Proposing a new batch method for assessment of biological activity in H_2S degrading biotrickling filters

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ABSTRACT

The proposed batch method consists on measuring the sulfate production rate (SPR) at maximum rate of a set of polyurethane cubes extracted from an ongoing pilot-scale biotrickling filter (BTF) for hydrogen sulfide (H_2S) removal. Saturation of the system was achieved by applying high gaseous pollutant concentrations. Under these operational conditions the measured activity is proportional to the concentration of H_2S degrading biomass (X_{SH}) present in the system. This method has been used to follow the performance of a pilot-scale BTF under selected conditions. The activity at the inlet zone of the packed bed was found to be between two and three times that measured at the outlet zone. An increase in elimination capacity of 14% corresponded to a very similar average activity increase in the reactor. In addition to this, the method provided a means by which the reactor recovery after a starvation period could be studied.

1 INTRODUCTION

The amount of active biomass present in a system greatly influences its buffering capacity in terms of pollutant elimination under varying operational conditions or disruptions. Biotrickling filters operating in wastewater treatment plants are generally exposed to a considerable variety of fluctuating conditions. Among these, natural variations in the waste air composition leading to varying inlet loads (Cox *et al*., 2002) and interruptions in the plant operation, e.g: breakdown of equipment or electrical failure (Gabriel *et al*., 2004), are the most common transient-state phenomena BTFs must face. The buffering capacity of these bioreactors has traditionally been assessed

by introducing artificial pollutant spikes at the gas inlet and by subjecting the reactor to pollutant starvation (Wani *et al*., 1998; Chung *et al*., 2007).

Different methods of determining biomass abundance or concentration and its activity in a bioreactor are found in the literature. Changes in the active cell number of microbial species are commonly assessed (Gabriel and Deshusses, 2003; Sercu *et al*., 2005) using plate counts to measure colony forming units (CFUs). Other authors, however, measure the protein content by the bicinchoninic acid (BCA) method to determine biomass concentration (Kan and Deshusses, 2005; González-Sánchez *et al*., 2006). For the determination of biofilm activity substrate-induced oxygen uptake rate (OUR) measurements are employed most. In this case, the biofilm is washed out from the packing and transferred to the liquid solution where the decrease in oxygen concentration is measured (Cox and Deshusses, 2002).

The objectives of this work were twofold: first of all, to propose a new batch method that enables the biological activity of hydrogen sulfide degrading BTFs to be followed through the measurement of sulfate production rates. Secondly, to demonstrate the suitability of this method of observing the changes in activity of a H_2S degrading pilot-scale BTF under the following selected applications: a) along the packed bed height for constant applied load; b) for increasing pollutant loads; c) for elimination capacity recovery after a 15 day starvation period; d) for increasing packed-bed temperature.

The information provided by this type of test, that is by the off-line assessment of the H_2S degrading biomass concentration, also promises to be very valuable for the calibration of mathematical models for H_2S removal in BTFs.

2 MATERIALS AND METHODS

2.1 Basic principles of the proposed methodology

The proposed method consists on measuring the maximum sulfate production rate of a set of polyurethane foam cubes placed in a batch reactor. First of all it is noted that the main difference between the proposed methodology for activity measurements and those found in the literature is that the biofilm is not washed and remains attached to the packing material. This situation is preferable since the presence of the whole biomass in the batch test is ensured. In addition to this, environmental conditions in the batch reactor are closer to those in the pilot reactor.

Secondly, the off-line assessment is carried out under maximum degradation rate conditions; that is, in a completely H_2S saturated system where the activity is maximum. In a continuous reactor, however, the actual activity is normally below its maximum. The stoichiometry and kinetics for substrate utilization and biomass growth are shown in Table 1 where C_{SH} (g S-H_2S·m^{-3}), C_{O2} (g O·m^{-3}) and C_{SO4} (g S-SO_4^{2-}·m^{-3})

are the hydrogen sulfide, oxygen and sulfate concentrations in the water phase; K is the maximum substrate utilization rate (g S·g COD^{-1}·day^{-1}); and K_{SH} is the half-saturation constant (g S-H_2S·m^{-3}).

Table 1.
Stoichiometry and kinetics of H_2S oxidation.

Process/Component	C_{SH}	X_{SH}	C_{O2}	C_{SO4}	Kinetics
Substrate utilization and biomass growth	-1	Y_{SH}	2-Y_{SH}	1	$K\frac{C_{SH}}{K_{SH}+C_{SH}}X_{SH}$

If kinetics are expressed in terms of biomass growth instead of substrate utilization, the K parameter is substituted by the term Y_{SH}·K = μ_{SH}, where Y_{SH} is the biomass yield coefficient (g COD·g S^{-1}) and μ_{SH} is the maximum specific biomass growth rate (day^{-1}). According to the above expression, for values of C_{SH} higher than three to five times K_{SH}, the term $C_{SH}/K_{SH} + C_{SH}$ can be approximated to unity, meaning that kinetics will be saturated. Under these conditions the maximum SPR will be proportional to μ_{SH}·X_{SH}. A completely saturated system implies that both the liquid and the biofilm are saturated. The gas to liquid mass flux can be described as q_{ex} (C_{gas}/H_{SH}·- C_{SH}) where q_{ex} is the mass exchange coefficient (m^3·day^{-1}) that depends on, among others things, the gas-liquid contact area; C_{gas} is the H_2S concentration in the gas phase; and H_{SH} is Henry's constant.

2.2 Description of the experimental set-up

The batch reactor employed for the activity tests consisted of a clear PVC column with an internal diameter of 0.15 m and a 0.29 m bed height (see Figure 1). For each SPR experiment 60 cubes (4-cm polyurethane foam) randomly picked from an ongoing H_2S degrading pilot-scale reactor described in detail elsewhere were used (Otegi *et al*., 2006). This number was considered to be representative enough of the studied location at the pilot plant. The batch reactor was fed through a mixing chamber with a mixture containing air provided by air pumps and pure H_2S from a cylinder. A theoretical inlet pollutant concentration of 1640 ppm was continuously applied for two hours. It was operated at an average constant air flow rate of 518 l·h^{-1} providing an empty bed residence time (EBRT) of 36 seconds. Two litres of recirculation liquid from the same BTF containing an initial sulfate concentration and nutrients were continuously recycled at a constant rate of 42 l·h^{-1}.Unreacted gaseous H_2S was absorbed by a sodium hydroxide solution.

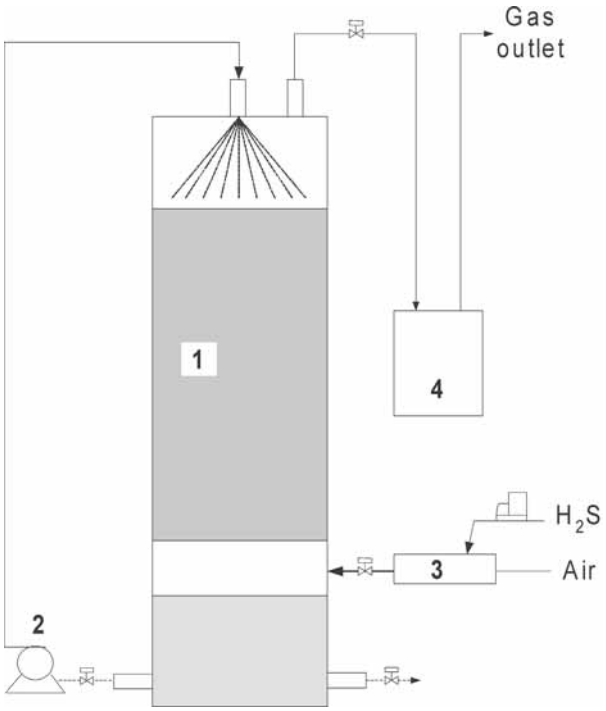

Figure 1. Schematic of the batch reactor.
1: PUF cubes; 2: recirculation pump; 3: mixing chamber; 4: NaOH solution

2.3 Batch methodology

The maximum SPR of the reactor was determined at different heights of the pilot plant packed-bed; namely at the inlet (INL), intermediate (INT) and outlet (OUT). In order to experimentally verify biological maximum degradation rate conditions in the batch reactor, specific SPR tests were carried out where theoretical inlet H_2S concentrations up to 3360 ppm were applied. The possible effect of the gas-liquid contact area on H_2S mass transfer was also studied by increasing the recycle liquid flow from 42 to 72 $l \cdot h^{-1}$. For these activity tests INL and OUT cubes were used. The tests showed identical results for biomass corresponding to the same height independently of the applied concentration (Figure 2) or recycle flow (Figure 3) indicating that for the studied operational conditions the proposed methodology succeeded at working under the desired maximum rate conditions.

Abiotic control tests in which PUF cubes containing no biomass were used were also carried out so that any possible non-biological sulfate formation could be disregarded (results not shown). For these, an inlet concentration of 1640 ppm was

tested under different temperature conditions. The kinetics for sulfate formation in the absence of biomass were found to be negligible.

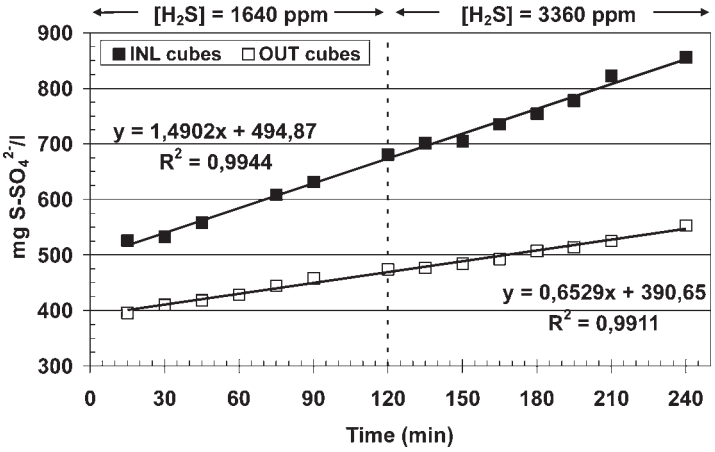

Figure 2. Influence of gaseous inlet H_2S concentration on SPR methodology (INL and OUT cubes).

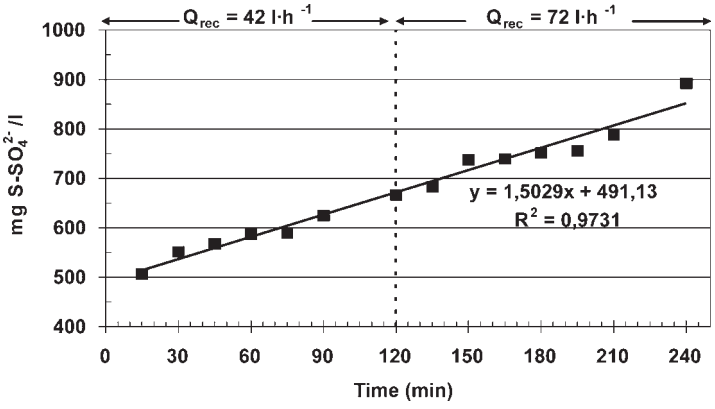

Figure 3. Influence of trickling rate on SPR methodology (INL cubes).

The biological activity results presented in this paper were obtained from SPR tests carried out to demonstrate selected specific applications of this methodology. Therefore, care should be taken when comparing rates corresponding to different applications to the overall elimination capacity of the ongoing pilot scale reactor because here the steady-state situation cannot always be ensured.

Water samples from the recirculation liquid were periodically withdrawn and immediately analyzed for pH and conductivity using a regular pH meter and a conductimeter (Crison). For sulfate content measurements a turbidimetric method was employed (APHA, 1995). Ammonia, phosphate and temperature measurements were also carried out at the beginning and end of each test to check nutrient availability and any temperature variations in the recycle liquid.

3 RESULTS AND DISCUSSION

3.1 Effect of reactor height

It is well known that BTF type reactors exhibit biomass distribution patterns along the packed bed height (Kennes and Veiga, 2001; Jin *et al.*, 2005). The usefulness of the proposed methodology was tested for biological activity measurements along the pilot-scale BTF packed-bed height. For that aim, SPR tests were carried out with INL, INT and OUT cubes at a relatively constant packed bed temperature (21±1). The activity value (or the biomass concentration) at the inlet zone of the packed bed was found to be roughly three times of that at the outlet zone as shown in Table 2. Accordingly, and as expected, polyurethane foam cubes extracted from an intermediate reactor height exhibited mid activity values.

In order to explain these results, it should be taken into account that the biomass X_{SH} is on the one hand proportional to Y_{SH}, Q and ΔS, where Q is the air flow rate ($m^3 \cdot d^{-1}$) and ΔS is the eliminated concentration for a selected packed bed volume ($g\ S \cdot m^{-3}$). However, at the same time, X_{SH} is inversely proportional to the detachment rate of the biofilm. As explained by Otegi *et al*. (2006) the ongoing pilot BTF was operated to achieve relatively high H_2S outlet concentrations giving rise to a relatively saturated system. For that reason, a lower biomass difference than the one measured experimentally would have been expected between the inlet and outlet zones. The higher difference observed herein is attributed to differences in the detachment rate, this parameter being higher at the outlet zone of the bed where water is trickled over more directly.

Table 2.
Activity values along the packed bed height of the BTF.

Origin of the packing	SPR ($mg\ S\text{-}SO_4^{2-} \cdot l^{-1} \cdot min^{-1}$)	R^2
INL	1.6142	0.97
INT	1.1481	0.90
OUT	0.5841	0.88

3.2 Effect of pollutant load

When subjected to a 30% load increase under relatively constant packed bed temperature conditions (21 ± 1ºC), the BTF showed an overall increase in elimination capacity of only 14% (see Table 3). The SPR measurements carried out with INL and OUT cubes revealed an increase in biological activity of 25% and 9%, respectively. From these result it can be stated that the average SPR increase observed along the reactor height (~ 17%) agrees reasonably well with the increase in the whole elimination capacity. This is believed to be a logical result because the maximum activity is proportional to the removed load.

Table 3.
Effect of load on activity values.

Origin of the packing	Applied load (g $H_2S \cdot m^{-3} \cdot h^{-1}$)	EC (g $H_2S \cdot m^{-3} \cdot h^{-1}$)	SPR (mg $S\text{-}SO_4^{2-} \cdot l^{-1} \cdot min^{-1}$)	R^2
INL	34.8	32.5	1.1920	0.99
OUT	34.8	32.5	0.5985	0.99
INL	45.1	36.7	1.4902	0.99
OUT	45.9	37.5	0.6528	0.99

3.3 Effect of a starvation period

The effect of a 15-day starvation period on the BTF performance was also tested. During that period no air or pollutant was fed to the reactor and only a low water trickling rate was maintained to prevent the biofilm from drying out. Operation of the reactor was restarted with an applied load of 7.3 g $H_2S \cdot m^{-3} \cdot h^{-1}$ which was gradually increased up to 40.5 g $H_2S \cdot m^{-3} \cdot h^{-1}$ by changing both the air flow and the inlet concentration (results not shown).

As shown in Table 4 the activity of INL cubes was measured one, two and almost six weeks after the starvation period began for a packed bed temperature range of 19 ± 1.5ºC. From the long starvation experiment an important activity loss was expected to happen at the reactor and this fact was confirmed by the low activity value measured in the SPR test carried out at the end of the first week of operation. A roughly two-fold increase in the elimination capacity of the continuous reactor (from 5.4 to 10.4 g $H_2S \cdot m^{-3} \cdot h^{-1}$) was similarly reflected in the batch tests as a double activity value. For the further increase in the overall elimination capacity of the reactor (from 10.4 to 40.5 g $H_2S \cdot m^{-3} \cdot h^{-1}$) the four-fold activity rise was also found to be almost proportional to the gained elimination capacity.

Table 4.
Reactor recovery after a starvation period.

Origin of the packing	Time from restart (days)	SPR (mg $S\text{-}SO_4^{2-}\cdot l^{-1}\cdot min^{-1}$)	R^2
INL	7	0.2359	0.93
INL	14	0.4926	0.98
INL	40	1.9479	0.99

3.4 Effect of temperature

Temperature is known to be an important parameter that affects physical absorption, biological oxidation, and especially microbial growth. Results corresponding to SPR measurements carried out to study the effect of this parameter on biological activity are summarized in Table 5. Cubes corresponding to the INL zone were used and the effect was studied for an 8ºC temperature difference. It was found that at 30ºC, the biological activity was three-fold of that measured at the lower temperature. As stated in the basic principles of this methodology, the measured maximum SPR is not only proportional to X_{SH} but to the product $\mu_{SH} \cdot X_{SH}$. Therefore, the observed three-fold rise in activity is attributed to both an increase in the value of μ_{SH} and X_{SH}.

Table 5.
Effect of temperature on biological activity.

Origin of the packing	Packed bed temperature (ºC)	SPR (mg $S\text{-}SO_4^{2-}\cdot l^{-1}\cdot min^{-1}$)	R^2
INL	30	5.2120	0.98
INL	22	1.5796	0.83

4 CONCLUSIONS

A new batch method has been proposed for maximum sulfate production rate determination of a set of polyurethane foam cubes taken from a continuous H_2S degrading BTF. From the results presented in this paper it can be concluded that the proposed method has proven to be a useful tool in following the H_2S degrading biomass concentration of a BTFs. This has been demonstrated through the satisfactory application of the methodology to selected conditions. Results have confirmed, for

example, that an activity (or biomass) gradient exists along the studied BTF packed bed. The activity at the inlet zone was found to be two to three times that of the activity measured at the outlet zone. In addition, the recovery of the activity in a reactor subjected to a long starvation period is proportional to the gained elimination capacity as the load is gradually increased.

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