exhausted, the results suggest substrate limitation. When feed was changed from F1 to F2, substrate mass flow (calculated by equation 2) decreased from 0.54 g/h to 0.22 g/h resulting on a decrease of TBR from 0.39 to 0.18 Kg/hm^3.

The results suggest polyurethane foam can be considered a suitable material as biomass support for continuous thiosalts bio-oxidation. With this inert support, packed bed bioreactor performance can be easily controllable and versatile regarding thiosalts concentration.

3.2. Scale-up.

With a design similar to B10 bioreactor, the B200 bioreactor (table 1) was analogously inoculated, operated and fed with F1 and F2 in two campaigns. The differences between these two bioreactors are only geometrical, mainly in height (15 cm for B10 and 197 cm for B200). Air flow rate was likewise constant, although for B200 was 1000 mL/min. Liquid flow rate was gradually increased in order to prevent an excessive substrate limitation, thereby promoting conditions for increasing TBR.

Figure 4 shows thiosalts concentration in inlet and outlet solutions and oxygen concentration. Figure 5 presents TBR obtained at each liquid flow rate tested.

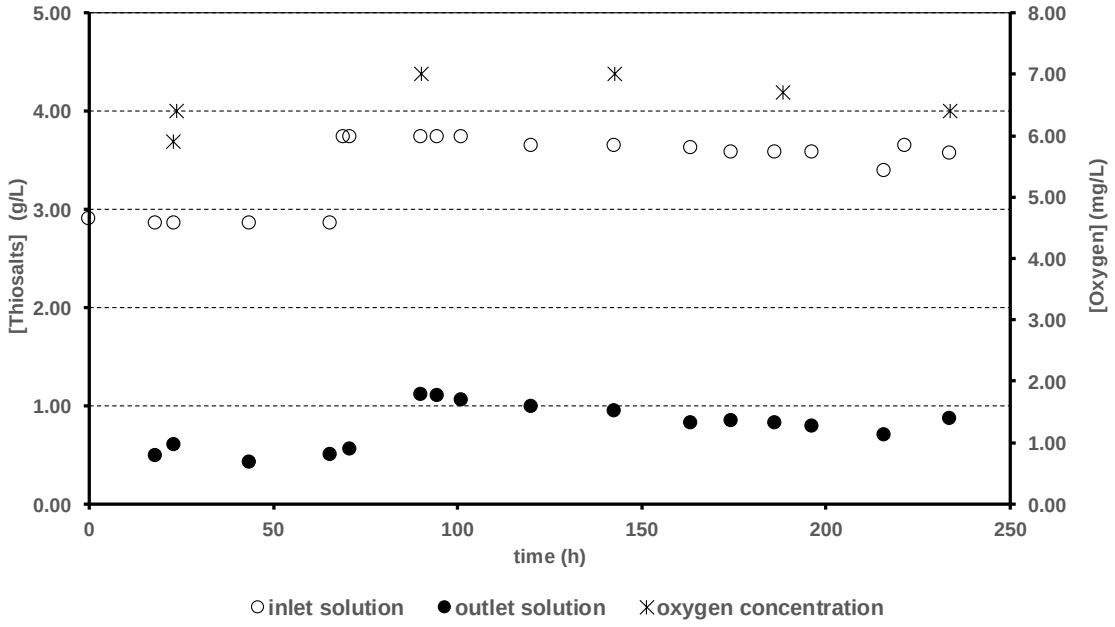

Figure 4: Thiosalts concentration in inlet and outlet solutions, oxygen concentration in solution. Bioreactor B200. Feed: F1. Liquid flow rate: 240 – 840 mL/h. Air flow rate: 1000 mL/min. Room temperature.

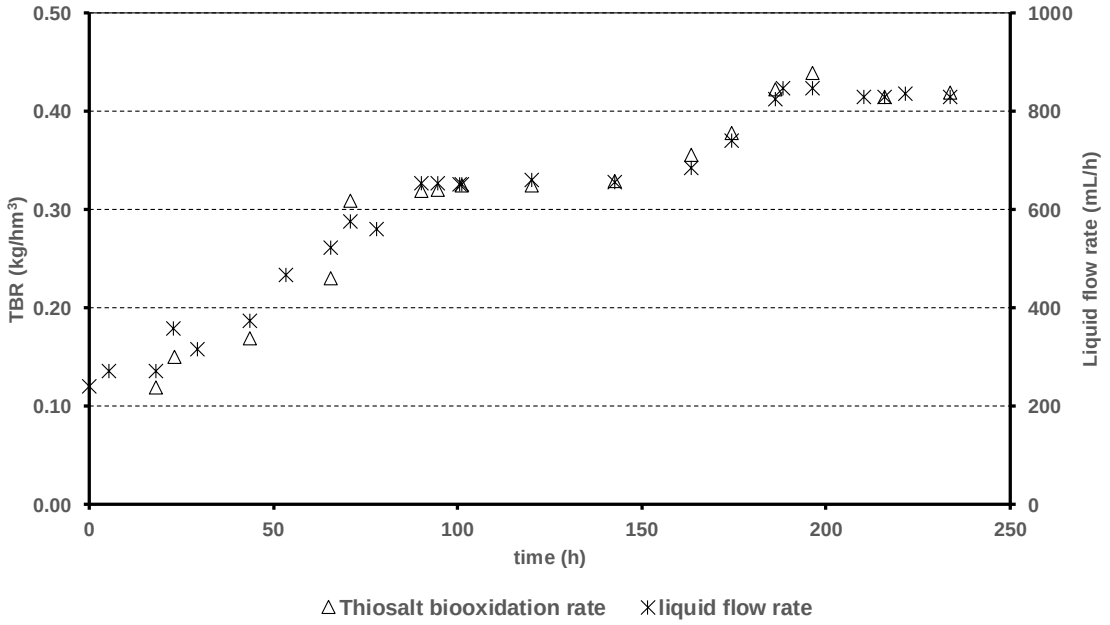

Figure 5: Thiosalts bio-oxidation rate. Bioreactor B200. Feed: F1. Air flow rate: 1000 mL/min. Room temperature.

Although complete bio-oxidation of thiosalts was not reached (figure 4), the operation was again limited by substrate, given that TBR quickly rose when liquid flow rate was increased (figure 5). In contrast, no aeration limitation was observed since oxygen concentration was always slightly lower than oxygen solubility, that is 7.1 mg/L (Mazuelos et al, 2016).

Figure 5 shows that two steady states were reached when liquid flow rate was close to 650 and 850 mL/h, denoting stability when liquid flow rate was kept constant. At highest liquid flow rate, TBR was close to 0.42 Kg/hm^3 with a thiosalts conversion of 77.5%.

Despite geometrical differences, similar TBR were obtained in B10 and in B200. If flow-dynamic were similar in both bioreactors, similitude in microbial activity inside them could be postulated.

A test was performed in order to determine residence time distribution in B200 when liquid and air flow rates were 820 mL/h and 1000 mL/min respectively. Literature reports ideal continuous stirred tank reactor model (CSTR) fits to experimental flow in continuous flooded packed bed bioreactors, although the longer the bioreactor is the closer to plug flow model (PF) the flow is; in this way, flow in bioreactors with size like B10 has been modelled by using CSTR model. For B200, Plug-flow reactor with a recycle loop model has been applied, since a behaviour of flow hybrid between PF and CSTR is postulated (Levenspiel, 2004, Fogler, 2006). In figure 6 conceptual diagram of this model is shown; k is an adjustable parameter which defines the recirculation ratio k/(k+1). When k = 0 we have PF model, and high values for k entails real flow like CSTR model.

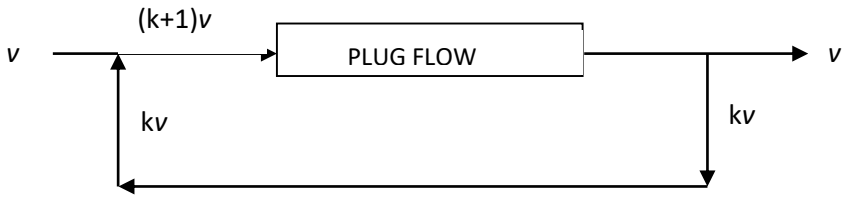

Figure 6: Conceptual diagram of plug-flow reactor with a recycle loop model.

For this model, normalised cumulative distribution function F(Θ) is given by equation (9):

$$1 - F(\theta) = \left[\frac{k}{k+1}\right]^{\theta(k+1)-1} \qquad (9)$$

In figure 7, 1-F(Θ) as a function of Θ is drawn for experimental and model data, when k was adjusted to 73. The curve of the model fits to experimental data (R^2=0.9990). This high value for k (recirculating ratio: 98.7%) allows to postulate flow like CSTR model.

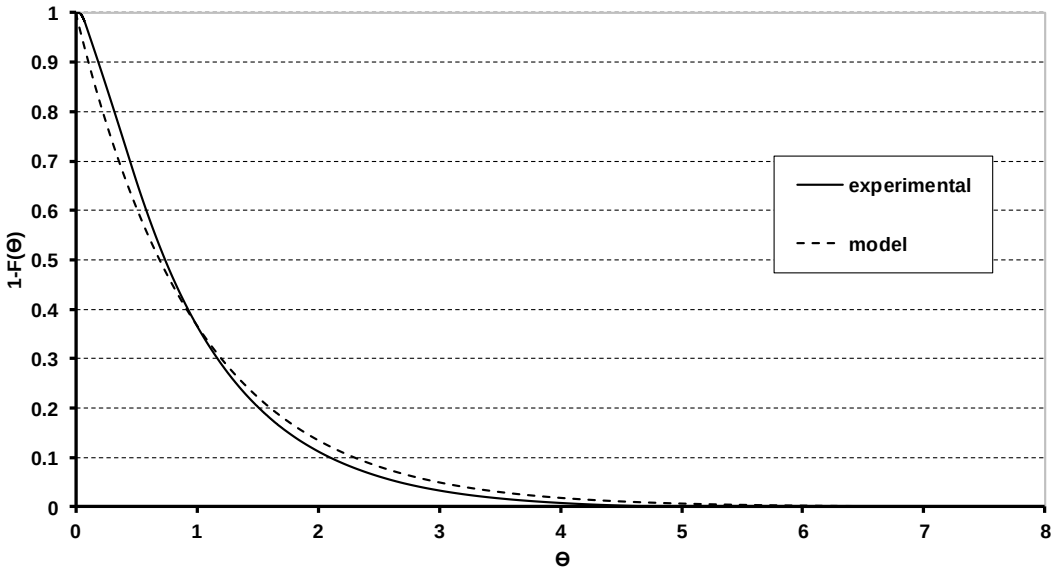

Figure 7: RTD for B200 bioreactor. Experimental data and plug-flow reactor with a recycle loop model. Liquid flow rate: 820 mL/h; Air flow rate: 1000 mL/min. Room temperature.

In figure 8, thiosalts concentration in inlet and outlet solutions when F2 was fed at different liquid flow rates are shown. Figure 9 presents the TBR obtained.

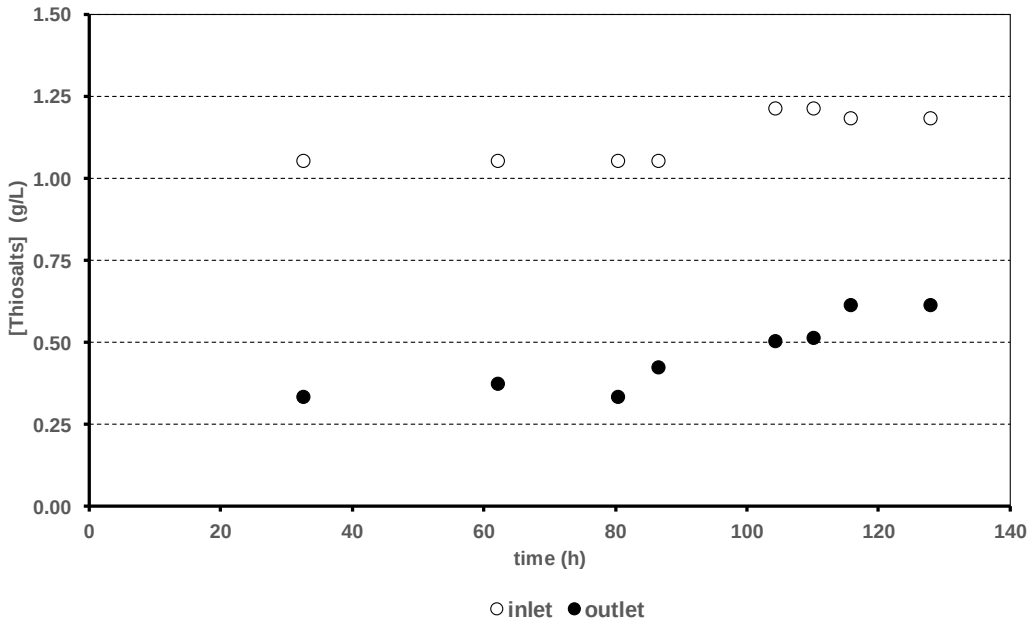

Figure 8: Thiosalts concentration in inlet and outlet solutions. Bioreactor B200. Feed: F2. Air flow rate: 1000 mL/min. Room temperature.

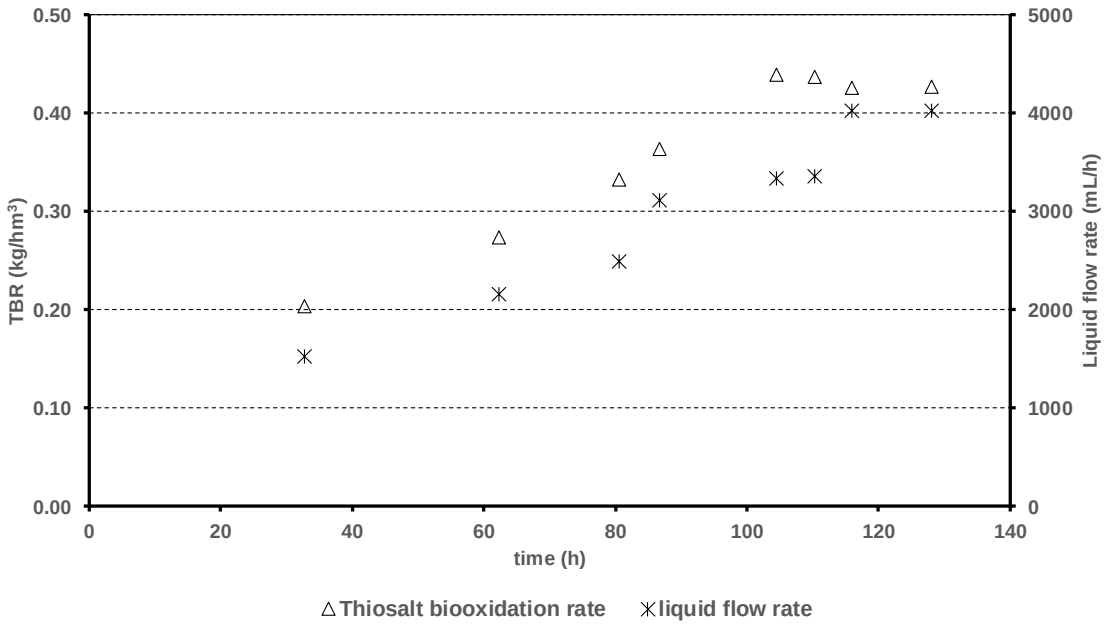

Figure 9: Thiosalts bio-oxidation rate. Bioreactor B200. Feed: F2. Air flow rate: 1000 mL/min. Room temperature.

Substrate limitation is observed again; bio-oxidation rate increased as liquid flow rate increased. In this campaign, TBR reached were similar to those obtained in preceding campaign (0.43 kg/hm3), but quintuplicating liquid flow rate (4 L/h), thereby decreasing residence time to 1.4 hours.

This design of bioreactor is versatile with respect to thiosalts concentration and liquid flow rate; it is feasible both, removing 75% of thiosalts in F1 with residence time lower than 6.5 h (figures 3 and 4) and removing 50% thiosalts in F2 (figures 7 and 8) with residence time lower than 1.5 h.

In order to study scaling up of bioreactor, it is interesting consider bio-oxidation rates per unit of base area instead of per working volume. For this purpose, TBR obtained in B10 and in B200 bioreactors were multiplied by its respective working volumes and, since they have different diameters, divided by respective base areas. Maximum bio-oxidation rates calculated in this way are 61 g/hm^2 for B10 and 719 g/hm^2 for B200, that is bio-oxidation rate is 12 times higher when height is multiplied by 13. The slight differences between these multipliers can be associated with running all experiments under substrate limitation conditions, which is typical for depuration targets.

It can be anticipated scaling-up for this kind of bioreactor can be simple and accurate.

3.3 Robustness.

Between the attributes necessary for implementation of bioreactors at commercial scale, functionality in the long term is required. B10 bioreactor was operated for 8000 hours in two campaigns. In figures 9 and 10 thiosalts concentration for inlets and outlet solution

and liquid flow rate are shown, when F1 and F2 were fed. In both campaigns air flow rate was 750 mL/min.

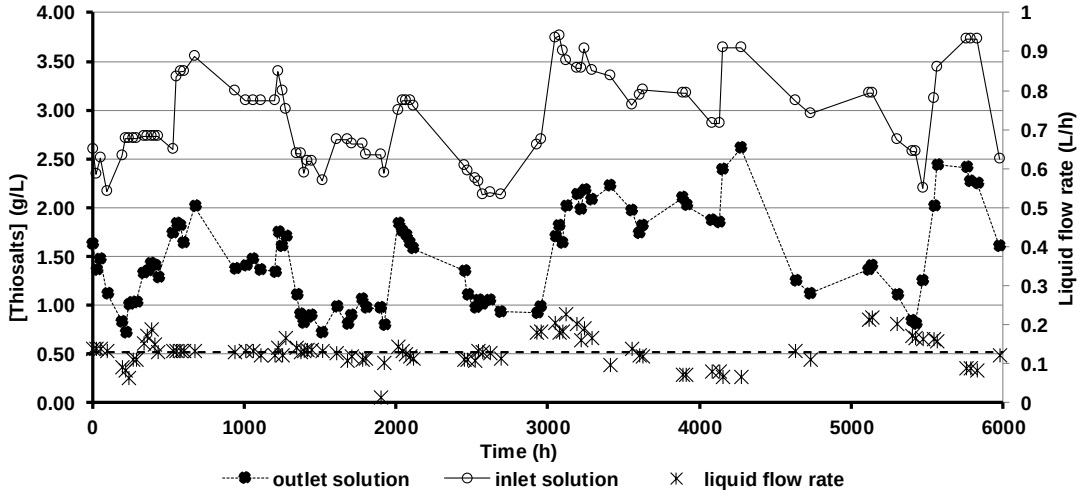

Figure 10: Thiosalts concentration in inlet and outlet solutions and liquid flow rate. Bioreactor B10. Feed: F1. Air flow rate: 750 mL/min. Room temperature.

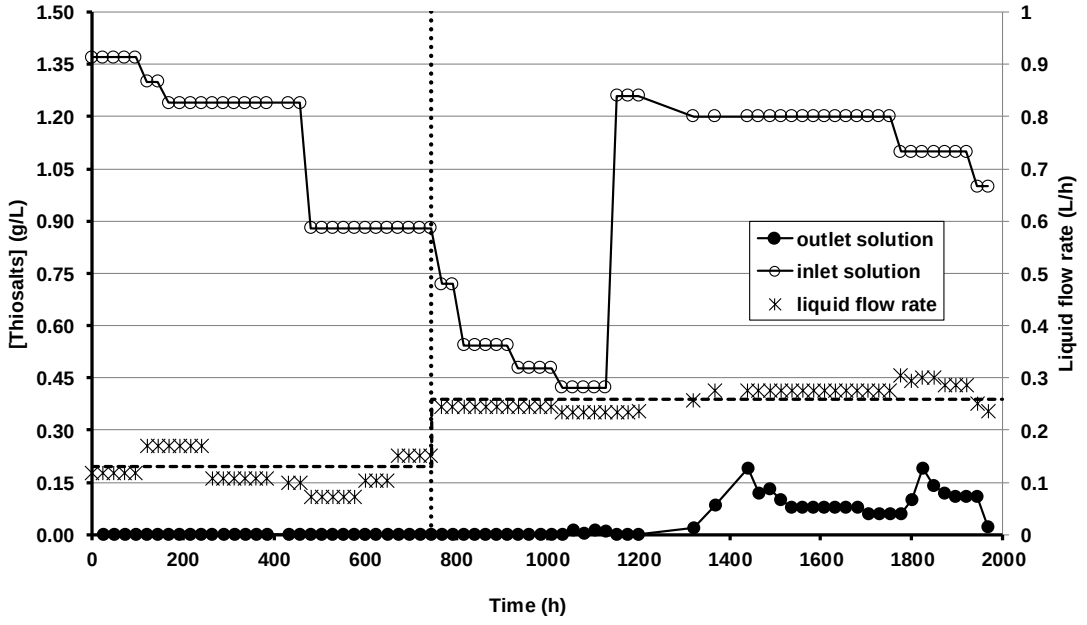

Figure 11: Thiosalts concentration in inlet and outlet solutions and liquid flow rate. Bioreactor B10. Feed: F2. Air flow rate: 750 mL/min. Room temperature.

For these tests, around 800 L of F1 and 400L of F2 were fed. Due to the duration of continuous operation was almost a year, several batches of real liquors were collected from the industrial plant at both cold and warm seasons. For this reason, Frequent and large fluctuations in feed can be observed in figures 9 and 10. It is interesting to underline in figure 10 similitude between curves of thiosalts concentration for inlet and outlet solutions. This analogy can be understood postulating a quick response given by the bioreactor in the face of changes in feed, with the implicit delay because of mix effect linked to CSTR model. This behaviour cannot be seen in figure 11 since most of the time thiosalts were completely removed.

This long operation, without interruptions and fluctuating feed, denotes robustness of this kind of design of bioreactor.

4. Conclusions.

Polyurethane foam is a suitable material as biomass support for continuous thiosalts bio-oxidation. It is a light material, thereby facilitating installation, maintenance and replacement of packed bed bioreactors. It is an inexpensive material that allows to get regular particles in shape and size according to design specifications.

Operation of bioreactors packed with polyurethane foam particles can be stable, easily controllable, versatile with respect to thiosalts concentration and robust in long term. Thiosalts conversion can be controlled from liquid flow rate and total removal of thiosalts

is feasible. Bio-oxidation rate of 0.42 kg/hm^3 can be achieved with residence times lower than 7 hours.

A new fast procedure for starting up of continuous bioreactor for thiosalts bio-oxidation has been proposed which allows to efficient continuous operation in less than a week.

Flow is close to CSTR model and scaling-up in height can be carried out from a simple geometrical proportionality.

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