

# Conversion of chemical scrubbers to biotrickling filters for VOCs and H<sub>2</sub>S treatment at low contact times

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## ABSTRACT

The purpose of this work was to evaluate the technical and economical feasibility of converting three in-series chemical scrubbers to biotrickling filters for the simultaneous removal at neutral pH of 10000 m<sup>3</sup>/h containing H<sub>2</sub>S and volatile organic compounds (VOCs) at a wastewater treatment plant (WWTP). The conversion was based on previous conversion protocols and mainly required of replacing the original packing material by a structured packing and recycle pumps, besides modifying the controls and operation of the reactors. Complete removal of H<sub>2</sub>S and VOCs on a routine basis was reached in a longer period of time compared to previous conversions reported. Under the conditions at the WWTP, i.e., a gas contact time of about 1.4 seconds per reactor and pH controlled between 6.5 and 6.8, inlet average concentrations below 10 ppm<sub>v</sub> of H<sub>2</sub>S and below 5 ppm<sub>v</sub> for VOCs were often completely degraded in the reactors. The first and second reactors played a major role in H<sub>2</sub>S removal. Long-term operation of the biotrickling filters proved the ability of the biotrickling filter to handle progressive load variations of H<sub>2</sub>S and VOCs. However, fast, sudden load changes often lead to reduced removal efficiencies. Odor removal showed average efficiencies above 80%. Limited outlet odor concentration was attributed to limited removal of VOCs, which was assessed through gas chromatography-mass spectrometry of selected gas samples. The conversion showed as economically viable taking into account the theoretical consumption of chemicals needed for the absorption and oxidation of both H<sub>2</sub>S and VOCs.

## KEYWORDS

Chemical scrubbers conversion; Biotrickling filter; H<sub>2</sub>S; VOCs; neutral pH

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## INTRODUCTION

The emission of volatile compounds to the atmosphere is a growing environmental and social issue, due to health and odor problem that often generates. In this sense, emissions of wastewater treatment plants (WWTPs) are regarded as one of the main odor pollution sources [Devai and DaLaune, 1999; Lebrero et al. 2011]. The composition of these emissions varies along the WWTP and is typically a complex mixture of reduced sulfur compounds, amines and low molecular weight organic compounds [Gabriel and Deshusses, 2003; Easter et al. 2005]. Different studies have focused on the identification of the principal malodorous compounds in these sources, revealing that hydrogen sulfide and ammonia are the two principal inorganic odorous compounds. However, the wide range of odor-causing organic compounds makes the analysis more complex [Pagans et al., 2007; Wang et al. 2010], and more specific studies are needed to identify volatile organic compounds (VOCs) in the emission [Rodriguez et al., 2012; Lebrero et al. 2013]. In any case, all these studies confirm the importance of integrating the control of the gaseous emissions in the treatment process of a WWTP.

The selection of the treatment technology for odor control is decided according to the technology efficiency and the cost optimization. The high efficiency at gas contact times as short as 1 or 2 seconds have made conventional chemical scrubbing as the most established technique at industrial scale. However, chemical scrubbing has important drawbacks, such as the high operating costs and the need to use hazardous, chemical products in the pollutants removal [Chung et al., 1997; Estrada et al. 2011]. This fact has resulted in studying the benefits of the biological treatment of these emissions under the same operational conditions (low empty bed residence time, EBRT). Gabriel and Deshusses (2003, 2004a, 2004b) demonstrated the technical and economical viability of converting chemical scrubbers to biotrickling filters. In addition, a ten-step conversion protocol was developed (Gabriel et al., 2005) as a general procedure for the conversion of chemical scrubbers, independently of the final application of the equipment. Following this procedure reduces the downtime of the scrubbers, with a variation depending on the complexity of the conversion which is the result of a case by case analysis.

Such procedure was applied on a series of chemical scrubbers operating in the Orange County Sanitation District (OCSD), California. These reactors were treating concentrations between 5 and 40 ppm<sub>v</sub> of H<sub>2</sub>S and below 5 ppm<sub>v</sub> of VOCs at EBRTs between 1.6 and 3 s. The performance of the converted biotrickling filters was successfully tested in the treatment of H<sub>2</sub>S under acidic conditions at low contact times. However, simultaneous removal of H<sub>2</sub>S and VOCs indicated that poor VOCs removal efficiencies could be obtained at pH close to 2 (Gabriel and Deshusses, 2003a). However, operation at neutral pH, where H<sub>2</sub>S absorption is favored (González-Shánchez et al, 2008), resulted in limited performance of the bioreactor in the long run in terms of H<sub>2</sub>S removal (Gabriel and Deshusses, 2003a). An additional drawback of the study was the large pressure drop produced by the open-pore cubes of polyurethane foam (PUF) used.

Despite the important number of experiences reported from the OCSD project, conversion of chemical scrubbers to biotrickling filters is a relatively unexplored topic.

Since some of the former obstacles have been recently overcome at pilot scale by Dorado et al. (2013), who showed that simultaneous ammonia and VOCs abatement could be successfully performed in biotrickling filters operating at low contact times (2-8 s) under neutral pH conditions with the use of a structured packing material that provides low pressure drop, the aim of the present work was to study the technical and economical viability of the conversion of chemical scrubbers to biotrickling filters, in an industrial facility, for the simultaneous treatment of H<sub>2</sub>S and VOCs at neutral pH and at low contact times (below 5 s).

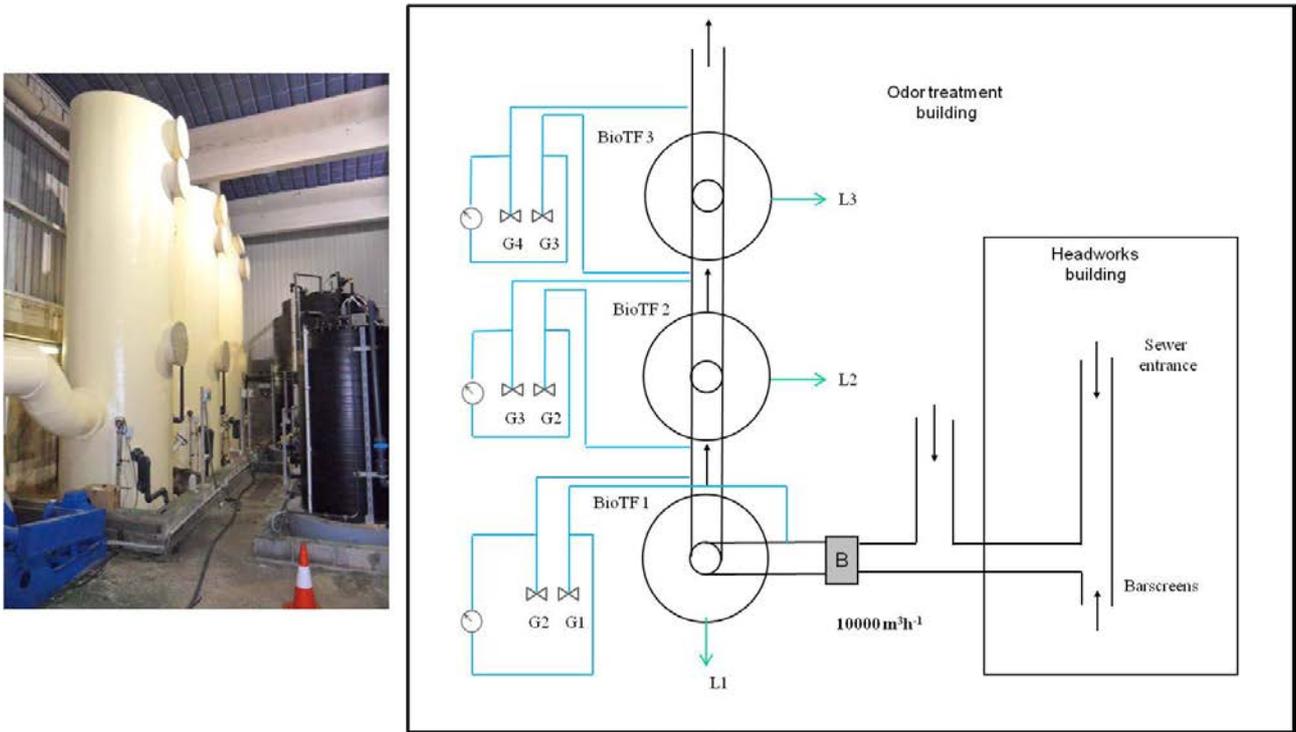
## **MATERIALS AND METHODS**

### **Biotrickling filters characteristics and operation**

The converted scrubbers were located at the Cubelles-Cunit WWTP (Barcelona, Spain). The original system consisted in 3 in-series chemical scrubbers for the treatment of the odor-laden air from the influent sewer trunk line (Figure 1). The converted scrubbers were identical reactors made of fiberglass reinforced plastic, with a bed volume of 4 m<sup>3</sup> (1.5 m of diameter and 2.3 m of high) each one, packed initially with 2" Pall rings, resulting in an EBRT of 1.44 seconds per reactor (Table 1). Prior to the conversion, the liquid trickling was carried out by the recirculation of the liquid from the 2 m<sup>3</sup> sump of the scrubber to the upper part of the bed by three centrifugal pumps that impelled the liquid at a flow rate of 25 m<sup>3</sup>/h. After the conversion the water recirculation flow rate and, consequently, the water trickling velocity were reduced by a factor of 5. Each chemical scrubber was also equipped with an industrial water line for make-up water supply, and a second line for chemicals supply. Polluted air was fed to the scrubbers by a fixed-speed centrifugal blower.

Prior to the conversion, the WWTP provided information regarding the H<sub>2</sub>S emissions treated during a 12 month period (Figure S1, Supplementary Information). Large seasonal variations indicated that the biotrickling filters should be flexible to adapt to the different conditions throughout the year. Also, the monitoring plan at the facility should consider such variation. Consequently, during the conversion, a pH and a level control loop were installed to accommodate biotrickling filters operation to the biological process. The sump level was the only parameter controlled initially in the chemical scrubbers. Minimum-level sensors were kept to ensure the safety operation of the pumps. This control was upgraded with the installation of medium- and high-level sensors which served to open or close the make-up water supply line when the lower or higher level switches were contacted, respectively. The pH control loop was modified in each reactor during the conversion according to Dorado et al. (2013) to allow regulating the make-up water flow rate by means of electrovalves. In addition to this, and to potentially avoid a lack of water renewal during auto-balanced pH

operation, an additional make-up water supply line manually regulated was used. On-off type controllers served to keep the pH between 6.5 and 6.8 by means of the renewal of the liquid phase.



**Figure 1.** Picture and schematic of the scrubbers once converted to biotrickling filters.

### Analytical methods

The BTF performance was assessed during 8 months by monitoring the main process variables, to ensure the correct operation of the biological process. Gas phase monitoring was carried out by the analysis of pollutants concentration as well as gas flow rates and reactors pressure drop. Gas sampling ports G1 to G4 (Figure 1) were used. H<sub>2</sub>S was measured at least twice a day at the entrance and exit of the system and at least once per week in between the reactors with portable electrochemical analyzers (Micro5, Gas Alert and MX6 IBrid, Industrial Scientific) with a resolution of 1 ppm<sub>v</sub> within a range of 0 to 200 ppm<sub>v</sub> and 0.1 ppm<sub>v</sub> within a range of 0 to 50 ppm<sub>v</sub> and a typical response time of 15s respectively. VOCs were measured at least once per week during the first months and once per day during the warmer months of the year with a portable photo ionization detector (MiniRae3000, Rae) with a resolution of 0.1 ppm in a range from 0 to 10000 ppm<sub>v</sub> and a response time of 3s. A 10.6 eV lamp was used.

Gas flow rates were measured at the entrance of the biotrickling filter system with a 1 meter Pitot tube coupled to an electronic manometer (MP-120, KIMO) with an accuracy of  $\pm 2\%$  within a range of 0 to 1000 Pa. Pressure drop through the beds was monitored daily with U-type water manometers. The temperature and relative humidity were measured for the gas phase on each of the sampling ports (entrance, in between reactors and exit) using a

Thermometer/Hygrometer (Testo 605-H1) with an accuracy of  $\pm 3$  %RH and  $\pm 0.5$  °C. Make-up water and water recirculation flows were monitored daily by means of rotameters. The pH was on-line measured with pH sensors (pH 28, Crison). Finally, liquid samples from the three reactors were taken weekly from sampling ports L1 to L3 (Figure 1) to analyze sulfate concentrations by ionic chromatography (ICS-2000, Dionex). Samples of industrial water from the plant were simultaneously analyzed to set the benchmark for sulfate production.

Periodically, samples from the entrance and exit of the system were collected in 1 L Tedlar<sup>®</sup> bags. Samples were analyzed by Solid Phase Micro Extraction (SPME) and Gas Chromatography – Mass Spectrometry (GC–MS) according to Scaglia et al. (2011) using deuterated p-xylene (99.9% atom deuterated p-xylene, Sigma Aldrich) as internal standard (IS) according to Davoli et al. (2003). Sample analysis was performed using an Agilent 7820 GC with a DB-624 capillary column (60 m length, 250  $\mu$ m internal diameter and film thickness of 1.4  $\mu$ m) coupled to a 5975C series MS. The carrier gas was helium. Samples were manually injected through the GC inlet injection port and run for 52 minutes. Compounds were tentatively identified by comparing their mass spectra with the NIST (USA) 98 library. The mass spectrometer was operated in full scan, in the m/z range of 41–200. The actual concentration in samples was calculated for representative analytes for each chemical class of VOCs. Quantification was based on total peak abundance area determined by an Agilent Technologies analytical software system.

Calibration was performed according to Dorado et al. (2014) by analyzing a set of standards of selected, representative analytes injected together with known amounts of the IS previously calibrated. Abundance ratios corresponded to the abundance response factors (IRF<sub>sc</sub>) later used to recalculate the actual concentration of the compound (C<sub>sc</sub>) based on concentration of IS added to the sample (C<sub>is</sub>), and the actual response of both the IS (A<sub>is</sub>) and the selected compound (A<sub>sc</sub>) (Eq. 1). Typical SPME/GC-MS detection limits are in the range of  $\mu$ gm<sup>-3</sup> (Larroque, Desauziers and Mocho 2006), which corresponds to around 0.1-0.2 ppb<sub>v</sub> at room temperature and atmospheric pressure for the typical molecular weights of odorant VOCs. According to Prenafeta-Boldú et al. (2012), all compounds identified were analyzed in terms of removal efficiency (RE) of the treatment system by comparing their peak abundance area (A<sub>sc</sub>) in samples taken from the inlet and outlet gas streams.

$$c_{sc} = \frac{C_{is} A_{sc} IRF_{sc}}{A_{is}} \quad (\text{Eq. 1})$$

Once per month, gas samples were taken from the inlet and outlet streams in a similar way as for the VOCs analysis. Samples were collected in <sup>®</sup>Nalophan bags and then delivered to Odournet on the same day for analysis and determination of odor concentrations by dynamic olfactometry according to the European standard (EN 13725, 2003).

## RESULTS

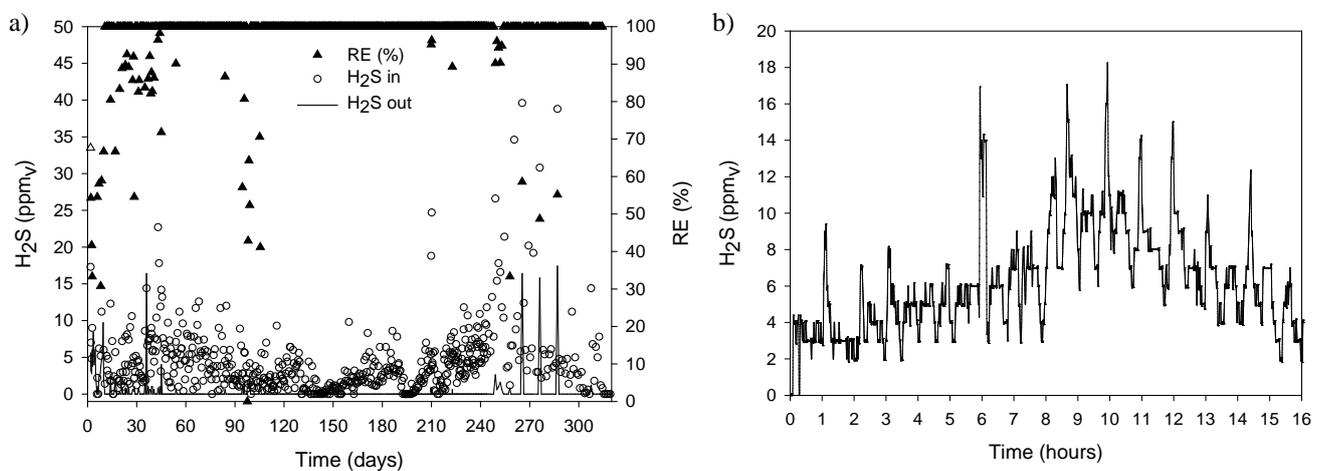
### Chemical scrubbers conversion

The conversion of the chemical scrubbers was based on the ten-step conversion protocol of Gabriel et al. (2004) and adapted to 7 steps to the current installation. First step consisted of replacing the old packing material, 2" Pall rings, by a structured packing material (FKP 158, Ecotec, Spain), with a surface area of  $320 \text{ m}^2/\text{m}^3$ , more suitable for the biological process because of its larger specific surface area (Devinny et al., 1999). The FKP 158 packing was made of polypropylene and consisted of moulded plastic panels with a honeycombs surface structure, each panel has a duct-shaped profile with  $45^\circ$  and  $90^\circ$  redirections while panels are arranged crosswise and are welded among each other. In a second conversion step, recirculation pumps were replaced by lower power ones (MPN-40-25-125, Ecotec, Spain) to decrease the recirculation flow rate from  $15 \text{ m}^3/\text{h}$  to  $3 \text{ m}^3/\text{h}$ . Modifications in the liquid line were completed by replacing the spray nozzles by pig tail nozzles which allow working with a higher solids concentration, and with the installation of 3 rotameters (VS1\_50H, PCE Instruments, France) to monitor the recirculation flow rate. Previous results in a pilot scale reactor (Dorado et al., 2013) were useful to define the new controls for pH and water supply regulation. Feed lines to the reactor were modified by uninstalling the chemicals supply lines, not necessary in the new configuration, and by installing 3 rotameters (VS1\_25B, PCE Instruments, France) and 3 seat valves (VVUFV\_DN 25, FIP) in the make-up water line. Also, a second industrial water line to be used for pH and level control was installed. The conversion was continued with the addition of the necessary ports for biological process monitoring. These ports were placed at the inlet and the outlet of each reactor, for gas phase, and in each recirculation line for the liquid phase. The conversion was finished by the installation of three electrovalves in the make-up water lines and their connection to the corresponding pH and level control loops. Costs were of 4854€ for the replacement of the old packing and installation of the new packing material; 3300€ for the replacement of the recirculation pumps; 2500€ for the conditioning and modification of the liquid feeding, recycle and gas lines; and 11000€ for the conditioning and upgrading of the instrumentation and control equipment. Also, around 5196€ were spent in labor costs for the conversion, which mainly correspond to subcontractors of Ecotec to perform all the conversion process.

### H<sub>2</sub>S removal performance

The technical viability of the full-scale system was evaluated after inoculation with aerobic sludge from the same WWTP. The sludge was recirculated during 48 hours to ensure biomass retention in the packing material. Afterwards, the air supply blower and make-up water supply were connected to start the routine operation of the biotrickling filters. The removal efficiency (RE) of the three-reactors system, namely total RE, showed an increase during the first days of operation (Figure 2a). During this period, three operation stages were distinguished. In the first stage, until day 10, bacteria introduced in the reactors acclimated to new conditions and started growing. In this period, REs in the range of

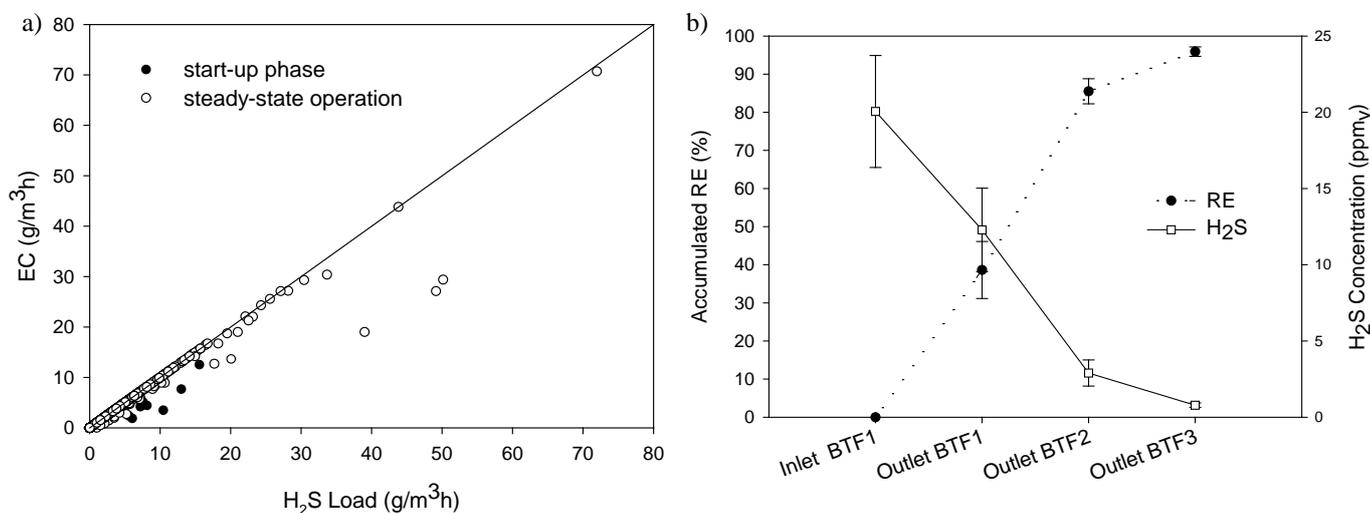
30% to 70% were found, which probably corresponded to chemical absorption in a large proportion. In a second stage between days 10 and 45, pollutants started to be biodegraded and REs systematically reached 100% most of the time at the end of this period. However, episodes of reduced efficiencies were observed due to inlet concentration peaks in this stage. Thereafter, the system operated under pseudo-steady-state conditions, being able to remove the entire load with an average RE above 99%. The system was subject to typical daily variations of the inlet load (Figure 2b) at any WWTP (Gabriel and Deshusses, 2003 PNAS; Sharma et al, 2008). The profile shows lower concentrations during the first hours of the day increasing to maximum values in the late afternoon with random sudden concentration peaks occurring along the day. Consequently, the inlet  $H_2S$  concentration was routinely measured twice per day to cope with the variation of the inlet  $H_2S$  load. It was important to consider that, even during days of low loads, the load variation could be significant.



**Figure 2.**  $H_2S$  removal performance a) Removal efficiency, inlet and outlet concentration vs. time and b) Inlet concentration variation along day 171 of operation (April 4<sup>th</sup>, 2013). Day 0 corresponds to October 15<sup>th</sup>, 2012.

The elimination capacity (EC) and RE as a function of the load supplied to the system was analyzed as well as these for each reactor separately. The pollutants load fed to the system ranged between 1 and 52  $g/m^3h$  for  $H_2S$ , with maximum  $H_2S$  loads of 70  $g/m^3h$ . This study showed that maximum system capacities in terms of  $H_2S$  removal were not achieved at the current conditions (Figure 3a). However, a different situation is encountered by analyzing the individual performance of each biotrickling filter. Bioreactors 1 and 2 treated the major part of the load, whereas seldom activity was observed in reactor 3 during the monitored period. Nevertheless, when concentrations were high enough, the third reactor exhibited removal as well (Figure 3b). This was corroborated with sulfate production data from the reactors. Average values were 557, 423 and 290  $mg SO_4^{-2}/L$  with standard deviations of 61, 101 and 65  $mg SO_4^{-2}/L$  for biotrickling filters one, two and three respectively. Compared to the average value of 172  $mg SO_4^{-2}/L$  (standard

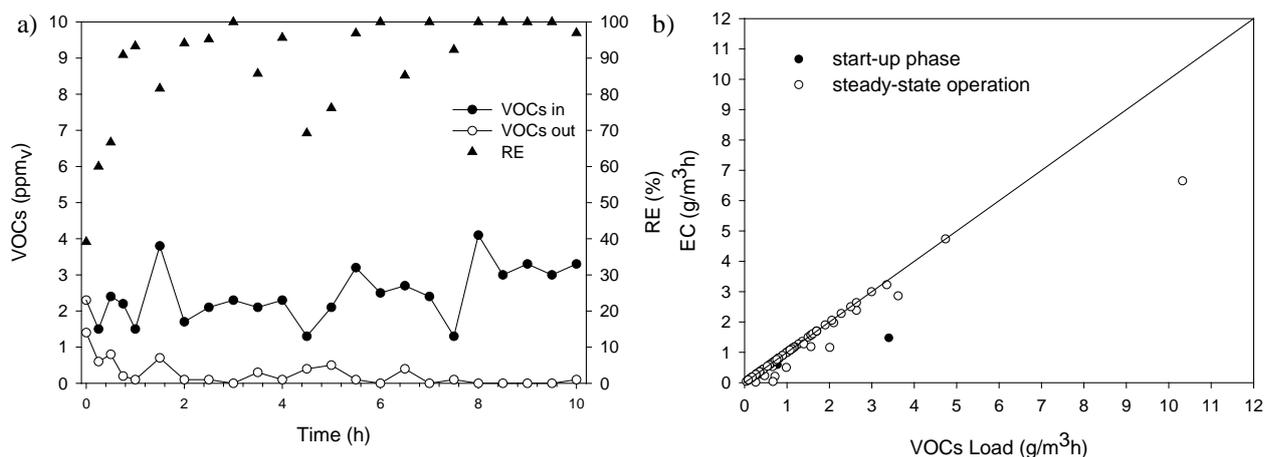
deviation of 17 mg SO<sub>4</sub><sup>-2</sup>/L) that corresponds to the industrial water from the WWTP. Consequently, biological activity was found in the three reactors.



**Figure 3.** Overall EC (a) and typical RE and H<sub>2</sub>S concentration profiles along the reactors (b). The removal profile corresponds to day 209 of operation (May 13<sup>th</sup>, 2013).

### VOCs and odor removal performance

VOCs removal was more limited compared to H<sub>2</sub>S (Figure S2, Supplementary Material), which is consistent with the hydrophobic character of the compounds and with the lower concentrations found along the monitored period compared to those of H<sub>2</sub>S. A similar trend to that of H<sub>2</sub>S was found for VOCs RE during the start-up of the reactors, even if the low sampling frequency for VOCs in that period hindered obtaining similar conclusions. In the long run, average inlet VOC concentrations ranged between 2-2.5 ppm<sub>v</sub> during the colder months of the year (around days 20 to 210 of operation corresponding to November 2012 to half May 2013). In particular, for the case of March and April 2013, average inlet VOC concentrations were lower than 0.5 ppm<sub>v</sub>. The highest average inlet VOC concentration was found during June 2013, with a value of 3.8 ppm<sub>v</sub>. Peak values identified were at 23.1 and 9.6 ppm<sub>v</sub> with RE of 87% and 44%, respectively. However, REs had even higher variability with an average RE of 78% in the overall operation period but a standard deviation of 30%. As more representative VOC RE, the RE in the hottest months of the year were 86%, 61%, 55% in June, July and August 2013, respectively. Moreover, some negative REs were observed during May to August 2013 (days 210 to 310 of operation). An example of the variability is shown in Figure 4a, which corresponds to a profile of the inlet and outlet concentrations and the RE along a day of operation. Inlet concentrations ranged from values between 1.5-4 ppm<sub>v</sub> whereas RE ranged between 40-100%. The elimination capacity as a function of the load is displayed on Figure 4b. A maximum EC seems to be reached at 6.6 gC/m<sup>3</sup>h.



**Figure 4.** a) Daily variation of the inlet and outlet concentration (04-06-2013). b) Overall EC of the VOCs.

Regarding odor removal, five samples were analyzed by means of dynamic olfactometry in an external laboratory (Odournet, Spain). Results are shown in table 2. According to portable sensors, measurements of  $\text{H}_2\text{S}$  and VOCs during all odor sampling episodes lead to RE of 100% except in the sampling of May 21<sup>st</sup>, in which a -4% RE for VOCs was found. In addition, the hypothesis of having residual odor due to the VOCs at the outlet was corroborated by GC-MS. Table 3 shows a list of the most frequent VOCs found by GC-MS. Several VOCs were found to be produced in the system. Four compounds were identified with higher outlet concentrations compared to their inlet values (2-Butanone, N,N- dimethyl, toluene and nonanal), being of particular interest toluene and nonanal, whose outlet concentrations exceeded their odor threshold as reported by Nagata (2003). Additionally, several VOCs with low odor thresholds such as methyl butyrate or decanal presented low REs. Therefore, it is notorious the fact that the residual odor of the gas stream was most probably due to non-eliminated (or even produced) VOCs, while the biologically treated  $\text{H}_2\text{S}$  contributes to the major part of the removal.

### Economical viability

Finally, an economical analysis was made to quantify the economic viability of the conversion. First, an initial investment of around 9000 € per reactor was estimated for the conversion. On the other hand, changes introduced resulted in operating costs (mainly reagents consumption) savings. A cost of  $7.4 \text{ € kg H}_2\text{S}^{-1}$  was calculated previously to plant modifications. Savings due to reduction of chemicals consumption were estimated under two different approaches: the theoretical consumption approach and the actual consumption approach. Costs of chemicals were  $0.174 \text{ € kg}^{-1}$  for NaOCl and  $0.310 \text{ € kg}^{-1}$  for NaOH. For the theoretical approach, stoichiometric values for complete absorption and oxidation of  $\text{H}_2\text{S}$  to sulfate were considered for the calculation of the consumption of chemicals (Card, 2001), which resulted in  $20.4 \text{ kg} \cdot \text{h}^{-1}$  of NaOCl and  $2.4 \text{ kg} \cdot \text{h}^{-1}$  of NaOH, which represents  $178704 \text{ kg NaOCl} \cdot \text{year}^{-1}$  and  $12264 \text{ kg NaOH} \cdot \text{year}^{-1}$ . Using the previously mentioned costs of chemicals, a total of  $34182 \text{ € year}^{-1}$  was estimated which

represents the annual savings for operating as biotrickling filters. Taking into account the conversion cost and annual savings, payback time was estimated in 9-10 months for the complete system. For the actual consumption approach, historical data provided by the plant (consumption of 8149 kg NaOH·year<sup>-1</sup> and 7812 kg NaOCl·year<sup>-1</sup>) was used to estimate yearly savings of 4000 €year<sup>-1</sup> in reagents with a payback time estimated of around 7 years.

## DISCUSSION

The retrofitting of the chemical scrubbers was made reusing the shell, the packing support and part of the wetted parts from the previous installation. These are minimum requirements needed for any retrofitting process to be economically feasible (Gabriel and Deshusses 2004). In the conversion performed herein a special interested was placed in upgrading the make-up water supply system since a larger amount of water was needed at neutral pH in a naturally proton producing process. The water supply system was designed to permit, in the one hand, the automatic regulation of the flowrate based on on-off controllers actuated according to the signal of pH and sump level sensors. In the other hand, a second line allowed manual regulation of the make-up water flowrate to ensure a minimum addition of water to the biotrickling filters. The total conversion cost of 26580€ for the three scrubbers converted were in the range of those of previous conversions (Gabriel and Deshusses, 2005; Prado et al., 2009). Conversion costs were considered as in-house costs since were assumed by Ecotec in the benchmark of the project. Costs of the engineering work performed by the members of the project and other indirect costs were not considered. Then, the conversion, if performed by a contractor, would double or triplicate the conversion costs (Gabriel and Deshusses, 2003).

Adding activated sludge from the WWTP to startup the bioreactors is a common, inexpensive strategy at industrial scale. However, the longer startup period needed compared to former conversions (Gabriel and Deshusses, 2003) was attributed to a combination of factors. Mainly, the structured packing material FKP 158 provides a medium specific surface area without much capacity to retain suspended solids during the inoculation process. Also, the low VOCs and H<sub>2</sub>S concentrations found did not produce a large biomass growth. Thus, limited biological capacity existed to face the daily variations of the inlet load during the startup. However, the system was able to cope with the daily fluctuations found once operating under pseudo steady-state conditions (Figure 2a). On the other hand, such open structure of the packing material, that limited the startup performance, was advantageous in the long run if the pressure drop of the system is considered. Average pressure drops of 2.2±0.8, 1.8±0.6, 1.7±0.5 cm of water column per meter of packed bed in the three reactors were significantly lower than that found for other typical packing materials such as PUF. Large pressure drops have been reported as a handicap to install PUF in previous conversions (Prado et al., 2009) due to

reduced gas flow rates and increased odor concentrations in the waste gas sources if the blower was not replaced. Thus, a reduced pressure drop lead to lower conversion and operating costs with the structured packing (Dorado et al., 2010b). The load was expected to increase as the temperature increased. In particular, 2013 was a relatively colder year as compared to previous ones (Figure 1S). For instance, from January to May (days 75 to 200) the average inlet H<sub>2</sub>S concentrations were within a range of 1.2 – 3.7 ppm<sub>v</sub> with concentration peaks up to 8-12 ppm<sub>v</sub> (Figure 2a). Concentrations were even lower for VOCs (Figure 2S). The system was able to handle these peak values without forfeiting the efficiency, though the system was not extremely demanded in terms of treatment capacity. The system adapted well to progressively increasing loads registered along June and July with average inlet H<sub>2</sub>S concentrations of 7.3 and 6.5 ppm<sub>v</sub> and maximum peak values of 26 and 40 ppm<sub>v</sub>, respectively. Mainly, maintenance tasks in other areas of the WWTP that lead to the converted scrubbers to suddenly handle additional emissions. In this case, the system was not always able to treat the loads without jeopardizing the efficiency. Such fast, sudden load changes questions the ability of the system to react to abrupt changes of the operating conditions.

Maximum H<sub>2</sub>S ECs obtained herein were around 70 g/m<sup>3</sup>h for H<sub>2</sub>S for the three biotrickling filters. Gabriel and Deshusses (2003) reported ECs up to 105 g/m<sup>3</sup>h for a similar system operating at contact times of 2s. PU foam as packing material was identified to play a major role for such success due to improved pollutant mass transfer. Although the inlet load to the overall system was always below 70 g/m<sup>3</sup>h, during episodes of high loads, maximum ECs were observed for reactor 1 at around 45 g/m<sup>3</sup>h. Assuming similar conditions for the three reactors, which would be reached if reactor 3 received a higher load on a routine basis, the maximum EC for the whole system would be expected to be around 135 g/m<sup>3</sup>h. Such EC<sub>max</sub> is in the range of these EC<sub>max</sub>s reported previously (Gabriel and Deshusses, 2003; Shinabe et al., 2000; Wu et al., 2001) thus confirming the suitability of the packing material tested herein. In terms of VOCs removal at short EBRT, ECs observed in the present study were considerably low compared to an EC<sub>max</sub> of 15 gC/m<sup>3</sup>h obtained during the pilot tests in a biotrickling filter operated at EBRTs of 2 to 8 seconds [Dorado et al., 2013] and average EC<sub>max</sub> around 18 gC/m<sup>3</sup>h for a biotrickling filter treating NH<sub>3</sub> and VOCs at 1 s EBRT [Prado et al., 2009]. The more hydrophilic nature of the pollutants tested together with a larger EBRT of the pilot reactor may be factors influencing the larger EC<sub>max</sub> obtained in Dorado et al (2013). In addition, the low concentration of VOCs tested herein may explain such lower performance. Reduced RE at low pollutant concentrations for H<sub>2</sub>S have been described to produce mass transfer limitation due to a reduced driving force between the gas and the liquid phase (Gabriel and Deshusses, 2003; Kim and Deshusses, 2005), which was even more limiting herein due to the hydrophobic nature of the VOCs. Further monitoring is warranted to corroborate the suggested limit of the system.

Regarding the negative VOC efficiencies registered, it is worth noticing that the high variability of the entrance and exit, paired with the non-simultaneous measurements could have lead to measurements that can be interpreted as

production of VOCs. This uncertainty could be improved if simultaneous sensors are used in both ports, which would give a more accurate picture of the situation. Another possibility is that some VOCs were stripped from the liquid phase to the gas phase, hence producing VOCs in the reactors. This hypothesis is supported by the fact that the liquid phase was continuously fed with the secondary effluent of the WWTP without further post-treatment as make-up water. Therefore, some organic compounds found such as toluene (Table 3), which are common compounds in different parts of a WWTP (Gostelow and Parsons, 2000; Dincer and Muezzinoglu, 2008) that are not biologically treated, may be stripped out from the liquid phase to the gas phase. Though, this has not been studied and is subject of further investigation. Further characterization of the gas stream should be performed to clarify the uncertain situation of the VOCs and determine whether the low ECs are related to mass transfer problems due to the low solubility of the compounds.

Although a quantitative relation between odor removal and the removal of a particular pollutant is often not feasible (Lebrero et al., 2013), several authors have correlated the removal of H<sub>2</sub>S with odor when H<sub>2</sub>S is the predominant pollutant (Akdeniz et al., 2012; Gostelow and Parsons, 2000). Probably, the majority of the odor removal found herein could be attributed to the biodegradation of H<sub>2</sub>S, while residual odor concentrations between 2400 and 7600 OU m<sup>-3</sup> were attributed to the VOCs at the outlet. In addition, the higher the inlet odor concentration, the higher the odor removal efficiency which confirms the ability of the reactors to progressively adapt to increasing pollutant loads. Overall, satisfactory odor RE were obtained even if further treatment is probably needed to ensure no impact of the treated gases in the vicinity, particularly in the hottest season of the year.

From a cost-benefit point of view, the initial investment of around 9000 € per reactor for the conversion was similar compared to 11340€ of similar scrubbers retrofitting reported in the literature [Gabriel and Deshusses, 2004]. Compared to a payback time of 2-4 years calculated for a similar retrofitting case (Gabriel and Deshusses, 2003), a payback time below one year assuming a theoretical reagents consumption is significantly lower; while the 7 years payback time considering the actual consumption of reagents is out of the range of a feasible investment. The latter situation is related to a reduced addition of chemicals decided by plant personnel compared to the theoretical value needed to completely stabilize the absorbed H<sub>2</sub>S. Due to the economical situation in the country, the WWTP experienced lower budgets and savings were made on different aspects, being reagents one of the cutouts. Therefore it is difficult to state whether this specific case of conversion was economically feasible or not. In any case, it is important to consider the fact that the economic feasibility of a conversion process not only depends on the value of the initial investment (which is a function of the modifications needed to adapt the equipment) but also on the operation and control of the process. Perhaps, in a healthier economical context, the operation in plant would have been different and the numbers would tell that the payback time and hence the economic feasibility of the conversion is convenient for the organization.

## CONCLUSIONS

The present work confirms the technical and economical viability of the conversion of chemical scrubbers into biotrickling filters. Despite the low contact time of the gas phase, the biological operation of the equipment was viable, showing that simultaneous treatment of H<sub>2</sub>S and VOCs is feasible operating at neutral pH with sustained efficiencies in the long-run. The structured packing material tested performed properly with estimated maximum capacities similar to those of polyurethane foam but with a much lower pressure drop. Still, larger startup periods are needed. Additionally, odor removal was successfully achieved, mainly due to H<sub>2</sub>S elimination but also attributed to VOCs removal. The remaining odor was attributed to incomplete removal of VOCs in the outlet stream. Regarding the economical aspect, biotrickling filters can generate important savings regarding the usage of chemicals, yet the feasibility depends on other external factors as well.

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