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Monitoring and performance of a desulphurizing biotrickling filter with an integrated continuous gas/liquid flow analyser

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ABSTRACT

Biological processes have proved to be suitable for desulphurization of energy-rich gases containing high loads of $H_2S_{(g)}$. However, monitoring devices for assessing such bioreactors performance are still scarce. In this work, an analytical system consisting in a flow injection analyser (FIA) for total dissolved sulphide ($H_2S_{(aq)} + HS^- + S^{2-}$) (TDS) and a continuous flow analyser with a gas diffusion step (GD-CFA) configuration for $H_2S_{(g)}$ have been used for on-line monitoring of a biotrickling filter for desulphurization of biogas mimics under aerobic conditions. Analyses were validated *versus* commercial sensors during real-time monitoring of the biotrickling filter performance under aerobic and anoxic conditions. During the aerobic period monitoring reported herein, the inlet H_2S concentration was stepwise increased from 2000 ppm_v (51 g H_2S m^{-3} h^{-1}) up to 8000 ppm_v of H_2S (215 g H_2S m^{-3} h^{-1}). Complementary off-line measurements of other sulphur species allowed assessing a sulphur mass balance, which indicated that S^0 production proportionally increased with an O_2/H_2S ratio decrease. Under the studied conditions, the maximum TDS concentration detected in the liquid phase was 3.08 mg S^{2-} L^{-1} while the maximum elimination capacity of the reactor was 201 g H_2S m^{-3} h^{-1} and the maximum removal efficiency was 100%. The FIA/GD-CFA results demonstrated that the proposed analytical system is reliable for on-line monitoring applications and can serve as a valuable tool to understand the complex mechanism of biological desulphurization.

1. Introduction

Flow injection systems are based in the automation of a standard, conventional analytical process. The sample to be analyzed is injected and dispersed into a continuous carrier solution flow that is directed to the detection system, in which a transitory signal peak is obtained. The detector identifies a baseline when no sample is present and a peak signal when sample is injected. The analytical response is the difference between peak heights and the baseline. Advantages of automated flow injection systems with respect to off-line processes are the speed, robustness and versatility, in addition to the low samples and reagents consumption and the low cost per analysis [1]. Flow injection systems are widely used for on-line process monitoring in water and waste water treatment, as well as in fermentation process, pharmaceutical, food industry and clinical analysis, among other applications [2–6]. The determination of sulphur species by flow injection systems have been intensively used, resulting in the development of reliable systems for the direct determination of sulphate (SO_4^{2-}), sulphite (SO_3^{2-}) and sulphide (S^{2-}) [6,7].

Desulphurization of energy rich gases, such a biogas, is required for energy recovery processes to prevent engines corrosion as well as for human health and environmental protection. Typical $H_2S_{(g)}$ content in biogas ranges from 0.1% to 0.5% v v^{-1} (1000–5000 ppm_v) but values as low as 0.0002% and as high as 2% have been reported [8]. Biological desulphurization processes have been proven to be a technically and economically effective alternative to traditional physicochemical processes, especially for low $H_2S_{(g)}$ concentrations [9–12], and also for ultra-high $H_2S_{(g)}$ concentrations, with elimination capacities as high as 280 g H_2S m^{-3} h^{-1} [13]. In particular, biotrickling filters work by passing a humid stream of contaminated air through a chemically inert packing material over which the aqueous phase is continuously trickled. The packing material is usually made of some synthetic or inert material, like plastic rings, open pore foam or lava rock. To avoid the accumulation of excess biomass and degradation by-products in the biotrickling filter, a control of the trickling liquid, the make-up water and the purge flow rates are recommended [14]. In desulphurizing biotrickling filters, biological sulphur oxidation occurs

Abbreviations: FIA, flow injection analysis; GD-CFA, gas diffusion-continuous flow analysis; TDS, total dissolved sulphide; SAOB, sulphide antioxidant buffer; ISE, ion selective electrode; HRT, hydraulic retention time; LR, loading rate; RE, removal efficiency; EC, elimination capacity; DO, dissolved oxygen; ORP, oxidation–reduction potential.

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according to Eqs. (1) and (2) [15].

$$HS^- + ½O_2 \rightarrow S^0 + OH^- \quad (1)$$

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+ \quad (2)$$

Therefore, the O_2/H_2S concentration ratio determines whether elemental sulphur (S^0) or SO_4^{2-} is produced during biological desulphurization. Further investigation in monitoring systems is required for the complete understanding of the complex biological and chemical processes that take place in biological desulphurization, with special attention to the dynamics of the operating conditions (e.g. contaminant concentration, oxygen supply, hydraulic residence time, empty bed residence time) and to the efficient real-time process monitoring.

The objectives of this work were to integrate the FIA/GD-CFA analyser to an existing biotrickling filter for on-line monitoring of total dissolved sulphide (TDS) ($H_2S_{(aq)} + HS^- + S^{2-}$) in the liquid phase and $H_2S_{(g)}$ in the gas phase and to validate the equipment under continuous operation to assess the performance of the reactor. To this aim, controlled experiments were performed by increasing the inlet $H_2S_{(g)}$ concentration to force TDS accumulation in the liquid phase. On-line values obtained by the FIA/GD-CFA system were validated with conventional commercial sensors in both liquid and gas phases.

2. Materials and methods

2.1. Standards and reagents

All aqueous solutions were prepared with deionized Milli-Q water (18 MΩ cm^{-1}). Reagents employed were of analytical grade. The sulphide antioxidant buffer solution (SAOB, pH 14) and the stock solution of S^{2-} (~1 mol S^{2-} L^{-1}), as well as standard solutions of S^{2-} were prepared as previously described [16–18]. Sulphide standard solutions covered a concentration range from 10^{-5} to 10^{-1} mol S^{2-} L^{-1} (0.32–3206 mg S^{2-} L^{-1}). Gaseous standards were prepared as described by Redondo et al. [18] covering a concentration range from 100 to 10000 ppm_v H_2S.

2.2. Experimental set-up

The analytical system configuration used for on-line monitoring of the biotrickling filter is shown in Fig. 1. Liquid samples are processed by a FIA configuration system (Fig. 1a), while gas samples are processed by a CFA configuration system containing a gas diffusion cell for selective $H_2S_{(g)}$ absorption (Fig. 1b). Both configurations share an ion selective electrode (ISE) for TDS detection (Fig. 1c). Further details on the ISE construction, conditioning and calibration procedures as well as on system configuration and operation can be found elsewhere [18,19]. Since the analyser described by Redondo et al. [18] was not prepared for on-line sampling, in the present work an in-line sampling filtration system and a continuous sample pH adjustment step were added. The bioreactor consisted in a packed bed with HD-QPAC (Lantec Products Inc., CA, USA) with a 4 mm × 4 mm grid opening cut to tightly fit inside the reactor as packing material. The reactor inner diameter is 0.071 m, with bed height of 0.53 m, resulting in 2.15 L reactor volume. The EBRT (empty bed residence time) was set to 180 s. The biogas mimics consisted in a mixture of $H_2S_{(g)}$ and $N_{2(g)}$, circulating in upflow, counter-current mode. Inorganic carbon was supplied in the liquid phase as $NaHCO_3$. Also, the reactor has an automated mineral medium addition and an auxiliary reactor for air supply and level control (Fig. 1). Details of the bioreactor setup can be found elsewhere [13,20].

Continuous analysis of the biotrickling filter with the FIA/GD-CFA system required of an in-line sampling filtration system for preventing any solid particle coming from the biotrickling filter recirculation line to enter the analytical system. A combination of a primary filtration unit by means of a tangential flow type filter (Mini-Ultrasette™; Pall Corporation, USA) with 3 μm pore size followed by a secondary filtration unit of a disposable direct flow type filter (DIF-MN-40; Headline Filters, UK) with 0.22 μm pore size was installed. Permeate from the tangential flow type filter was returned to the biotrickling filter recirculation line (Fig. 1). Filtration to 0.22 μm pore size was selected to avoid any undesirable biofilm formation in the electrode surface and in the tubing system of the analyser.

Since desulphurizing bioreactors may operate in a wide range of pH [21,22] and have important pH changes during operation if pH is not controlled [22–24], the FIA/GD-CFA system was equipped with an in-line pH adjustment step for liquid samples (Fig. 1a) to provide robustness to the FIA system. Since the optimal pH for the ISE is 14 [18], the sample stream was mixed with a metered flow of SAOB (pH 14) before the injection valve. The optimal flow rate, and consequently the dilution ratio, was selected based on the lowest pH value allowed by the biotrickling filter pH control system (pH 6). Different tubing combinations were tested, resulting in a minimum SAOB/sample flow rate ratio of 0.13, which corresponded to a pH adjusting solution flow rate of 0.26 mL min^{-1}.

2.3. Experimental conditions and bioreactor monitoring

Under normal operating conditions, an inlet $H_2S_{(g)}$ concentration of 2000 ppm_v (load of 51 g H_2S m^{-3} h^{-1}) was fed to the biotrickling filter under excess oxygen supply. Dry air is fed by a digital mass flow controller into the bottom of the auxiliary aeration unit and is bubbled by means of a fine bubble diffuser directly to the liquid phase. Also, a gas contact time of 180 s and an average hydraulic retention time (HRT) for the liquid phase of 51 ± 6 h were maintained. pH was controlled by means of an on/off controller in the range 6–6.5. Under such conditions, the desulphurizing capacity of the biotrickling filter monitored produces no TDS accumulation in the liquid phase [13]. Thus, different experiments under anoxic (not shown) and aerobic conditions were performed in which the biotrickling filter inlet $H_2S_{(g)}$ was increased and the HRT reduced to force accumulation of significant amounts of TDS in the liquid phase. Overall, experiments allowed measuring $H_2S_{(g)}$ concentrations in the outlet gas phase up to 6500 ppm_v and TDS up to 37 mg S^{2-} L^{-1} in the liquid phase, thus covering the range of concentrations of the FIA/GD-CFA analyser. In the experiments under aerobic conditions reported herein, the HRT was reduced to 9 h while the inlet $H_2S_{(g)}$ concentration was step-wise increased each 120 min to 4000 ppm_v (108 g H_2S m^{-3} h^{-1}), 6000 ppm_v (162 g H_2S m^{-3} h^{-1}) and 8000 ppm_v of H_2S (215 g H_2S m^{-3} h^{-1}). Later, normal operating conditions were resumed.

For the FIA/GD-CFA system validation, two commercial sensors were employed; one for the liquid phase and the other one for the gas phase. The FIA was validated by a sulphide ISE combined with an Ag/AgCl electrode as reference (VWR™ sympHony™ 14002-790; VWR International Inc., USA) installed in the waste line right after the constructed ISE electrode. The GD-CFA was validated by an electrochemical commercial $H_2S_{(g)}$ sensor (Sure-cell; Euro-Gas Management Services Ltd., UK) installed in the biotrickling filter outlet gas line.

In addition to the FIA/GD-CFA analyses, liquid samples were taken every 20 min from the liquid phase for off-line SO_4^{2-} and $S_2O_3^{2-}$ analyses. Samples were filtered in 0.22 μm disposable filters and measured using an ICS-1000 Ion Chromatography system with an IonPac AS9-HC column (Dionex Corporation). On-line liquid phase monitoring also included pH and oxidation–reduction potential (ORP) (PH 28, Crison Instruments, Spain) and dissolved oxygen (DO) (oxi340i, WTW, Germany) measurements.

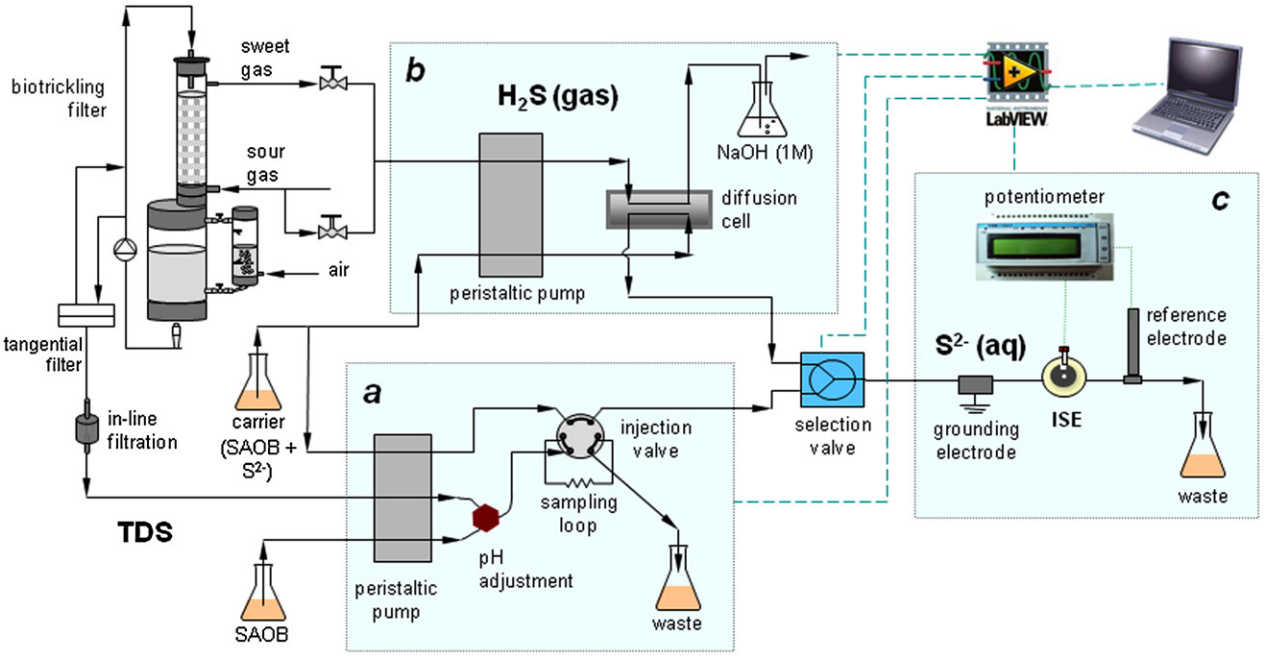

Fig. 1. FIA/GD-CFA analytical system for on-line monitoring of a desulphurizing biotrickling filter. (a) FIA system for TDS determination in the liquid phase. (b) GD-CFA system for $H_2S_{(g)}$ determination in the gas phase. (c) Detection system.

3. Results and discussion

3.1. On-line monitoring with the FIA/GD-CFA system

Monitoring data of the complete experimental period under aerobic conditions as acquired by the FIA/GD-CFA system are shown in Fig. 2. The electrode baseline presented a gradual increase along the monitored period, as normally observed in flow injection analysers when operating in continuous mode [19]. Thus, the total peak (FIA configuration) and plateau (GD-CFA configuration) heights were calculated considering the correspondent baseline for each cycle.

During the experiment, the analytical system was programmed for continuous on-line determination of TDS in the liquid phase and to sample the gas phase twice per each inlet concentration step (at minute 70 and 110 of each interval of 120 min). The selection valve of the analytical system (Fig. 1) was used for automatically switching from the FIA to the GD-CFA configuration. As shown in Fig. 2 inset, the selection valve change produced a sharp increase in the system response, probably as a consequence of a signal noise instant disturbance. Thus, an extended time for the baseline stabilization is needed during gas samples analysis, consequently leading to a decrease in the gas analysis frequency. Under alternat-

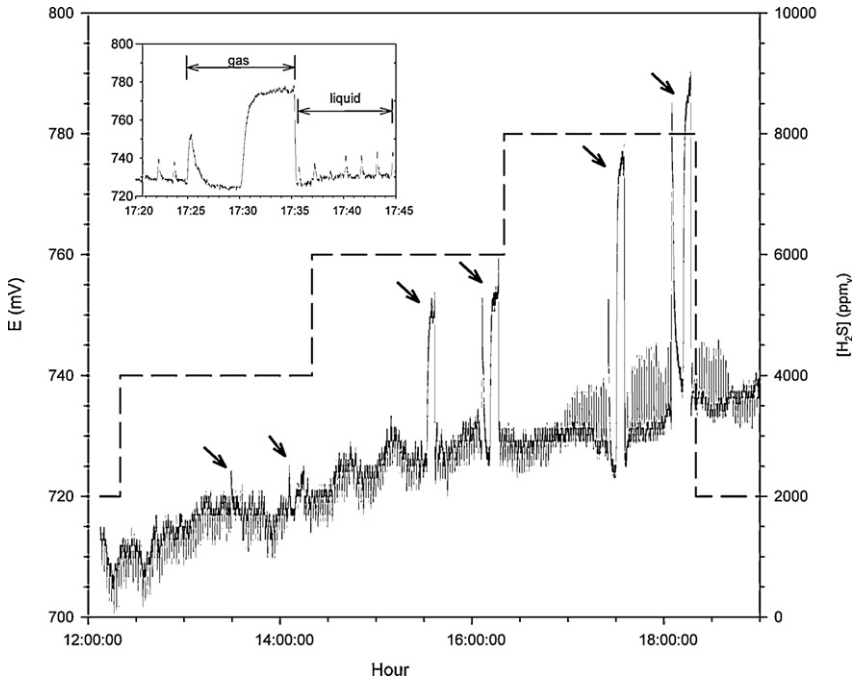

Fig. 2. Experimental FIA/GD-CFA on-line monitoring data. Dotted line indicates inlet $H_2S_{(g)}$ concentration. Arrows show gas phase CFA determination of two samples for each inlet concentration step. Inset shows detailed data of a 25-min period.

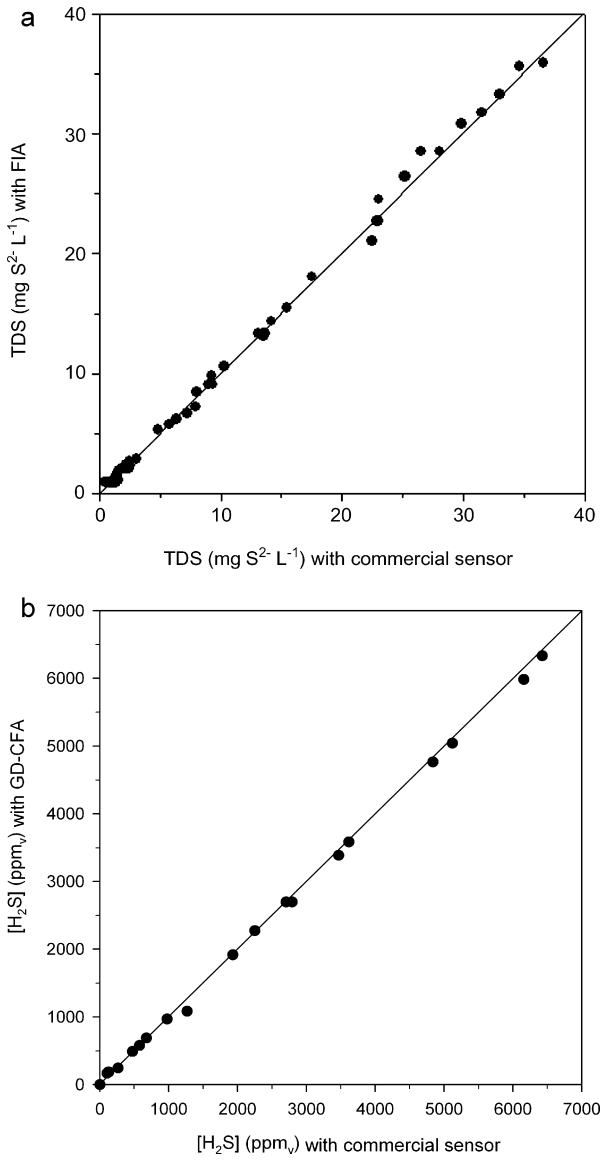

Fig. 3. Linear regression test to compare the FIA/GD-CFA experimental data and commercial sensors results for (a) TDS in the liquid phase and (b) $H_2S_{(g)}$ in the gas phase.

ing operating conditions, the gas analysis time is 8 min on average (4 min for baseline stabilization and 4 min for maximum signal stabilization), while 90 s are needed for liquid samples analysis. However, the custom-made program for data acquisition and for controlling the selection valve can be easily adapted for any gas or liquid phase sampling frequency configuration including continuous, full-time gas phase or liquid phase monitoring.

The analyser was validated by comparing its results for gas and liquid samples from the biotrickling filter with those obtained with commercial sensors. Fig. 3a for the FIA configuration and Fig. 3b for the GD-CFA configuration demonstrate, by the linear regression test, that no significant differences were observed at 95% confidence level. In the linear regression test for the FIA, a slope of 1.0 ± 0.0 and intercept of 0.0 ± 0.2 was obtained. For the GD-CFA, a slope of 1.0 ± 0.0 and intercept of 16.8 ± 36.4 was obtained. Thus, the analytical results can be considered acceptable for both liquid and gas phase measurements for the concentration range studied. Calibrations performed in this study resulted in a detection limit of $1.5 \times 10^{-5} \pm 0.9 \times 10^{-5}$ mol S^{2-} L^{-1} for the FIA analyser and 159 ± 57 ppm_v H_2S for the GD-CFA configuration.

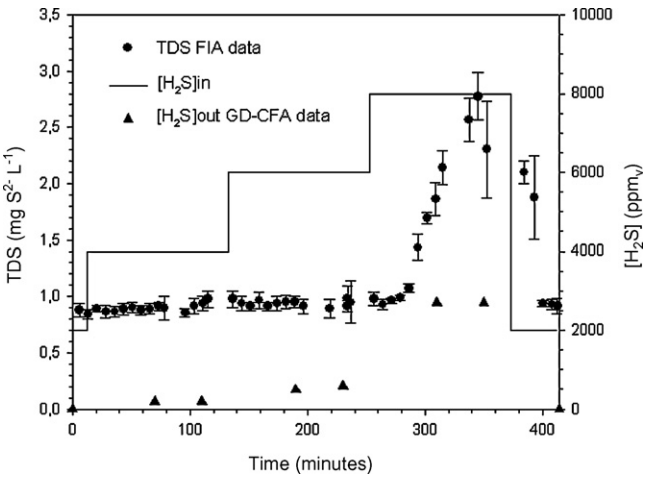

Fig. 4. TDS and $H_2S_{(g)}$ concentration profiles obtained with the FIA and the GD-CFA. Error bars indicate 95% confidence interval.

It is worth mentioning that the filtration step employing a first tangential filtration unit plus a direct flow filter element was in use for more than 80 h without showing any significant clogging of the filter element. Such configuration revealed enough in the present case, for the filtration of 0.12 L h^{-1} with a concentration of total suspended solids <2 mg L^{-1}. According to this and the fact that the liquid sample pH was adjusted on-line to 14, the 0.22 μm could have been avoided in the present application. However, sulphur-oxidizing bacteria are known to grow in a wide range of pHs from 1 to 11 [10,25], thus the second step filtration might be necessary in the long-run to protect the FIA/GD-CFA system.

According to the HRT in the present reactor during the experiment (9 h), FIA data averages in periods of approximately 7.5 min (i.e. 5 data) were considered throughout the experiment as shown in Fig. 4. Until minute 280, the TDS concentration was close to the FIA detection limit. Major TDS accumulation was only detected during the 8000 ppm_v H_2S step in which TDS concentration experienced a significant gradual increase until reaching maximum average concentrations of 2.8 mg S^{2-} L^{-1}. Once the inlet concentration of 2000 ppm_v H_2S was restored, TDS concentration immediately decreased, reaching values below the FIA detection limit after 1 h. Also, no significant response of the $H_2S_{(g)}$ outlet concentration was obtained in the GD-CFA system during the 4000 ppm_v H_2S step with outlet $H_2S_{(g)}$ concentrations close to the GD-CFA detection limit. Later, the outlet gas concentration gradually raised to a maximum value of 3074 ppm_v H_2S. Similarly to TDS, the $H_2S_{(g)}$ outlet concentration sharply decreased once normal operating conditions were restored, reaching values close to zero 1 h after normal operation resumption.

3.2. Overall biotrickling filter performance

Parameters typically used to characterize biotrickling filters performance are the loading rate (LR, g H_2S m^{-3} h^{-1}), the removal efficiency (RE, %) and the elimination capacity (EC, g H_2S m^{-3} h^{-1}) [10]. Overall, the performance of gas-phase bioreactors is commonly characterized by the relation between the applied LR and the respective EC and RE. Results are shown in Fig. 5a and b for the biotrickling filter under study. LR ranged from 51 to 215 g H_2S m^{-3} h^{-1}, generally considered a high load. Since the FIA/GD-CFA system was programmed to mainly analyse the liquid phase in the experiment presented herein, monitoring results of the commercial sensor allow seeing the dynamics of EC and RE during the experiment (Fig. 5a). Except for the 4000 ppm_v H_2S step, each step lead to a decrease in the RE, which was more significant

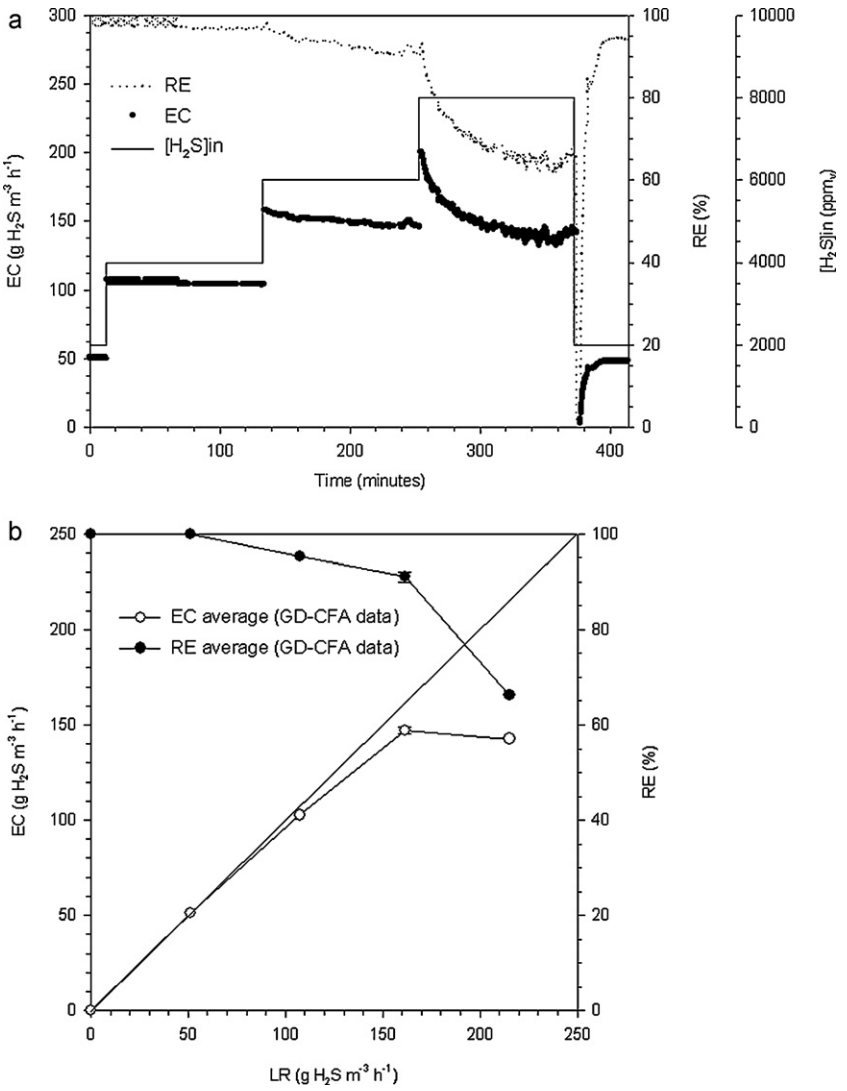

Fig. 5. (a) Evolution of EC and RE calculated using data of the $H_2S_{(g)}$ commercial sensor. (b) Average EC and RE *versus* LR calculated using data from GD-CFA.

once the reactor had reached the 8000 ppm_v H_2S step. Oppositely, the EC exhibited a marked increase right after each inlet concentration increase. However, a progressive decrease of the EC was found along the 6000 ppm_v H_2S step, and a sharp decrease was found along the 8000 ppm_v H_2S step, the latter due to the quick saturation of the sorption capacity of the liquid phase. When normal operating conditions resumed, the EC and RE suddenly dropped to zero for a period of around 3 min, which corresponds to the gas residence time of the reactor. Still, since some TDS had accumulated in the liquid phase, 18 min were required to achieve EC and RE values equivalent to the previous inlet concentration step.

The maximum instant EC registered was 201 $g\,H_2S\,m^{-3}\,h^{-1}$ (Fig. 5a), while the maximum averaged EC was 150 $g\,H_2S\,m^{-3}\,h^{-1}$ (Fig. 5b). The RE was initially 100% and kept close to 98% during the 4000 ppm_v H_2S step. During the 6000 ppm_v H_2S step, the RE was approximately 92% and dropped to a minimum average value of 68% during the highest LR period. However, RE quickly recovered to close to 95% as soon as the 2000 ppm_v H_2S step resumed, indicating a fast recovery of the biotrickling filter capacity. Overall, results indicate that such biotrickling filter configuration under the operating conditions tested herein is able to handle high, transient $H_2S_{(g)}$ loads with effective desulphurization of a wide range of concentrations. In terms of monitoring, the FIA/GD-CFA proved sufficient for assessing the overall performance of the reactor (Fig. 5b), even if continuous monitoring of the gas phase is recommended for assessing short transient periods dynamics (Fig. 5a).

3.3. Sulphur fate

Although desulphurization efficiencies and the reactor capacity can be assessed with the FIA/GD-CFA analyser, the information provided by the analyser needs complementary data to understand the complex performance of the biotrickling filter in terms of sulphur fate. In the liquid phase, the biotrickling filter has in-line sensors for pH, DO, ORP and temperature. Monitoring results during the experimental period are shown in Fig. 6.

An on–off control algorithm allowed maintaining the pH value between 6 and 6.5 during the whole experiment. The DO profile from a DO sensor located in the recirculation line after the aeration unit shows that the maximum oxygen consumption took place during the highest $H_2S_{(g)}$ inlet concentration, as expected. After inlet conditions were restored, DO rapidly recovered the initial value. It is worth mentioning that a DO sensor located in the sump of the reactor showed a value of 0 $mg\,O_2\,L^{-1}$ throughout the experimental period, indicating that oxygen availability was limited at some point along the depth of the reactor. Regarding the ORP profile, a gradual decrease for each concentration step was encountered, from the initial value of −40 mV to −50 mV, −150 mV and −300 mV

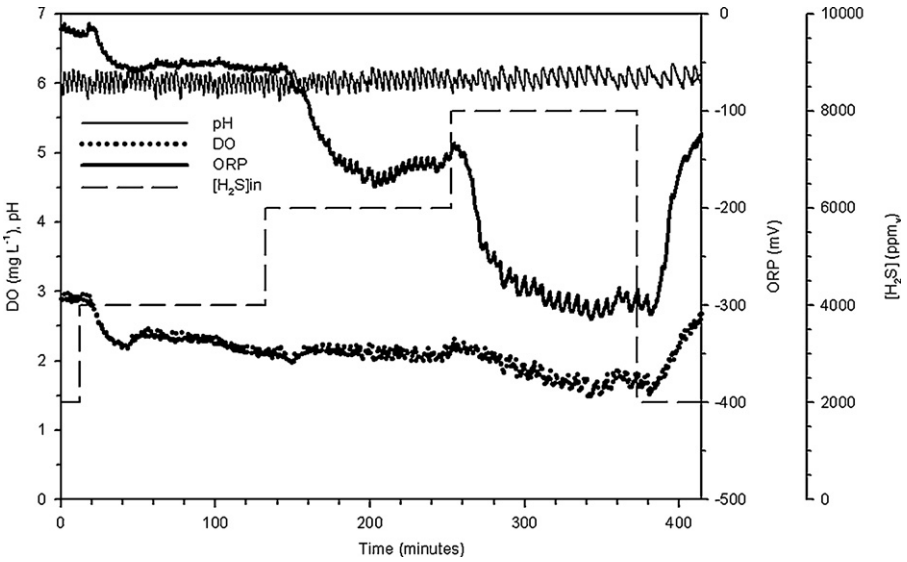

Fig. 6. In-line monitored parameters in the biotrickling filter during the experimental period.

for inlet $H_2S_{(g)}$ concentrations of 4000, 6000 an 8000 ppm_v H_2S, respectively. The initial value of −40 mV is consistent with the presence of SO_4^{2-} as main product of the $H_2S_{(g)}$ oxidation. ORP values between −250 and −400 mV indicate TDS accumulation and are in the range usually reported for S^{2-} oxidation to S^0 [13]. At this point, one can speculate if the limitation in the performance was due to mass transfer or to biological activity. Although profiles in Fig. 4 seem to indicate a mass transfer limitation during the 4000 and 6000 ppm_v H_2S steps, the ORP profile (Fig. 5a) and average TDS concentrations of 0.90 ± 0.02 and 0.94 ± 0.02 mg S^{2-} L^{-1} along the 4000 and 6000 ppm_v H_2S steps, respectively, indicate that the reactor was biologically limited.

Ionic sulphur species profiles measured in the recycle liquid are shown in Fig. 7. The SO_4^{2-} concentration profile shows a slight tendency to decrease from around 340 mg S-SO_4^{2-} L^{-1} to around 270 mg S-SO_4^{2-} L^{-1} at the end of the 8000 ppm_v H_2S step, indicating that the high load applied lead to a decrease in the biological SO_4^{2-} production. According to Fortuny et al. [13], the O_2/H_2S supplied ratio under this conditions (5.60, v v^{-1}) lead to a S^0 production due to oxygen limitation. Interestingly, still after resumption of the normal conditions, the SO_4^{2-} concentration kept decreasing down to around 245 mg S-SO_4^{2-} L^{-1}, even if the biological oxidation limitation due to the O_2/H_2S ratio applied had recovered to values corresponding to complete SO_4^{2-} production (23.60, v v^{-1}) [13]. Such delay may be explained by the hydraulic conditions of the liquid phase coupled to a delay in the reactivation of the biological mechanisms that lead to SO_4^{2-} production. The $S_2O_3^{2-}$ concentration kept close to zero until minute 260 of the experiment and then started to increase until 4 mg S-$S_2O_3^{2-}$ L^{-1} at the end of the 8000 ppm_v H_2S step, showing a maximum value of 6.8 mg S-$S_2O_3^{2-}$ L^{-1} at the end of the monitoring period. Thiosulphate formation by chemical oxidation was driven by TDS accumulation [20] not only during the maximum LR period but also after resumption of the initial LR.

A sulphur mass balance was performed to calculate the S^0 concentration by subtraction, as previously described [26]. The amount of sulphur as S-S^0 and S-SO_4^{2-} produced, as well as the total sulphur removed by biological activity (S-H_2S) are shown in Fig. 8. The DO/S^{2-} ratio in the liquid phase was calculated, representing the DO available at the top of the reactor, which could be

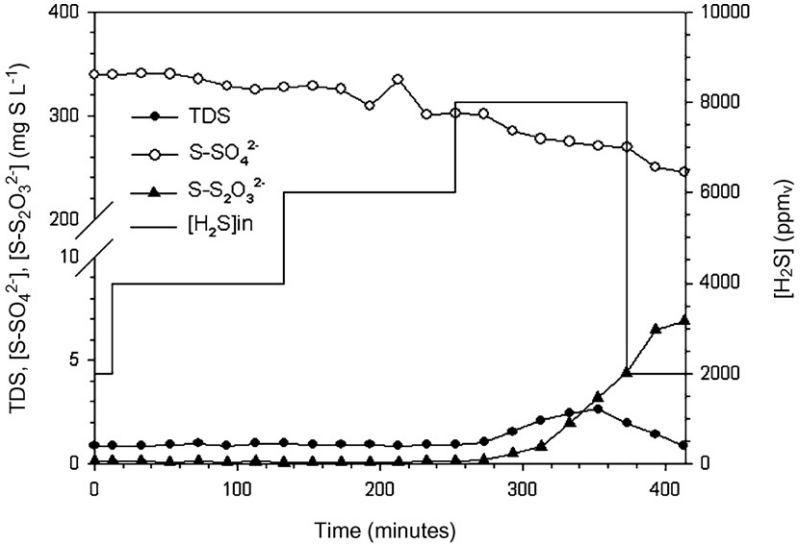

Fig. 7. Sulphide, sulphate and thiosulphate concentration monitoring.

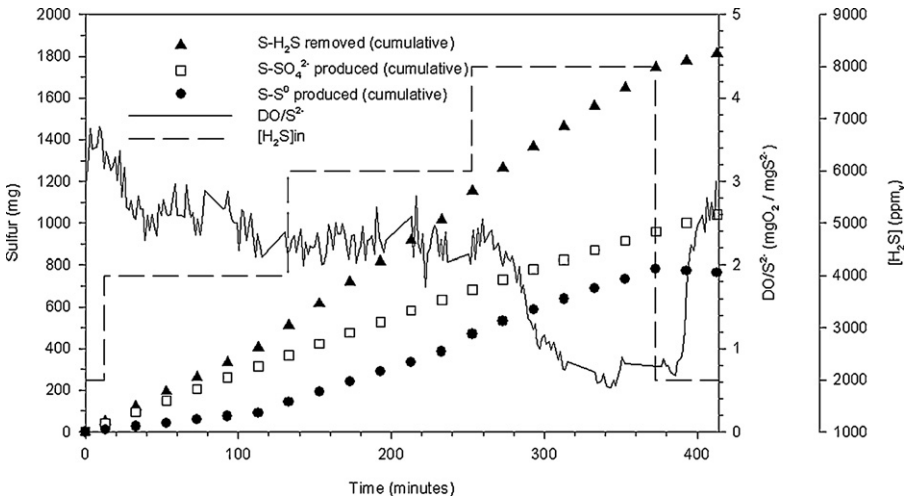

Fig. 8. Sulphur mass balance and DO/S^{2-} ratio in the biotrickling filter reactor during the experimental period.

Table 1
Sulphate and sulphur production as a function of the O_2/H_2S supplied ratio and DO/S^{2-} ratio.

H_2S in (ppm_v)	LR ($g\,H_2S\,m^{-3}\,h^{-1}$)	$O_2/H_2S_{supplied}$ ($v\,v^{-1}$)	S-SO_4^{2-}/S-H_2S removed (%)	S-S^0/S-$H_2S_{removed}$ (%)	DO/S^{2-} ($mg\,O_2/mg\,S^{2-}$)
2000	51	23.6	100	0	2.96–3.66
4000	108	11.2	78–80	20–22	2.09–3.37
6000	162	7.5	62–72	28–38	1.74–2.83
8000	215	5.6	55–59	41–45	0.53–2.54
2000	51	23.6	56–57	43–44	0.68–3.01

related to the capability of the system to produce either SO_4^{2-} or S^0 (Fig. 8) according to the stoichiometric relation obtained from Eqs. (1) and (2). Theoretically, a DO/S^{2-} ratio lower than 0.5 indicates that S^0 is the main product while a value higher than 2 indicates that the main product is SO_4^{2-}. Interestingly, even when the calculated DO/S^{2-} ratio reached values higher than 2 $mg\,O_2/mg\,S^{2-}$, sulphur mass balance results suggested a concomitant production of SO_4^{2-} and S^0. These results confirm the existence of an important DO gradient inside the filter bed, and perhaps in the biofilm, leading to the depletion of oxygen at the bottom part of the reactor where, probably, only S^0 was being produced. Although not studied, gas circulation in upflow mode, in counter-current to the liquid phase circulation may increase the potential of S^0 production in the reactor compared to a co-current operation. In the latter scenario, the oxygen availability would be larger at the entrance of the reactor where the H_2S concentration reaches its maximum value.

Sulphur mass balance results indicate that S^0 production started from the beginning of the 4000 ppm_v H_2S step (108 $g\,H_2S\,m^{-3}\,h^{-1}$), when the O_2/H_2S supply ratio was 11.2. However, S^0 accumulation suffered a notable increase during the 6000 and 8000 ppm_v H_2S steps (162 and 215 $g\,H_2S\,m^{-3}\,h^{-1}$, respectively), when O_2/H_2S supply ratio was 7.5 and 5.6, respectively, which is considered as a limiting value for aerobic biological desulphurization [20]. At the end of the highest LR period, a total amount of 783 mg S-S^0 were produced from 1747 mg S-H_2S removed. It is worth mentioning that as soon as normal operation was resumed (2000 ppm_v H_2S inlet concentration, O_2/H_2S supply ratio of 23.6), the S^0 production ratio instantly decreased while SO_4^{2-} production noticeable increased, confirming that during highest LR period, the limited O_2/H_2S ratio avoid the complete biological S^{2-} oxidation [15].

Sulphate and elemental sulphur production can be expressed as a ratio to the removed $H_2S_{(g)}$ (Table 1). Elemental sulphur production is clearly enhanced by oxygen limitation, as can be seen in Table 1. Differently to the results obtained by Fortuny et al. [13], SO_4^{2-} production selectivity is higher than S^0 production for equivalent LR, since the oxygen supply system was improved from gas-phase air injection to an aeration column previous to the biotrickling filter, enhancing the O_2/H_2S supplied ratio [27]. As noticed in Fig. 8, minimum and maximum values of the DO/S^{2-} ratio shown in Table 1 confirm that even when the oxygen supplied in the top part of the reactor is higher than the stoichiometric requirements for the production of SO_4^{2-}, S^0 was being produced in the intermediate and bottom parts of the reactor. Results show that optimization of the oxygen supply in such bioreactor configuration is warranted for improving desulphurization capacities.

4. Conclusions

A flow-based analytical system consisting on a FIA configuration for TDS analysis and a GD-CFA configuration for $H_2S_{(g)}$ analysis with a single ISE electrode for S^{2-} was proved to be suitable for on-line monitoring of a desulphurizing biotrickling filter reactor treating high loads of biogas mimics. Electrodes were successfully validated by comparing them to commercial sensors. On-line monitoring of TDS in the liquid phase and $H_2S_{(g)}$ in the gas outlet is essential information for understanding the biotrickling filter performance. In general, the biotrickling filter under study presented a fast recovery of their treatment capacity after load increase perturbations. Although sulphur mass balances results indicate that under oxygen limiting conditions the formation of S^0 is favoured over SO_4^{2-}, results demonstrate that direct supply of oxygen into the liquid phase is an useful way to improve the desulphurization capacity of biotrickling filters.

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