Feasibility of S-rich streams valorization through a two-step biosulfur production process

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ABSTRACT

A bioscrubbing process named SONOVA has been developed, tested and assessed herein to valorize flue gases containing SO_x. The process consists in a first scrubbing stage, to absorb and oxidize SO_2 to sulfate, followed by a two-step biological stage. It consists of (1) an up-flow anaerobic sludge (UASB) reactor to reduce sulfate to sulfide with crude glycerol and (2) a continuous stirred tank reactor (CSTR) to partially oxidize sulfide to elemental sulfur (S^0). SONOVA integrates the reutilization of resources, using the effluent of the biological stage as a sorbent agent and the residual heat of flue gases to dry the product. S^0 is then obtained as a value-added product, which nowadays is produced from fossil fuels. In this research, SO_2 concentrations up to 4000 ppm_v were absorbed in 2 s of gas contact time in the spray-scrubber with removal efficiencies above 80 %. The UASB reduced up to 9.3 kg S-Sulfate m^{-3} d^{-1} with sulfide productivities of 6 kg S m^{-3} d^{-1} at an hydraulic retention time (HRT) as low as 2h. Finally, CSTR was fed with the UASB effluent and operated at HRT ranging from 12h to 4h without biomass wash-out. Sulfide was fully oxidized to S^0 with a productivity of 2.3 kg S m^{-3} d^{-1} at the

lowest HRT tested. Overall, this research has explored not only maximum capabilities of each SONOVA stage but has also assessed the interactions between the different units, which opens up the possibility of recovering S^0 from harmful SO_x emissions, optimizing resources utilization and costs.

Keywords: Biosulfur, bioscrubber, SOx emissions, integral process, UASB, flue gas valorization

1. INTRODUCTION

The combustion of sulfur containing matter results in SO_x formation which causes health impacts, acid deposition in the environment and visibility depletion if released to the atmosphere (EPA, 2019). Pigments industry, coal-based power generation plants or waste incineration facilities are some examples of the industries generating SO_x containing emissions. Pigments industry, in particular, utilizes a wide diversity of chemical compounds in innumerable formulations to manufacture products such as Ultramarine blue and Prussian blue, pigments which are mainly synthesized from sulfur and other additives such as natural clay or copper, respectively (Eastaugh et al. 2007). The Global pigments market size was valued at 20023 million USD in 2015 registering a Compound Annual Growth Rate (CAGR) of 4.1 % during the forecast period 2022 (Nathwani, 2016). Unfortunately, this industry generates harmful waste effluents since most of the manufacture processes occur at extreme conditions of temperature (up to 1000 ºC - 1200 ºC). As an example, the synthesis of S based pigments generates large amounts of SO_2 emissions, besides other byproducts such as nitrogen oxides and particles, that must be treated before their release to the atmosphere.

One of the most implemented treatment to remove SO_x from flue gases is wet flue gas desulfurization (WFGD) which (1) is costly due to the use of alkaline absorbents and (2) produces an alkaline sulfate-sulfite rich effluent that must be further treated before its

release to the environment (Srivastava and Jozewicz, 2001). In this sense, there is an arising need to propose and develop environmentally friendly and feasible technologies, both from technological and economical points of view, to valorize S-rich emissions. This is the case of SO_x contained in flue gases or S-rich waste liquid effluents, that could be transformed into elemental sulfur, a value-added product currently obtained from the petrochemical industry. Still and all, the high operating costs of recovery processes, together with demanding energy inputs, and in particular low market acceptance of the recovered material, handicap resource recovery (Kataki et al., 2016).

To this aim, a promising integrated bioscrubbing process, namely the SONOVA process, is proposed in this work to valorize SO_2 contained in flue gases**.** The process consists of: (1) the scrubbing of SO_2 from flue gas using slightly alkaline absorbents, and the treatment of scrubber liquor through (2) the biological reduction of sulfite and/or sulfate to sulfide (using crude glycerol as carbon source and catalyzed by sulfate reducing bacteria) and (3) the partial oxidation of sulfide to elemental sulfur (performed under micro-aerophilic conditions and catalyzed by sulfide oxidizing bacteria). The biological stage of this process (sulfate reduction and sulfide partial oxidation) could be also applied to the treatment of sulfate-laden effluents, even without organic content, such as pulp and paper industry effluents or saline wastewater. The competitiveness of the overall bioscrubbing process proposed in this work is based on the use of biological processes to recover elemental sulfur as a value added product reusing energy (energy contained in flue gases can be reused for elemental sulfur drying) and resources (the effluent from the bioscrubbing process can be reused for boosting SO_x absorption). In general, the most well-known application of S-rich effluents valorization, instead of to recover elemental sulfur, is to treat acid mine drainage (AMD) since this type of waste contains metals, commonly precious or heavy metals, and sulfate. The biological reduction of sulfate

contained in AMD allows precipitating metals with sulfide to afterwards be valorized or not depending on the added value of the recovered metals (Christensen et al., 1996; Jong and Parry, 2003; Neculita et al., 2007). Apart from this last application, only few studies can be found in the literature focused on sulfur recovery from SO_x emissions or S-rich effluents (Chuang et al., 2005; Jiang et al., 2013; Sun et al., 2018; Zhang et al., 2018), and most of them require either using easily biodegradable and/or expensive carbon resources or treating low S loads (< 2 kg m^{-3} d^{-1}). Jiang et al. (2013) reported excellent results applying the SANI process although required sewage and nitrogen sources to valorize S-containing effluents. Zhang et al. (2018) reported a smart alternative to the SANI process, targeting biosulfur production, to treat specifically sulfate-deficit wastewater and also required the use of domestic wastewater for sulfate reduction; and Sun et al. (2018) developed a novel bio-FGD system configuration to eliminate SO_2 and NO from flue gases although requiring the application of a quartz sulfur condenser to separate the final product and concluding that, the process could be profitable if the operational parameters could be further optimized and if wastewater was available. Other studies propose both biological steps (sulfate reduction and sulfide oxidation) in a single reactor with successful results and less investment costs but probably with complex downstream procedures for sulfur recovery or low sulfur purities (Philip and Deshusses, 2003; Xu et al., 2012).

Regardless the product targeted from S-rich effluents valorization, the supply of an organic carbon source is required if the first biological step, i.e. the reduction of sulfate, is performed heterotrophically. Many organic sources have been used in other studies to reduce sulfate such as VFAs (Celis-Garcia et al., 2007; Garcia-Solares et al., 2014), ethanol (Nevatalo et al., 2010) or lactate (Bertolino et al., 2014) among others (Liamleam and Annachhatre, 2007). However, industrial applications are every time more limited by

the costs of the carbon source to get not only technically feasible processes but also economically feasible processes. The use of wastes is an economical alternative to efficiently reduce sulfate (Jian et al., 2013; Barrera et al., 2014; Fernandez-Palacios et al., 2019; Mora et al., 2018; Sahinkaya et al., 2013). As an example, crude glycerol, an organic waste that has been traditionally valorized as biogas through anaerobic digestion (Lopez et al., 2009; Viana et al., 2012) or as biohydrogen through dark fermentation (Haron et al., 2018), has been also proven to be a potential electron donor for sulfate reduction (Mora et al., 2018; Santos et al., 2018; Fernández-Palacios et al., 2019). Crude glycerol is an attractive waste for being an inexpensive carbon source and highly available since it is the byproduct of the biodiesel production process. As reported by Kolesarova et al. (2011) and Yang et al. (2012) a surplus of crude glycerol is forecasted due to the growth of the biodiesel industry. Crude glycerol is also impure since it can contain methanol, soaps, FAMEs (fatty acid methyl esters) and inorganic elements (calcium, phosphorous, magnesium, sulfur). However, in the SONOVA process the utilization of crude glycerol avoids the supplementation of nutrients and trace metals to the anaerobic sludge, which are generally necessary in anaerobic digestion processes (Singh et al., 1999), since they are all contained in the organic source.

Regarding partial sulfide oxidation (the last step of the SONOVA process) several works have been published reporting elemental sulfur recovery with suspended biomass (Krishnakumar et al., 2005; Zytoon et al., 2014; Zhang et al., 2018). However, few of them treats effluents from sulfate reduction processes using waste organic effluents, which implies the presence of by-products from biological degradation and, frequently, high free ammonia loads besides the absence of nitrate or nitrite. Moreover, the quality of the elemental sulfur produced is not usually determined; neither proposed or tested the downstream procedure to recover and purify biosulfur, which is important since it is the

126 final product of the process. This is the main reason why sulfide oxidizing biomass is
127 cultivated as a suspended culture in a continuous stirred tank reactor (CSTR) in this study,
128 instead of being cultivated as an immobilized culture.
129 Then, the aim of this research was to demonstrate the feasibility of a bioscrubbing process
130 to valorize SO_2 contained in flue gases through the development, operation and
131 optimization of a sequential Scrubber-UASB-CSTR system to obtain a valuable product,
132 as is elemental sulfur, using crude glycerol. The process proposed in this work is
133 challenging since it targets not only the optimization of SO_2 absorption but also the sulfate
134 reduction minimizing the production of methane. The process also couples the cultivation
135 of suspended sulfide oxidizing biomass to separate more efficiently the elemental sulfur
136 produced. Furthermore, the development of this research allowed obtaining the maximal
137 capabilities of each of the stages besides valuable data from different operating scenarios.

138 2. MATERIALS AND METHODS

139 2.1 Experimental setup and assays performed to assess SO_2 absorption efficiencies

140 A lab-scale spray-scrubber was constructed and operated separately to characterize the
141 wet-absorption of SO_2 under different operating conditions. Detailed information and the
142 schematic of the absorption unit is presented in the Supplementary Material (Section S1,
143 Figure S1).
144 A series of absorption assays were performed with two different sorbents (1) slightly
145 alkaline solution and (2) effluent of the biological process. The second sorbent was used
146 in order to evaluate the effect of its composition over the SO_2 absorption efficiency
147 compared to that obtained with the alkaline solution. The characterization of SO_2 wet-
148 absorption was performed by assessing the influence of both the gas contact time and gas-
149 absorbent (L/G) ratio. The experimental conditions of wet-absorption tests are shown in
150 Table 1.

Table 1. Experimental conditions tested during the characterization of SO_2 absorption

Absorbent	Inlet SO_2 (ppmv)	L/G (L/m^3)	Gas contact time (s)	$pH_{initial}$
Alkaline absorbent	2000	5 - 15	0.6 - 4	8.0
Bioprocess effluent	2000 - 4000	5 - 15	0.6 - 4	7.4

Since the SONOVA process considers the recovery of energy from flue gases to obtain a dry bioproduct, the temperature of flue gases to be valorized is anticipated to be below 80ºC. A set of experiments was previously performed at temperatures ranging from 40ºC to 80ºC to assess the SO_2 removal efficiency (see Table S1). It was proven that under the conditions set in the present study, temperature was not affecting the performance of the absorption unit and hence this parameter was not controlled.

A Labview interface was used for the monitoring of SO_2 concentration at the outlet gas and pH and ionic conductivity in the liquid effluent. Experiments were performed until constant SO_2 concentration, feeding fresh absorbents continuously to ensure constant pH and composition in the liquid phase during SO_2 absorption. The performance of the SO_2 absorption process was evaluated in terms of removal efficiency. To ensure experiments accuracy, three replicate measurements were made, obtaining relative errors below 5%. In this paper only average values are shown.

2.2 Experimental setup and operating conditions for biosulfur production

The experimental setup for biosulfur production, from a mimic of S-rich wastewater, consisted of a sequence of two reactors (Figures S2 and S3, Supplementary Material). The first reactor was an up-flow anaerobic sludge bed (UASB) reactor for sulfate reduction with a total volume of 2.5L and an effective volume (sludge bed volume) of 1L. Start-up and initial operation of the UASB were performed as described in a previous

work (Fernández-Palacios et al., 2019). As previously reported (Mora et al., 2018), the optimal conditions found to promote sulfidogenesis from a methanogenic granular sludge using crude glycerol as the organic carbon source were: T=35ºC, pH=8.5, COD/S-Sulfate ratio above 7.0 g O_2 g^{-1} S-SO_4^{2-}, microaerophilic conditions and sulfide concentrations under 250 mg S^{2-} L^{-1}. Nevertheless, COD/S-Sulfate ratio in the influent was set below 6 g O_2 g^{-1} S-SO_4^{2-} since it has been demonstrated that the limitation of COD promotes sulfidogenesis and minimizes biogas production in sulfidogenic UASB reactors (Mora et al., 2018). The UASB was fed with synthetic mineral medium for a better evaluation of biosulfur production from a controlled sulfate-rich influent. Detailed information about the experimental setup and operating conditions can be found in the Supplementary Material (section S2).

The second reactor was a glass-made continuous stirred tank reactor (CSTR) with a volume of 6 L. The CSTR was used for biosulfur production, under microaerophilic conditions, from the partial oxidation of sulfide produced in the UASB. Then, the influent of the CSTR was the effluent of the UASB. Moreover, the supernatant of the CSTR effluent was tested as liquid absorbent for SO_2 removal in the absorption unit (Table 1, bioprocess effluent). Microaerophilic conditions in the CSTR were assured by transferring the oxygen from the headspace to the liquid phase through mechanic agitation. The pH in the reactor was monitored and registered.

The startup of the UASB-CSTR system was performed with two different inocula to speed up the startup of both reactors with specific biomass. The UASB was inoculated with settled granular sludge from an anaerobic digester treating wastewater in a paper recycling company. As reported by Pol et al. (2004), the use of granular sludge allows loading rates in UASB reactors far beyond the common loading rates applied in conventional activated sludge processes due to two main factors: a) the superior settling

characteristics and b) the high specific activities of granular sludge. On the contrary, the CSTR was inoculated with 6 L of sulfide oxidizing sludge obtained from a bioscrubber for biogas desulfurization.

The abovementioned reactors were operated under pseudo-steady conditions in order to assess the feasibility of the process. Two different sets of short-term assays were performed in the experimental setup to explore the limits of the two-step bioprocess. The first set was performed in the UASB during 60 h and consisted of varying the sulfate inlet concentration every 12 h (from 100 mg S L^{-1} to 1000 mg S L^{-1}) maintaining a COD/S-Sulfate ratio of 15 g O_2 g^{-1} S. The second set of assays was performed in the CSTR during 4 days and consisted of decreasing the HRT (from 12 h to 4 h) by changing the liquid level and hence the reaction volume in the CSTR. In Table 2 the summary of the operating conditions and the short-term assays conditions are presented.

Table 2. Conditions tested in the two-step experimental setup for biosulfur production

	Period I	**Period II**	**Ending period**	**SLR Assays**	**HRT** Assays**
Reactor	UASB	UASB	UASB	UASB	CSTR
Time (d)	0 - 99	99 - 115	115-120	65	117-120
HRT_{UASB} (h)	1.81±0.25	2.19±0.14	2.29±0.25	1.74	2.14±0.18
HRT_{CSTR} (h)	12	12	12	12	12 8 6 4
S inlet (mg S L^{-1})	235±17		451±7	100 250 500 750 1000	398±2

SLR ($kg\ S\ m^{-3}\ d^{-1}$)	2.42±0.54	2.47±0.39	4.63±0.48	1.4 3.5 7.0 10.5 14	0.8 1.2 1.6 2.4
OLR ($kg\ O_2\ m^{-3}\ d^{-1}$)	10.23±2.29	12.72±1.12	15.3±1.63	22 53 98 151 200	2.8 4.2 5.5 8.3
COD/S ($g\ O_2\ g^{-1}\ S$)	3.90±0.89	5.35±0.61	5.63±0.68	15	3.5

**SLR and OLR are sulfate and organic loading rates calculated taking into account the granular sludge bed volume. **Values calculated for HRT assays in the CSTR take into account the inlet sulfide and COD concentrations contained in the UASB effluent.*

The ending period consisted of increasing both the SLR and OLR in the system, maintaining the COD/S-Sulfate ratio, to increase the COD concentration in the effluent of the UASB and, subsequently, to assess the COD removal efficiency in the CSTR during the HRT assays. The SLR range treated in the CSTR during the HRT assays is refered to the sulfide loading rate considering the concentration of sulfide present in the effluent of the UASB during the HRT assays. The OLR range treated in the CSTR during the HRT assays was also calculated based on the COD concentration present in the effluent of the UASB during the HRT assays.

2.3 Jar tests for biosulfur precipitation and sedimentation

A series of jar tests were performed with different combinations of coagulants and flocculants to assess the precipitation and sedimentation efficiency of biological sulfur. Each test was performed at room temperature (18-20 ºC) with 200 mL of effluent from the CSTR (pH = 7.4). Agitation cycles of 1 min mixing at 200 rpm followed by 1 min mixing at 70 rpm and 15 min without mixing were applied to evaluate the performance

of each additive added to the samples. Two different cationic coagulants were initially tested, one with linear molecular structure (FL4820) and another with slightly branched molecular structure (FL3050) both supplied by SNF Group, France. Five different concentrations of each coagulant were applied (from 0.1 to 1 %), as recommended by the supplier. The supernatant turbidity was also analyzed at the beginning and at the end of each test to assess the efficiency of the process. Afterwards, the coagulant showing better results, in terms of % settled solids, was combined with different dosages of cationic (from 0.03 to 0.3 % of FO435, SNF Group, France) and anionic (from 0.1 to 1 % of HIMOLOC, Derypol, Spain) flocculants, as recommended by the suppliers. Settled solids, obtained from those tests showing optimal results, were also analyzed to determine sulfur purity and hence to assess the effect of coagulant and flocculant addition to the quality of the final product.

2.4 Analytical methods

2.4.1 Liquid phase analyses

Sulfate (SO_4^{2-}) and thiosulfate ($S_2O_3^{2-}$) concentrations were analyzed off-line by ion chromatography using suppressed conductivity detection (ICS-2000, Dionex Corporation). Chemical Oxygen Demand (COD) was analyzed off-line using COD commercial kits and a photometer (Lovibond®). Ionic conductivity and pH were continuously measured in the scrubber with a multi-analytic probe (Multi 3420, WTW, Germany). Oxidation-reduction potential (ORP) and pH were monitored in the UASB and CSTR with probes (Crison pH5333 and ORP5353, Hach Lange, Spain) connected to a multimeter (Crison MM44, Hach Lange, Spain). Sulfide concentration was analyzed off-line with a sulfide selective electrode connected to a benchtop meter (Symphony, VWR) after conditioning the samples with sulfide antioxidant buffer (SAOB). The SAOB composition was (g L^{-1}): ascorbic acid (35) and EDTA (67) dissolved in NaOH (2M).

VFA were analyzed by gas chromatography (7820A, Agilent Technologies) equipped with a DB-FFA column and using a flame ionization detector (FID) with helium as carrier gas. Prior to VFA analyses, samples were prepared as follows (Montpart, 2014). A volume of 0.6 mL of sample was pipetted to a 1.5 mL glass vial. Afterwards, 0.15 mL of a preserving solution and 0.75 mL of deionized water were added to the vial and kept at -20 ºC until analyzed. The preserving solution was meant to deproteinize the sample and to be used as internal standard. It contained (g/L): $HgCl_2$ (2), ortophosphoric acid (33.7) and hexanoic acid (2) (internal standard).

2.4.2 Gas phase analyses

SO_2 concentration in the outlet gas phase of the scrubber was performed using an electrochemical SO_2 sensor (SO2-B4, Alphasens, UK) with a measuring range from 0 to 2000 ppmv. The measurement of higher SO_2 concentrations required flue gas dilution, performed by two flowmeters (2100, Tecfluid, Spain). CH_4, CO_2 and H_2S contained in the gaseous effluent of the UASB were analyzed by gas chromatography (HP 5890, Hewlett Packard) equipped with a Porapack Q column and a thermal conductivity detector (TCD) with helium as carrier gas. The volume of the gas produced in the UASB reactor was analyzed following the Gas Bag Method (GBM) presented in Ambler and Logan (2011) using gas chromatography (7820A, Agilent Technologies) equipped with an HP-Mole Sieve column, a thermal conductivity detector (TCD) and using argon as the carrier gas. The GBM procedure consisted basically of measuring the initial composition of the collected gas in the bag, adding a known volume of tracer gas (nitrogen gas in this case) and analyzing the new composition. From these two analyses (before and after the tracer injection) the initial volume of gas could be calculated from mass balances (Baeza et al., 2017).

2.4.3 Solid phase analyses

The sludge contained in the riser of the UASB was sampled after 50 days of operation and was analyzed, together with a biosulfur sample, to obtain the granular size distribution (GSD) using laser diffraction based technology (Mastersizer 2000, Malvern Panalytical Ltd.) and total and volatile suspended solids (TSS and VSS, respectively) following the standard method analysis (APHA, 2005). Biosulfur (centrifuged sample from the CSTR) and sedimented solids from jar tests were also analyzed to obtain the main characteristics of the product. Sulfur purity was determined from the elemental analysis of centrifuged and lyophilized samples with a Flash EA 2000 CHNS instrument (Thermo Fisher Scientific) connected to a microbalance (MX5, Mettler Toledo). In the case of biosulfur, a thermogravimetric analysis (TGA) was also performed using a differential scanning calorimeter (449 F1 Jupiter, NETZSCH) in order to assess the effect of heat and air over the stability of biosulfur. DSC allows measuring enthalpy changes in samples due to changes in their physical and chemical properties as a function of temperature or time. Information about the melting point of biosulfur or the energy associated to its oxidation can be obtained with TGA.

3. RESULTS AND DISCUSSION

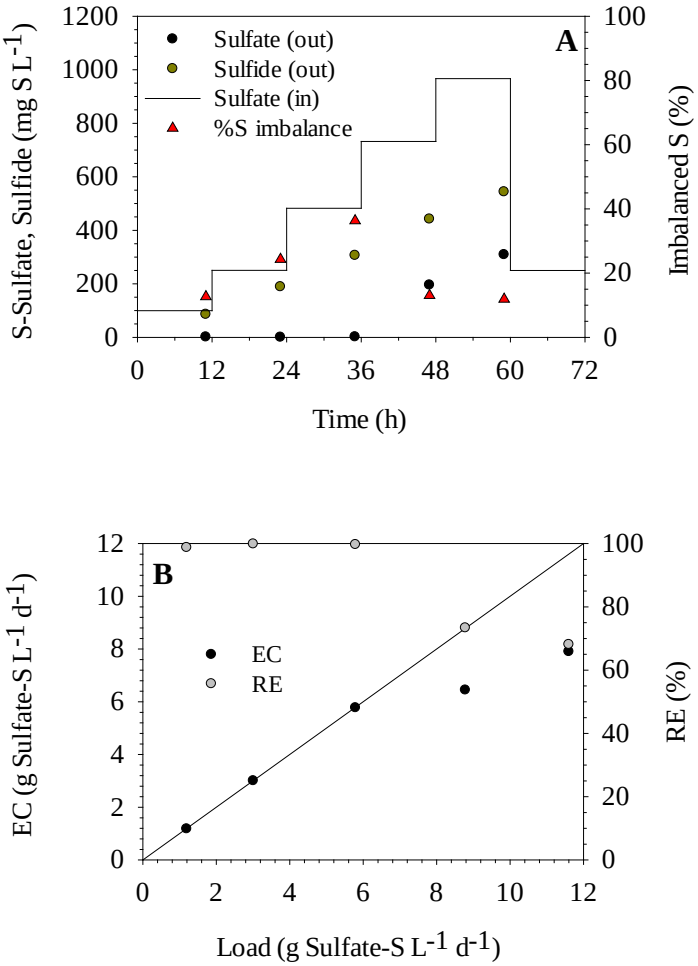
3.1 Technical feasibility and operation limits of the biological units

The technological feasibility of the sequential UASB-CSTR experimental setup utilized for biosulfur production was assessed in this work. Both reactors were connected from the beginning of the operation and their performance monitored during 120 days. In the Supplementary Material (section S3) the overall performance of the biological units is described in detail.

Short-term SLR assays (Table 2) were performed after 65 days of operation when the S-RE achieved in the UASB was 100 %. The results obtained from this first set of short-

term assays in the UASB are presented in Figure 1. As can be observed in Figure 1A, the S-EC of the UASB reactor, operated at such a low HRT (2h) and under non limiting COD availability, allowed treating inlet concentrations of sulfate as high as 1000 mg S L^{-1} with 68.1 % S-RE (maximum elimination capacity of 389 mg S L^{-1} h^{-1} or 9.3 kg S m^{-3} d^{-1}). This value is comparable to that obtained by Bijmans et al. (2008) (9.7 kg S m^{-3} d^{-1}) using formate and higher than the S-EC obtained by Nagpal et al. (2000), Nevatalo et al. (2010) and Kaksonen et al. (2006) using ethanol at 30-35 ºC (S-EC up to 3.8 kg S-Sulfate m^{-3} d^{-1}). The high S-EC obtained in this work is most probably related with the absence of the liquid phase recirculation during the UASB operation. The presence of sulfide in the recirculation could interfere negatively in the hydrolysis of crude glycerol, mainly happening in the first part of the sludge bed as previously reported by Fernandez-Palacios et al. (2019), worsening the performance of the UASB.

Regarding the sulfur mass balance it was observed that sulfide production did not correspond to sulfate reduction. As can be observed from the experimental data presented in the Supplementary Material (section S3), sulfur imbalance tends to increase when COD increases. This phenomenon is caused by the production of organosulfur compounds, which leads to require further research in order to enhance the yield of sulfate reduction to sulfide, instead of to other intermediate compounds. The production of intermediate compounds, such as organosulfur compounds, causes a decrease of elemental sulfur productivity and an increase of oxigen consumption in the CSTR.



326 **Figure 1.** Sulfate loading rate assays performed in the UASB. A) Sulfate and sulfide
327 concentrations in each hydraulic steady state and B) S-EC and S-RE obtained in each hydraulic
328 steady state.

329

330 On the other hand, the HRT assays (Table 2) were performed at the end of the operation,
331 once the SLR and OLR were doubled (Ending period, Table 2). The aim of this last
332 operation period was to obtain higher COD concentration in the effluent of the UASB
333 since until day 115 the COD was almost depleted (section S3, Figure S4B, Supplementary
334 Material). The COD increase allowed assessing 1) the competence between heterotrophic
335 and autotrophic bacteria and 2) the COD removal efficiency (COD-RE) in the CSTR

under different HRT. In Figure 2, the results obtained from this second set of short-term assays are presented.

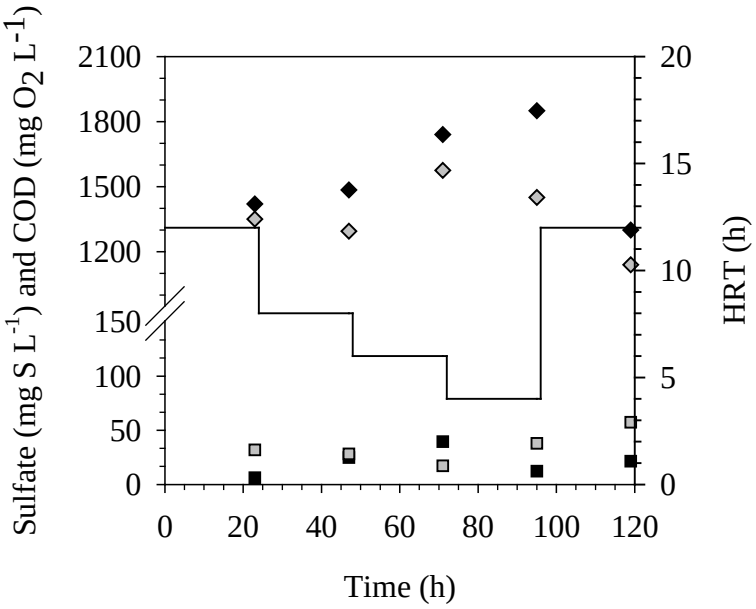


Figure 2. HRT assays performed in the CSTR. HRT (solid line), sulfate in the influent (black square), sulfate in the effluent (grey square), COD in the influent (black diamond) and COD in the effluent (grey diamond).

Sulfide was not detected at any HRT tested. Sulfate in the effluent of the CSTR was similar or higher than sulfate in the influent which indicated the full capacity of the culture to oxidize partially sulfide to sulfur. Sulfur productivities up to 95 mg S L^{-1} h^{-1} (or 2.3 kg S m^{-3} d^{-1}) were obtained at the lowest HRT tested (4 h). COD was also monitored and it was observed that the CSTR had a certain capability of COD degradation although the maximum removal efficiency calculated was 26.3 % at the lowest HRT tested. On the one hand, this result could indicate that heterotrophic bacteria were outcompeting SOB for the oxygen. However, the high dilution rate set in the CSTR together with the increasing SLR could also improve the adsorption of the organic matter on the surface of the elemental sulfur particles (Meerburg et al., 2015). As has been reported in other

studies, biosulfur has hydrophibicity and contain organic compounds on its surface such as long-chain polythionates or proteins (Kleinjan et al., 2003). Then, biosulfur composition and structure probably enhanced COD adsorption improving COD-EC and COD-RE at such a low HRT (4 h).

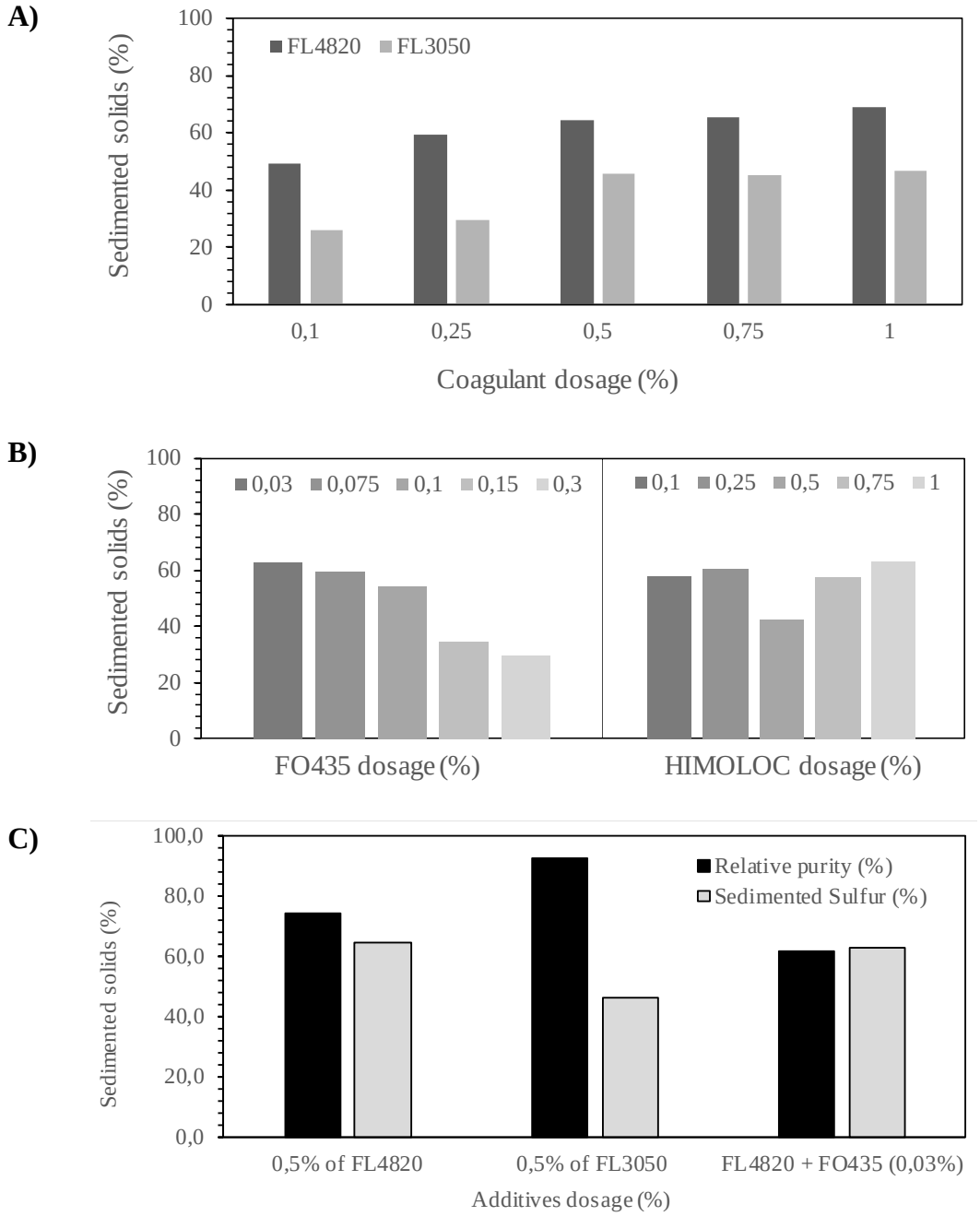
VSS concentration in the CSTR at HRTs of 12 h and 4 h was 660±10 mg L^{-1} and 555±7 mg L^{-1} which confirmed, together with the absence of sulfide and the production of sulfate, that the biomass was not washed-out at such a low HRT (4 h). The TSS and VSS concentrations at each HRT had alike values indicating that the suspended matter sampled in the CSTR was only organic (mainly biomass and sulfur).

3.2 Biosulfur quality and recovery process

Biosulfur was analyzed to obtain more information about the characteristics of the product and to propose an adequate procedure for its recovery. The analysis of the particle size distribution was performed as a first step. From this analysis a volume weighted mean of 39.8 µm, with a specific surface area of 0.748 m^2 g^{-1}, was obtained. This size was much bigger (10x) than that reported by Janssen et al. (2009) and Kostrytsia et al. (2018) for biosufur particles, although biosulfur produced in this study did not show any settling capacity in 1 h of Imhoff test.

The elemental analysis of biosulfur was also performed to obtain its purity and organic content. Two samples of suspended biosulfur were centrifuged at 10000 rpm during 2 min. The humidity content measured after the centrifugation of both samples was 46 %. Then, the first sample was lyophilized and homogenized (S_1, named raw biosulfur). The second sample was also lyophilized and homogenized after the layer of biomass deposited on the centrifuged sulfur was removed (S_2). The result of the elemental analysis is presented in Table S2 (section S4, Supplementary Material).

Sulfur content in S_1 was 87.5 %, which could be already adequate for some applications of this product. Instead, the sulfur purity in S_2 was almost 95 % with carbon content lower than 3.5 %. This result indicates that an effective centrifugation of both solids could be an adequate treatment to have a biosulfur with high quality; however, costs associated to this specific separation process are considerably higher than those required for sedimentation. As mentioned above, raw biosulfur sedimentation through the addition of chemical agents (coagulants and flocculants) is an economical alternative to centrifugation. In this case, Jar tests were certainly helpful to evaluate the % of biosulfur recovery (% of sedimented solids) and its final purity (Figure 3) after a coagulation-flocculation-sedimentation process. As can be observed in Figure 3A, the addition of the coagulant FL4820 had better results in terms of percentage of sedimented solids (SS) compared to coagulant FL3050. FL4820 presented at least 50 % of SS with the lowest dosage (0.1 %), while the addition of FL3050 uniquely generated 46.8 % of SS at the highest dosage tested (1 %). Although the optimal dosage of FL4820 was 0.5 % (64.4 % of SS), flocculation tests (Figure 3B) were performed with the maximal dosage tested since that was the one showing the highest % of SS (68.8%). In Figure 3B it can be observed that the addition of flocculants did not improve the % of SS. Results obtained with FO435 showed that the addition of cationic flocculants even worsened the % of SS, which was 49.3 % with a dosage of 0.03 % FO435. A different behavior was observed with the addition of HIMOLOC; nevertheless, the maximum % of SS (63.3 % of SS) obtained at the highest dosage (1 %) was still lower than that obtained adding uniquely the coagulant FL4820. These results highlighted the positive effect that minimal dosages of coagulant have over the sedimentation of solids without requiring other additives.



402 **Figure 3.** Effect of coagulants and flocculants over the sedimentation and quality of biosolids
403 produced in the CSTR. A) Addition of coagulants (FL4820 and FL3050) and B) addition of
404 flocculants (FO435 and HIMOLOC) combined with 1 % of FL4820 and C) comparison of purity
405 and % of settled sulfur obtained from the tests showing best results.

406

407 Other studies have been conducted to investigate the colloidal biogenic sulfur
408 flocculation. However, it is still a great challenge. As an example, Chen et al. (2015)

obtained successful results under different conditions than those set in this study. They found that the biogenic sulfur could be efficiently flocculated and separated although at pH 4.73, stirring speed of 129 r/min and a flocculant dose of 2.42 mg polyaluminum chloride mg^{-1} S. Jansen et al. (1996) also reported the difficulties associated to the aggregation of biosulfur (due to the multiple functional groups that it has) and the need to operate sulfide-oxidizing bioreactors at high loading rates to enhance the settleability of the sulfur sludge. Yuan et al. (2014) stated that the colloidal nature of biosulfur requires the addition of cationic coagulants to be separated. This is the same result obtained in the present study although worst % of sedimented solids have been obtained, probably due to the characteristics of the UASB effluent (salts, organic matter and organosulfur compounds content). As can be observed, a wide range of results about the recovery of biogenic sulfur are available in the literature indicating that there is not a definitive solution for all the biosulfur producing systems.

Settled solids from tests performed with 0.5 % of coagulant addition (both FL4820 and FL3050) and with FL4820 and 0.03 % of FO435 were analyzed to obtain the sulfur purity (Figure 3C). The elemental analysis of the settled biosulfur confirmed that the addition of coagulant and flocculants presented better % of SS than those obtained with the unique addition of FL3050, although the sulfur purity in the product was not so satisfactory (61.5 % sulfur purity). Dosages of 0.5 % of FL3050 presented high sulfur purities, nevertheless the % of SS was only 45.9 %. Then, the best performance was obtained with the addition of FL4820, which allowed obtaining a product with a sulfur purity of 74.3 % and 64.4 % of SS. However, a better approach is required to separate as much biosulfur as possible with the less investment in chemicals dosage which worsen the economic benefits of the process and the quality of the final product. Then, further studies should be conducted in

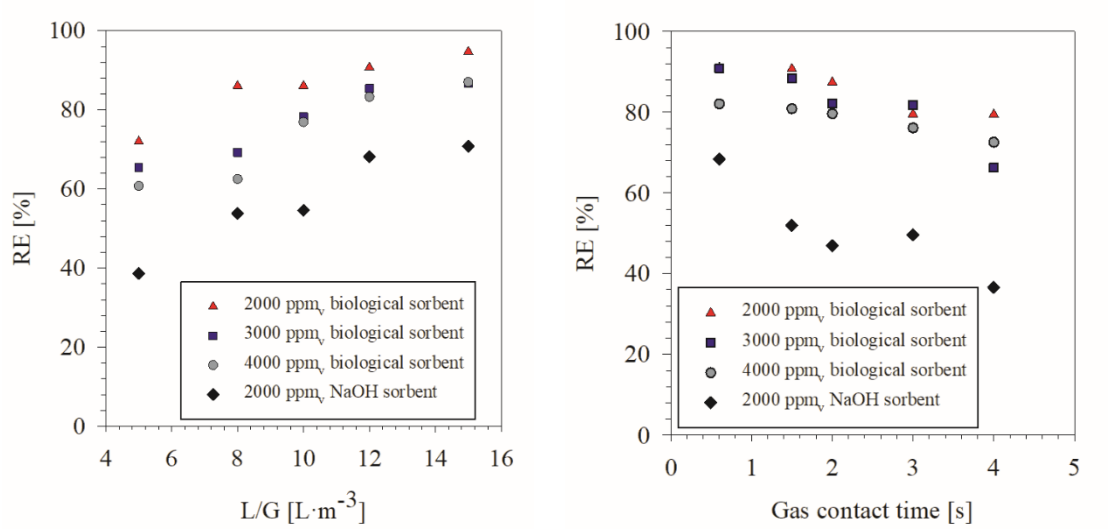
433 order to test tailor-made coagulants and flocculants for this specific application in order
434 to achieve higher % of SS and biosulfur purities.
435 Finally, the thermogravimetric analysis of non-lyophilized S_1 was performed since
436 lyophilization is not considered an economically feasible alternative to treat a product
437 without an important added value such as pharmaceutical or food products. To obtain
438 dried biosulfur a thermal treatment should be done. However, biosulfur could be melted
439 and oxidized to SO_2 when heated in the presence of air. For this reason, the
440 thermogravimetric analysis was performed not only with air but also with an inert gas. In
441 Figure S6 (section S5, Supplementary Material) the results from the gravimetric analysis
442 are presented. Profiles shown in Figure S6A (thermogravimetry performed with inert gas)
443 revealed that the melting point of biosulfur was 125ºC and, also, that biosulfur was
444 volatilized over 175ºC. From Figure S6B (air) it was observed that, biosulfur was
445 oxidized to SO_2 at 225ºC (enthalpy of -4513 J g^{-1}). Then, it was concluded that an
446 appropriate process to recover biosulfur from the CSTR could be a sequence of settling
447 after coagulant addition and air drying at T<100ºC. However, further research should be
448 done in order to obtain higher % of biosulfur recovery and to assess the effect of chemical
449 agents addition over the characteristics of the final product.

450 **3.3 Assessment of the SO_2 absorption system**

451 Results obtained from the absorption tests performed in the lab-scale spray scrubber under
452 different conditions are presented in Figure 4. It can be observed that L/G ratio and gas
453 contact time had a strong influence over the RE for each SO_2 concentration and type of
454 sorbent tested.

455

A) **B)**



456 **Figure 4.** Removal efficiencies of SO_2 absorption. A) At a gas contact time of 0.6 s depending
457 on the L/G ratio and B) at a L/G ratio of 7.5 L m^{-3} depending on the gas contact time.
458
459 The RE of 2000 ppm_v of SO_2 using a slightly alkaline absorbent prepared from a NaOH
460 solution at pH 8.0 rose from 38.7 to 70.9% when L/G ratio was increased from 5 to 15 L
461 m^{-3}. The value of RE obtained in the spray-scrubber revealed low mass transfer of SO_2
462 from gas to liquid phase at a gas contact time of 0.6 s. The increasing volumetric flowrate
463 of the absorbent increased the diameter of the droplets inside the scrubber and thus the
464 gas-liquid interface, reducing mass transfer limitations and enhancing absorption
465 efficiency. On the other hand, the increment of the contact time from 0.6 to 10 s (at a
466 constant L/G ratio of 7.5 L m^{-3}) resulted in a strong RE decay, from 68.4 to 20.6%. At a
467 constant L/G ratio, turbulences in gas-liquid contactor are increased at high gas flowrate,
468 enhancing SO_2 mass transfer to the liquid bulk.
469 The residual alkalinity contained as dissolved carbonate in the bioprocess effluent was
470 favorably used in the absorption unit to reduce reagents consumption and operational
471 costs, as well as to improve SO_2 RE. Results obtained using specifically this absorbent
472 for SO_2 removal showed an improvement on RE between a 25 and a 50%. Then, treating
473 2000 ppm_v of SO_2 at a gas contact time of 0.6 s had associated a RE increase to 94.7 %

and 72.0 % at a L/G ratio of 15 and 5 L m^{-3}, respectively. In the same way, SO_2 absorption at a L/G ratio of 7.5 L m^{-3}, and at gas contact time between 0.6 and 4 s, also presented higher RE (ranging from 91.0 and 74.4 %). The performance of the bioprocess effluent as an absorbent for SO_2 treatment was also evaluated at higher SO_2 concentrations. The removal efficiencies for the treatment of 3000 ppm_v of SO_2 were only 8-9% lower than the obtained for a flue gas of 2000 ppm_v of SO_2. Additionally, almost an identical absorption efficiency was observed treating 4000 ppm_v of SO_2. These results highlighted the suitability of residual alkalinity contained in the bioprocess effluent for SO_2 absorption, obtaining higher RE than using NaOH based absorbent. The reuse of bioprocess waste as regenerated absorbent enabled the reduction of reagents consumption in the absorption unit. In addition, buffer capacity of the regenerated absorbent allowed higher efficiencies also for the treatment of high SO_2 loads. Therefore, the use of bioprocess effluent as absorbent showed an excellent performance to reduce fluctuations in scrubber RE due to variations in SO_2 inlet concentration.

3.4 Economical feasibility of the SONOVA process implementation: the pigments industry as a case study

The integrated process for SO_2 bioscrubbing proposed in this work (SONOVA process) has opened a window of opportunity to valorize sulfur contained in flue gases, which are generated in this type of industrial activities. The technical feasibility of the integrated SO_2 bioscrubbing process has been already demonstrated in this work; however, it is also essential to assess the economic feasibility of the integrated process before it is implemented at larger scales. For this purpose, a case study is proposed to calculate investment costs, operational costs and the return on investment associated to a hypothetical project. The operational conditions of the case study process are presented

498 in Table S3 (section S5, Supplementary Material), which are based on the findings
499 reported in this work.
500 The biogas production from the UASB was also estimated to be 10% of the liquid effluent
501 treated in the unit. The dimensions of the process and the treatment capacity could target
502 the valorization of up to 20000 $m^3\ h^{-1}$ of flue gas, with SO_2 concentrations ranging from
503 3000-4000 ppmv. Considering that any company generating flue gases with SO_2 must
504 have already installed a scrubber to treat the emissions, the capital costs and operating
505 costs of the S-rich effluent valorization process have been estimated in 2,021.000 USD
506 and 1,471.897 USD per year, respectively (Aeris Tecnologías Ambientales, SL). Annual
507 savings in sulfur, natural gas, sodium hydroxide and waste management have also been
508 estimated in 400100 USD. This result means that the return on investment would be 5
509 years, specifically for the case study proposed in this work. Table 3 shows a summary of
510 the operational costs associated to the industrial activity considered in this case study
511 before and after the implementation of SONOVA.
512
513 **Table 3.** Operational costs of an industrial activity producing 20000 $m^3\ h^{-1}$ of flue gas with SO_2
514 concentration ranging from 2000 to 3000 ppm_v before the implementation of the SO_2 bioscrubber
515 (case A) and after the implementation of the bioscrubber (case B)

Treatment technology	Concept	Consumption	Cost	Operational costs (USD $year^{-1}$)
CASE A: Scrubber	Elemental sulfur	870 Tn $year^{-1}$	150 USD Tn^{-1}	130 500
	Natural Gas	1 871 323 Nm^3 $year^{-1}$	0.354 USD Nm^3	662 448
	NaOH 50%	1529 Tn $year^{-1}$	527 USD Tn^{-1}	805 783
	Waste management	50605 m^3 $year^{-1}$	5.4 USD m^{-3}	273 267
			TOTAL ANNUAL COSTS	**1 871 998 USD**
CASE B: SONOVA	Elemental sulfur[1]	350 Tn $year^{-1}$	150 USD Tn^{-1}	525 000
	Natural Gas[2]	1 697 223 Nm^3 $year^{-1}$	0.354 USD Nm^3	600 817
	NaOH 50%[3]	844 Tn $year^{-1}$	527 USD Tn^{-1}	445 038
	Waste management[4]	0 m^3 $year^{-1}$	5.4 USD m^{-3}	0
	Crude Glycerol	2 660 Tn $year^{-1}$	100 USD Tn^{-1}	266 002

Electricity[5]	1 191 360 kW year^{-1}	0.088 USD kW^{-1}	104 840
		TOTAL ANNUAL COSTS	**1 471 897 USD**

[1]Recovered sulfur from the SONOVA process is reused as a raw material for pigments production resulting in operational savings. [2]Methane produced in the UASB supplies part of the natural gas purchased for the production process resulting in operational savings. [3]Alkalinity contained in the recirculated effluent reduces chemicals supply in the scrubber resulting in operational savings. [4]S-rich effluent generated in the scrubber is not treated through a waste management external company but valorized resulting in operational savings. [5]Electricity requirements associated uniquely to the implementation of the SONOVA process mainly for pumping and aeration.

4. CONCLUSIONS

Overall, the process proposed in this study to produce biosulfur from flue gases containing SO_2 and crude glycerol has been demonstrated to be feasible from the technological point of view. A polluted gas with SO_2 concentration ranging from 2000 ppm_v to 4000 ppm_v has been optimally treated in a spray-scrubber, obtaining RE higher than 80 % at a gas contact time as low as 2 s, by reusing the effluent generated in the biological stage (CSTR). Moreover, sulfur loads up to 9.3 kg S m^{-3} d^{-1} were treated in the UASB setting an HRT of 2h. The CSTR was fed with the effluent from the UASB and operated at an HRT as low as 4h resulting in 100% of sulfide partial oxidation.

On the other hand, the economic analysis performed in this study showed that an industrial activity generating 20000 m^3 h^{-1} of flue gas, with SO_2 concentration ranging from 2000 to 3000 ppmv, would have a ROI of 5 years with the implementation of the integrated SO_2 bioscrubber. Moreover, the recirculation of the liquid effluent (consumption of chemical agents reduced by almost 50 %) besides the recovery of elemental sulfur from flue gases (60 % of the raw material recovered applying the SONOVA process) makes this technology, not only technologically and economically feasible, but also beneficial from the environmental point of view.

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