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Co-treatment of H_2S and toluene in a biotrickling filter

Huub H.J. Cox, Marc A. Deshusses*

Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, USA

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Abstract

Biological treatment is an emerging technology for the treatment of publicly owned treatment works (POTWs) off-gases. Most of POTWs off-gases contain H_2S and a wide range of volatile organic compounds (VOCs). Since co-treatment of odors and VOCs in biotrickling filters is a relatively unexplored area, the simultaneous biotreatment of H_2S and toluene (as the model VOC) was investigated. The experimental setup included two identical biotrickling filters, one operated at pH 4.5 and the other one was operated at pH 7.0. High concentrations of H_2S (up to 170 ppm_v) and toluene (up to 2.2 $g\,m^{-3}$) were supplied to determine the influence of the pH on the maximum performance. A rapid startup (a few days) was observed for both toluene and H_2S removal in the neutral-pH biotrickling filter. In the acidic biotrickling filter, toluene degradation also started immediately but at a lower rate. However, after several weeks of operation, the toluene elimination capacity (EC) at low pH reached a steady value identical to this found in the neutral-pH biotrickling filter. H_2S did not affect toluene degradation at concentrations up to 170 ppm_v at either pH. At a volumetric load of 100 $m^3\,m^{-3}\,h^{-1}$, maximum elimination capacities of 70 g toluene $m^{-3}\,h^{-1}$ (at 1.7 $g\,m^{-3}$ toluene) and 20 g $H_2S\,m^{-3}\,h^{-1}$ (at 170 ppm_v H_2S, the highest concentration tested) were observed. Microbial counting and activity measurements indicated the development of different microbial populations in the reactors. In the neutral-pH biotrickling filter, a population developed which had a limited tolerance to low pH. The population in the acidic biotrickling filter showed a broader pH range for removal of H_2S and toluene. Overall, the results presented indicated that effective co-treatment of H_2S and VOCs can be obtained in a single-stage biotrickling filter.

Keywords: Waste air treatment; Biotrickling filter; Odor; H_2S; VOC; POTW; Biofilter

1. Introduction

Hydrogen sulfide (H_2S) is the principal odorous component in off-gases from publicly owned treatment works (POTWs). It causes odor nuisance at concentrations as low as about 8 ppb_v [1] and corrosion problems in sewer systems [2]. POTW off-gases also contain a wide range of other odorous compounds, air toxics and volatile organic compounds (VOCs). These include reduced volatile sulfur compounds, ammonia, benzene, toluene, chloroform, dichloromethane, trichloroethylene, and other VOCs [3–5]. Of the air toxics, toluene is the most frequently detected. Concerns about odor nuisance to the surrounding communities as well as the implementation of more stringent regulations are forcing POTWs to treat their off-gases. In most cases, treatment is accomplished in caustic/hypochlorite or caustic/peroxide scrubbers. However, chemical scrubbers are expensive to operate and relatively inefficient for the treatment of compounds other than H_2S. This is why biological treatment of POTW off-gases is increasingly considered as an alternative to chemical scrubbing [6].

Biotreatment of off-gases relies on pollutant-degrading microorganisms to oxidize organic and inorganic gases or vapors. The two most promising bioreactors for air pollution control are biofilters and biotrickling filters. Biofilters are essentially compost beds through which the contaminated air is passed [6,7]. The contaminants are absorbed and degraded by naturally occurring mixed cultures immobilized on the packing. Biotrickling filters work in a similar manner to biofilters, except that an aqueous phase is trickled over the packing, and that the packing is usually made of some synthetic or inert material, like plastic rings, open pore foam, or lava rock. The trickling solution contains essential inorganic nutrients such as nitrogen, phosphorous, and potassium, and is usually recycled [8].

Many studies have investigated the removal of either H_2S or VOCs as single pollutants in biofilters and in biotrickling filters. VOCs such as toluene can be effectively removed at rates up to 100 grams per cubic meter reactor bed per hour ($g\,m^{-3}\,h^{-1}$) [9,10]. H_2S is also rapidly degraded in biofilters and in biotrickling filters [1]. However, in biofilters, accumulation of sulfate from the oxidation of H_2S

* Corresponding author. Tel.: +1-909-787-2477; fax: +1-909-787-2425.
E-mail address: mdeshuss@engr.ucr.edu (M.A. Deshusses).

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often causes a decrease of the performance in the long run [11,12].

Relatively little is known on the treatment of off-gases that contain both H_2S and VOCs. H_2S is generally oxidized by *Thiobacillus* species that exhibit optimum activity at acidic pH [2]. However, most *Thiobacillus* species are autotrophic organisms and, therefore, they do not use VOCs as a carbon source for growth. On the other hand, VOCs are degraded by heterotrophic microorganisms, which are thought to be most effective at a neutral pH. These apparently conflicting pH optima for microbial activity are a challenge for developing bioreactors for removing both H_2S and VOCs.

One solution is treatment in a two-stage process as proposed by Devinny et al. [3]. In the first stage, H_2S is oxidized in a biotrickling filter which pH is allowed to decrease as a result of sulfate accumulation. The H_2S-free off-gas is then passed through a neutral-pH biofilter for the removal of VOCs. Considerable savings could possibly be made if H_2S and VOC removal was combined in one bioreactor. Recent research at POTWs has shown that H_2S and low concentrations of VOCs can be co-treated in biofilters without pH control and letting the pH decline [4,13,14]. Experiments with a pilot-scale biotrickling filter were less successful [13]. In particular, the removal of VOCs was poor, although the biotrickling filter was operated at a neutral pH. Further research in understanding the performance and limits of H_2S and VOC co-treatment in biotrickling filters was warranted.

We investigated the use of biotrickling filters for the co-treatment of high loadings of H_2S and toluene. As the pH was expected to be the most critical parameter, two identical biotrickling filters were operated but at different pH. The effect of pH on the acclimation of the process culture and on the co-treatment performance of H_2S and toluene is reported and discussed.

2. Materials and methods

2.1. Experimental setup

Two laboratory-scale biotrickling filters were used. One was operated at pH 7.0 (Reactor 1) and the other one was operated at pH 4.5 (Reactor 2). The equipment was similar to this used in a previous study [9] except for the supply of H_2S and for the pH control (see below). The principal characteristics and the standard operating parameters of the biotrickling filters are summarized in Table 1 and a schematic representation is shown in Fig. 1. The pH was maintained within ± 0.3 units by a Cole-Parmer (Vernon Hills, IL) pH controller, which regulated the automatic addition of 0.5 M NaOH to each reactor. Each biotrickling filter was filled with 1 kg of 1 in. polypropylene Pall rings (Koch Engineering, Wichita, KS) resulting in a bed volume of 10-l. Gas flow ($1\,m^3\,h^{-1}$) was cocurrent with the trickling liquid. Toluene was introduced into the gas stream by saturating a side air stream by sparging into a bottle filled with pure toluene. H_2S was introduced by passing the gas stream over a HCl solution into which a solution of Na_2S was dripped. H_2S concentrations ranging from 0 to 170 ppm_v were obtained by changing the Na_2S concentration and/or the dripping rate. Except for the pH of the recycle liquid and the medium composition (Table 1), both biotrickling filters were operated in an identical way. The sequence of the experiments is presented in Table 2.

Table 1
Experimental setup and operating parameters of the biotrickling filters

Design	
Bed height and internal diameter	55×15.2 cm
Bed volume	10 L
Packing	1 kg polypropylene 2.5 cm (1 in.) Pall rings
Recycle liquid volume	4.5 L
Gas/liquid flow	Cocurrent
pH control	Automatic, addition of 0.5 M NaOH
Operation	
Gas flow rate (EBRT[a])	$1\,m^3\,h^{-1}$ (36 s)
Volumetric loading[b]	$100\,m^3\,m^{-3}\,h^{-1}$
Toluene inlet concentration	Variable, up to $2.25\,g\,m^{-3}$
H_2S inlet concentration	Variable, up to 170 ppm_v
Superficial liquid velocity	$5.6\,m\,h^{-1}$
Recycle liquid pH	Reactor 1: 7.0, Reactor 2: 4.5
Medium feed rate	$100\,ml\,h^{-1}$
Medium composition	Reactor 1 (per l): 0.54 g KH_2PO_4, 1.05 g K_2HPO_4, 0.5 g NH_4NO_3, 1 g NaCl, 0.26 g $MgSO_4$, 0.025 g $CaCl_2{\cdot}2H_2O$, 1 ml trace elements solution. pH = 6.9 Reactor 2 (per l): same as Reactor 1, but with 1.25 g KH_2PO_4 and no K_2HPO_4. pH = 4.3

[a] Empty bed retention time = bed volume/gas flow rate.
[b] Gas flow rate/bed volume.

2.2. Analytical methods

Toluene and CO_2 were analyzed by injecting grab samples into an HP 5890 GC equipped with capillary and packed columns, and with FID and TCD detectors [9]. H_2S was determined with a Jerome 631-X hydrogen sulfide analyzer (Arizona Instruments, Tempe, AZ). Microbial counts were done by serial tenfold dilutions of recycle liquid and biofilm samples in $8.5\,g\,l^{-1}$ NaCl, and subsequent plating on various media. Heterotrophs were counted on plate count agar (Difco), yeasts and fungi on oxytetracycline glucose yeast extract agar (respectively 0.1, 20, 5 and $20\,g\,l^{-1}$), toluene-degraders on mineral medium (see Table 1) solidified with $8\,g\,l^{-1}$ agarose (toluene supplied to the gas phase during incubation), and autotrophic sulfur-oxidizers on thiosulfate agar [15] (no carbon source other than atmospheric CO_2 was provided). All media were prepared at both pH 4.5 and 7.0 for separate enumeration of acidophilic and pH-neutral species. For activity measurements of the biofilm, samples were suspended in the recycle liquid

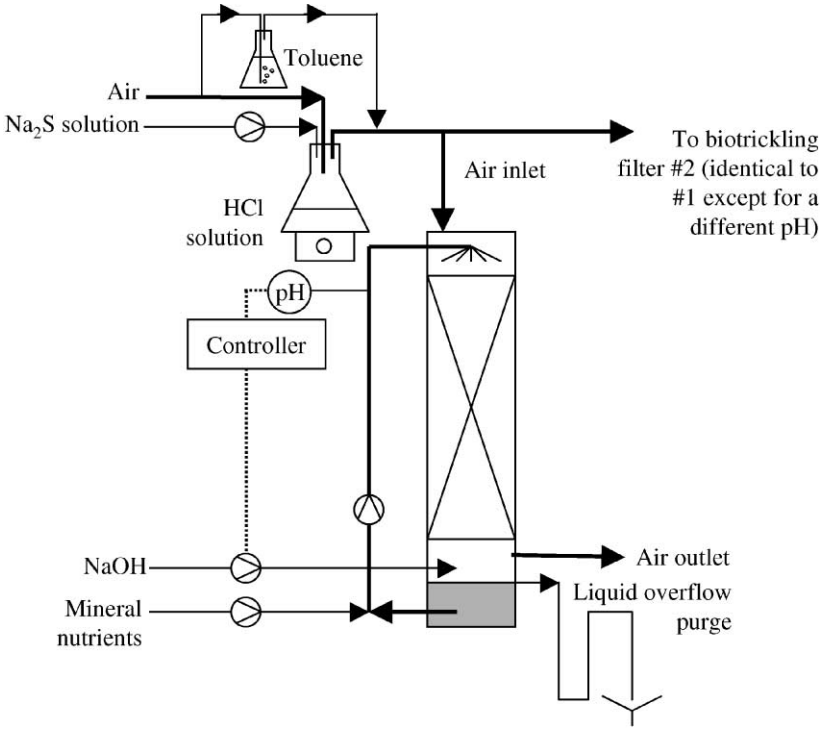

Fig. 1. Schematic representation of the experimental setup (only one biotrickling filter is shown).

and analyzed for substrate-induced oxygen uptake rates (OURs) at various pH. After adjustment of the pH with HCl or NaOH, 2.5 ml sample were placed in a custom-made vessel fitted with an oxygen electrode (YSI, Yellow Springs, OH) and saturated with air at room temperature. Substrate-induced OURs were measured after the addition of aqueous solutions of toluene, Na_2S or $Na_2S_2O_3$. The initial concentrations for OUR determinations were 0.19 mM toluene, 0.27 mM Na_2S or 0.14 mM $Na_2S_2O_3$. OUR values were corrected for the endogenous respiration. Sulfide concentration in the recycle liquid was determined in duplicate with an assay-kit from CHEMetrics (Calverton, VA).

3. Results and discussion

3.1. Startup with toluene as only pollutant

On the first day of operation, both biotrickling filters were inoculated with biomass from a toluene-degrading biotrickling filter [9] and toluene as sole pollutant was passed through the reactors. Fig. 2 shows the startup at the two different pHs. In both biotrickling filters, biodegradation of toluene started within 1 day, but toluene removal at pH 4.5 was only about 30% of the rate at pH 7.0. Microscopic examination of the recycle liquid showed rapid

Table 2
Experimental design

Day	Experiment
0–22	Startup with toluene as the sole pollutant (reactors controlled at pH 4.5 and 7.0, respectively)
16–19	Performance versus load curve, toluene sole pollutant
22–42	Introduction of 7.7 ppm_v H_2S while maintaining toluene at 0.3–0.5 $g\,m^{-3}$
57	Response to re-introduction of H_2S after a 7 day break
69–110	Steady-state performance with 1 $g\,m^{-3}$ toluene and 0–170 ppm_v H_2S
139–140	Microbial counting and characterization of the recycle liquid and biofilm
151	OUR[a] experiments with the biofilm
162	Reactor cleaning; restart with toluene and H_2S (reactors controlled at pH 4.5 and 7.0, respectively)
169–210	Steady-state performance experiments with slow changing pH
210	Reactor cleaning; restart with toluene and H_2S (reactors controlled at pH 4.5 and 7.0, respectively)
236	Response of the biotrickling filters to a sudden change of the pH
272–273	Measurement of sulfide in the recycle liquid at standard operation

[a] Oxygen uptake rate.

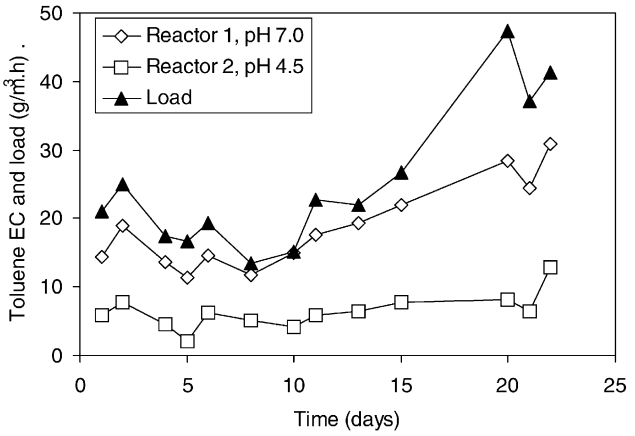

Fig. 2. Toluene loading and EC (= air flow × (inlet − outlet concentration)/bed volume) during the startup phase of the two biotrickling filters at a constant empty bed retention time (EBRT) of 36 s. Toluene (sole pollutant) inlet concentration fluctuated between 0.13 and 0.47 g m^{-3}.

development of a very diverse microbial population at pH 7.0, including various protozoa. The microbial population at pH 4.5 was less diverse, but not unexpectedly, contained a relatively high concentration of yeasts.

Performance versus load curves (Fig. 3), were determined on days 16–19, i.e., before complete acclimation, by stepwise increasing the toluene concentration while maintaining a constant volumetric loading. Clearly, the low pH severely inhibited toluene degradation in Reactor 2, which only reached a maximum elimination capacity (EC) of about 10 g m^{-3} h^{-1}, even at very high toluene loadings (>100 g m^{-3} h^{-1}). The maximum toluene degradation in Reactor 1 (pH of 7.0) was about 70 g m^{-3} h^{-1}, which is comparable to the rates observed in several other biotrickling filter studies. It is worth mentioning that at the time of this experiment, Reactor 1 contained about twice as much biomass as Reactor 2 (335 and 155 g wet biomass, respectively). Assuming uniform coverage of the packing, these amounts correspond to biofilm thicknesses of about 150 and 70 μm, respectively. This is expected to be sufficient for achieving high removal rates. Hence, the low toluene degradation rate at pH 4.5 was probably not caused by a limiting amount of biomass, but rather by a low specific microbial activity at pH 4.5. As discussed further in the paper, as acclimation of the process culture proceeded, the performance of Reactor 2 increased significantly over time until it equaled this of Reactor 1.

3.2. Introduction of low H_2S concentrations to toluene-degrading biotrickling filters

On day 22, supply of H_2S was started at an average concentration of 7.7 ppm_v, while maintaining an inlet toluene concentration of 0.3–0.5 g m^{-3} and the removal of toluene and H_2S was monitored over a period of 20 days. The H_2S concentration selected is representative of POTW off-gas, while the toluene concentration is 2–20 times higher than the total VOC concentration in POTW off-gas. These operating conditions were carefully chosen. Toluene was deliberately supplied in great excess to allow for the determination of a possible effect (positive or negative) of H_2S on toluene removal. This would not necessarily be possible if the experiment was performed at 99+% removal of the contaminants. Fig. 4 shows that removal of H_2S started immediately and was close to 100% in both reactors less than 5 days after H_2S introduction. Inoculation of biotrickling filters was apparently not required for a rapid startup of H_2S removal, probably because *Thiobacillus* and other H_2S oxidizing species are quite ubiquitous. Although inoculation was not required, the startup time of 5 days (Fig. 4) indicates that some adaptation towards H_2S degradation was required. This was either growth of the specific H_2S oxidizers, or acclimation of

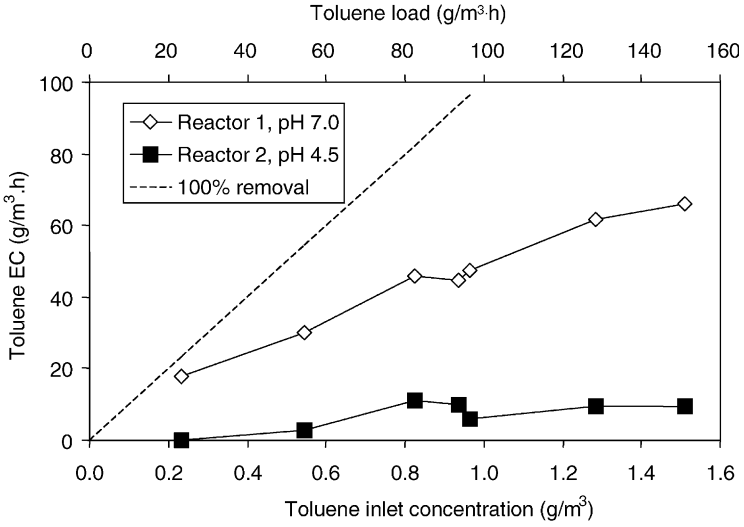

Fig. 3. Influence of the toluene inlet concentration on the EC during the startup phase, with toluene as the single pollutant (volumetric gas load 100 m^3 m^{-3} h^{-1}). The dashed line represent 100% removal of the toluene feed.

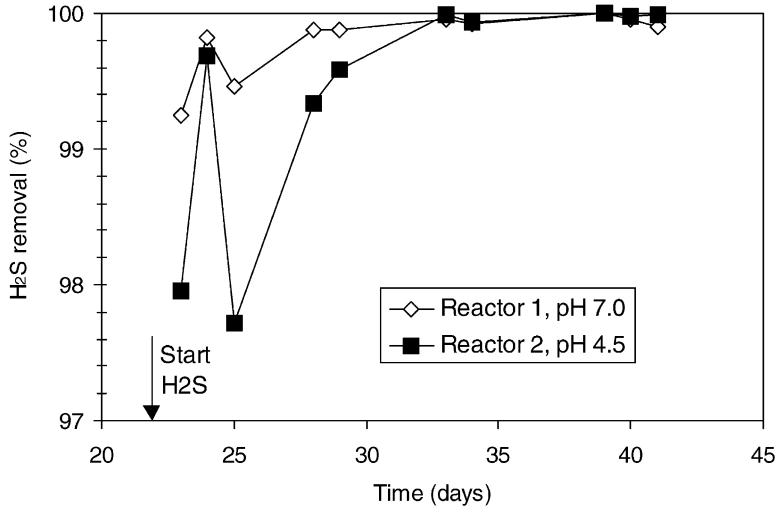

Fig. 4. H_2S removal efficiency in the presence of toluene. H_2S (7.7 ppm_v) was started on day 22 (arrow) in toluene-degrading biotrickling filters. Toluene concentration was 0.3–0.5 $g\,m^{-3}$, EBRT was 36 s.

the existing population. Such adaptation was not observed in an experiment performed 1 month later under similar conditions (inlet concentration: 8 ppm_v, same conditions as above). The removal of H_2S was monitored upon restarting the system after 7 days without H_2S. In that experiment, no breakthrough of H_2S was observed and the outlet concentration always remained under the detection limit [16]. While inoculation of the biotrickling filter was not needed here, inoculation is recommended when H_2S is the sole pollutant, or for very high load applications. Under the conditions tested herein, removal of H_2S was not affected by the pH once a steady state was reached. However, it should be noted that the H_2S loading during this experiment (about 1 $g\,m^{-3}\,h^{-1}$) was far less than the maximum EC in either reactors (see next sections). Hence, possible effects of the pH may have remained undetected since only the outlet gas was monitored. Toluene removal was not affected by the presence of H_2S (not shown). Toluene elimination capacities remained virtually the same as during startup with toluene only.

3.3. Steady-state performance at high loads of toluene and H_2S

Since no cross-inhibition effect of H_2S and toluene was observed at low concentrations, toluene and H_2S concentrations were increased. The objective was to evaluate the maximum performance of the systems and to determine possible toxic effects of high H_2S concentrations on toluene removal. The toluene concentration was set to 1 $g\,m^{-3}$, and H_2S concentrations were gradually increased from 0 to 170 ppm_v. As explained in the previous section, these conditions were specifically chosen to allow for a positive identification of possible pollutant interactions. Besides varying the H_2S concentration, all other operating conditions were kept constant for at least 3 days to ensure steady state, and pollutant removal and NaOH consumption rates were determined. The results are presented in Figs. 5 and 6 and in Table 3.

In Fig. 5, the EC of toluene is plotted as a function of the inlet concentration of H_2S for both the low-pH and the neutral-pH biotrickling filters. Clearly, toluene degradation was not affected by H_2S up to a concentration of at least 170 ppm_v. A remarkable finding illustrated in Fig. 5 is that the low-pH biotrickling filter exhibited a markedly higher toluene elimination than during the startup phase (compared to Fig. 3). The most probable explanation for this is that slow adaptation of an acid-tolerant toluene-degrading culture occurred in the reactor. Once this population reached a sufficient density, effective removal of toluene occurred. In fact, toluene elimination was about 15% higher at low pH than at neutral pH. This finding suggest that a strict control of the pH at a near neutral value is not necessarily required for efficient removal of easily biodegradable VOCs such as toluene in biotrickling filters.

Fig. 6 presents the data on H_2S removal in the two biotrickling filters. They were not statistically different. At a volumetric loading of 100 $m^3\,m^{-3}\,h^{-1}$, H_2S removal was complete up to an inlet concentration of about 50 ppm_v in both reactors. This corresponds to a H_2S EC of 7 $g\,m^{-3}\,h^{-1}$. The EC increased to 20 $g\,m^{-3}\,h^{-1}$ at an inlet concentration of 170 ppm_v, but the removal efficiency decreased to 70–80%. Higher elimination capacities (but lower removal percentages) would probably have been obtained if further increases in the H_2S inlet concentration had been performed. For comparison, a survey of literature data on H_2S removal in biofilters and biotrickling filters indicates that elimination capacities vary greatly with reported values ranging from 8 to 140 $g\,H_2S\,m^{-3}\,h^{-1}$ [1].

The fate of H_2S was further investigated. Sulfide concentrations in the recycle liquid was measured at the two operating conditions. The analysis revealed that dissolved sulfide

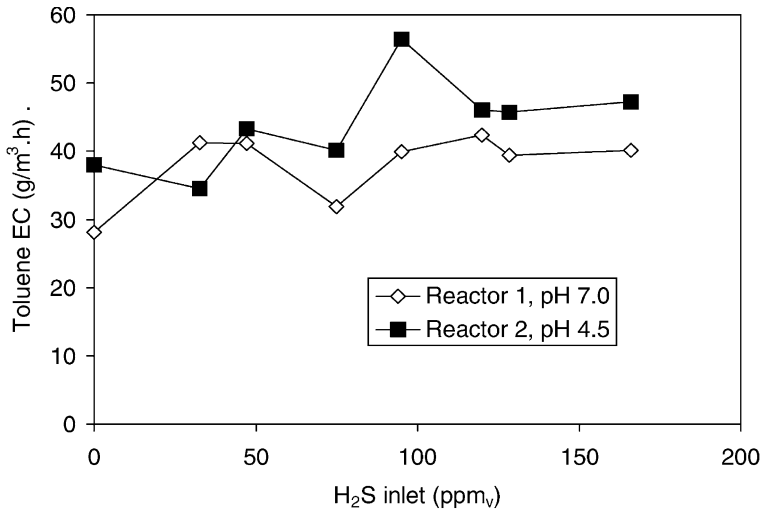

Fig. 5. Influence of the H_2S concentration on toluene removal (inlet 1 g m^{-3} toluene, toluene loading 100 g m^{-3} h^{-1}).

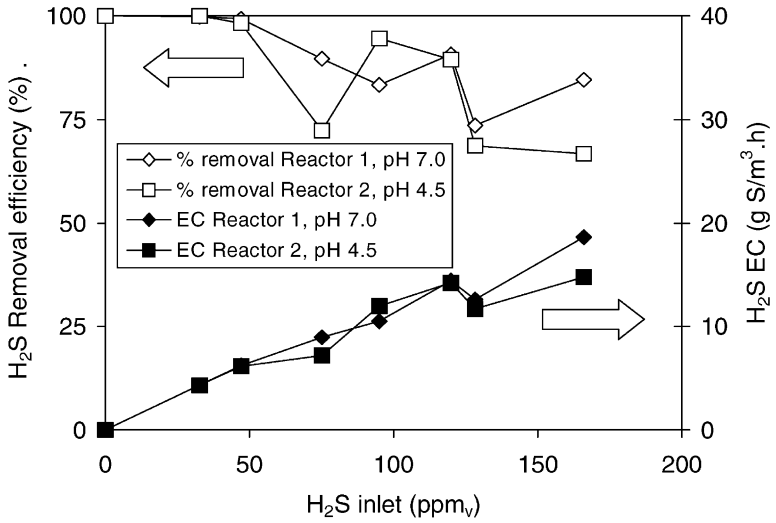

Fig. 6. H_2S removal efficiency and EC as a function of the inlet concentration and during co-treatment with 1 g m^{-3} toluene.

remained below 0.10 ppm at H_2S inlet concentrations of 20 and 70 ppm_v (Table 3). Hence, the amount of H_2S removed via the liquid purge was insignificant compared to the total amount removed from the waste gas and should not be a concern for industrial application. Data on the consumption of NaOH (Fig. 7) provided further insight as to the fate of sulfide. As expected, alkali consumption increased at higher H_2S inlet concentrations and higher degradation rates. Fig. 7 also compares the amount of NaOH consumed with the calculated amount needed for neutralization in case all the H_2S removed is completely oxidized to sulfuric acid. In both reactors, this ratio is close to 100% which strongly suggests

Table 3
H_2S removal by biological oxidation and via the liquid purge

Parameter	Reactor 1, operated at neutral pH		Reactor 2, operated at pH 4.5	
	29 December 1999	30 December 1999	29 December 1999	30 December 1999
H_2S in inlet air (ppm_v)	20	70	20	70
H_2S in outlet air (ppm_v)	0.003	8.1	0.002	3.1
H_2S in recycle liquid (ppm)	0.10	0.045	0.09	0.06
H_2S load (g m^{-3} h^{-1})	2.83	9.92	2.83	9.92
H_2S EC (g m^{-3} h^{-1})	2.83	8.77	2.83	9.48
H_2S removed via liquid purge (g m^{-3} h^{-1})	0.001	0.00045	0.0009	0.0006

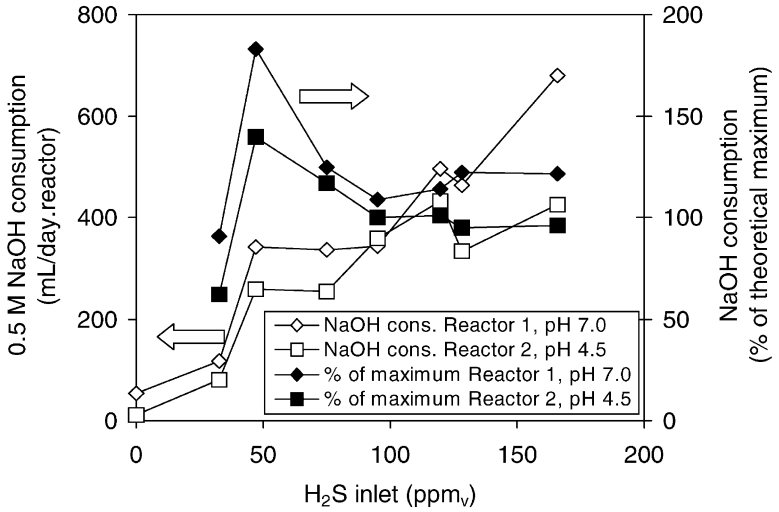

Fig. 7. Influence of H_2S concentration on NaOH consumption. Full symbols represent the ratio of the actual NaOH consumption to the theoretical consumption if removed H_2S is completely oxidized to sulfuric acid.

that H_2S is completely oxidized to sulfuric acid both at pH 4.5 and 7.0.

3.4. Characterization of microbial populations and activity measurements

In order to develop an explanation to some of the observed phenomena, a basic characterization of the process culture was attempted using simple plating techniques. Plate counting on solid media has the limitation that only viable cells capable of growth on the selected media will be counted. These may only constitute a minor fraction of the total population present in the biotrickling filter. Nevertheless, plate counting allows one to rapidly assess the microbiota of biotrickling filters. The results in Table 4 indicate that Reactor 1 operated at neutral pH contained a microbial population with a strong preference for a neutral pH. Counts on pH 4.5 media were several orders of magnitude lower than on pH-neutral media. This is an indication that operation of biotrickling filters at neutral pH caused selective enrichment of species capable of growing only at neutral pH. On the other hand, Reactor 2 operated at low pH contained relatively similar proportions of acid-tolerant and pH-neutral microorganisms, indicating that this reactor may have broader pH range for degradation of H_2S and toluene. This was confirmed by activity measurements of the biofilm in OUR experiments (Figs. 8 and 9). The biofilm from Reactor 1 oxidized toluene, Na_2S and $Na_2S_2O_3$ with maximum activity at pH 6–8, whereas at pH 4.5 microbial activity was

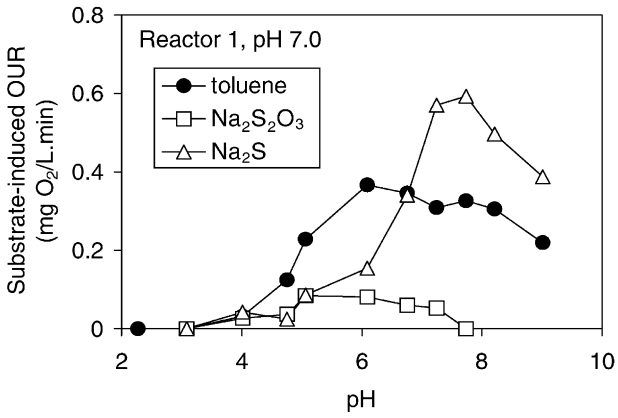

Fig. 8. Influence of the pH on the substrate-induced OURs by suspended biofilm from Reactor 1 operated at neutral pH.

Table 4
Counts (log counts/ml) of microbial populations in the recycle liquid and biofilm suspension; each class of microorganisms was counted on media with pH 4.5 and 7.0

Population	Reactor 1, operated at pH 7.0 (log CFU/ml)				Reactor 2, operated at pH 4.5 (log CFU/ml)			
	Recycle liquid		Biofilm		Recycle liquid		Biofilm	
	pH 4.5	pH 7.0	pH 4.5	pH 7.0	pH 4.5	pH 7.0	pH 4.5	pH 7.0
Total heterotrophs	3.8	7.5	5.3	7.7	6.5	7.1	6.6	7.3
Total yeast and fungi	3.7	4.2	5.2	5.9	5.0	6.2	6.3	6.6
Toluene-degraders	3.8	7.4	5.3	7.5	6.3	6.9	6.9	6.9
Autotrophic S-oxidizers	4.0	7.2	5.8	7.6	6.9	7.2	7.1	7.2

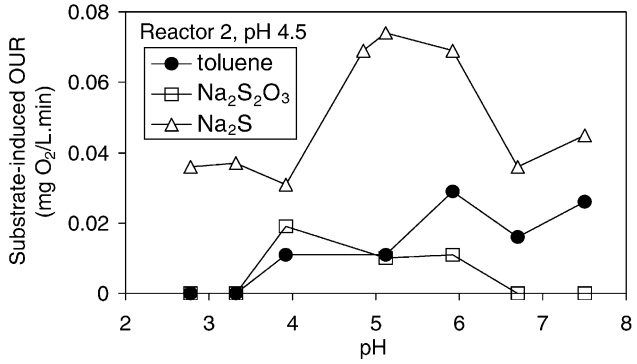

Fig. 9. Influence of the pH on the substrate-induced OUR by suspended biofilm from Reactor 2 operated at pH 4.5.

very low (Fig. 8). Biofilm from the low-pH reactor exhibited a much broader pH range for microbial activity (Fig. 9). It should be noted that the absolute values of OUR of Figs. 8 and 9 were quite different. This is because the two biofilms had different specific activities and because different concentrations of biofilm were used for OUR measurements.

3.5. Short-term sensitivity to a change of the pH

The effect of pH was further investigated in pH shock experiments. The pH of the recycle liquid of the neutral-pH reactor and of the low-pH reactor was temporarily lowered to set values of 3.8 and 2.6, respectively. Standard operation was continued throughout the experiment, and the performance of biotrickling filters was determined before, during and after the pH change. As shown in Fig. 10, the reactor previously operated at a neutral-pH showed a drastic decrease of the removal rate of both H_2S and toluene when the pH was lowered to 3.8. Such a response was expected, since plating experiments had shown that the number of acid-tolerant microorganisms in this reactor was low (Table 4).

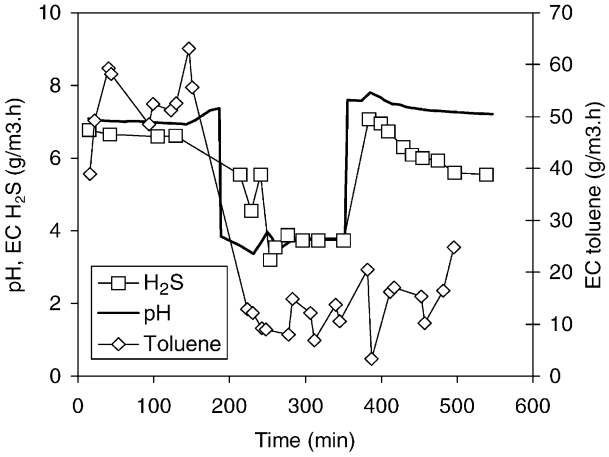

Fig. 10. Effect of a temporary decrease of the pH (set values 7.0 → 3.8 → 7.0) on H_2S and toluene removal in Reactor 1, normally operated at pH 7.0.

Readjustment of the pH to its original value immediately restored H_2S removal, but toluene removal remained low (Fig. 10). Apparently, the short-term low pH incursion had a different effect on the toluene and H_2S degrading microorganisms in Reactor 1. It is interesting to compare this experiment with another one where the pH of Reactor 1 was gradually decreased to a value of 2.1 over 33 days (not shown). Under these slowly changing conditions, the EC of toluene and H_2S was not affected, most probably because it allowed time for pH resistance mechanisms to develop or more likely it allowed sufficient time for acid-tolerant species to grow.

The pH shock experiment of Reactor 2 is shown in Fig. 11. The low-pH reactor was much less sensitive to a pH change, and the removal of H_2S and toluene was relatively unaffected (Fig. 11). Thus operation at low pH results in the establishment of biotrickling filters with a faster and more stable response to a change of the pH.

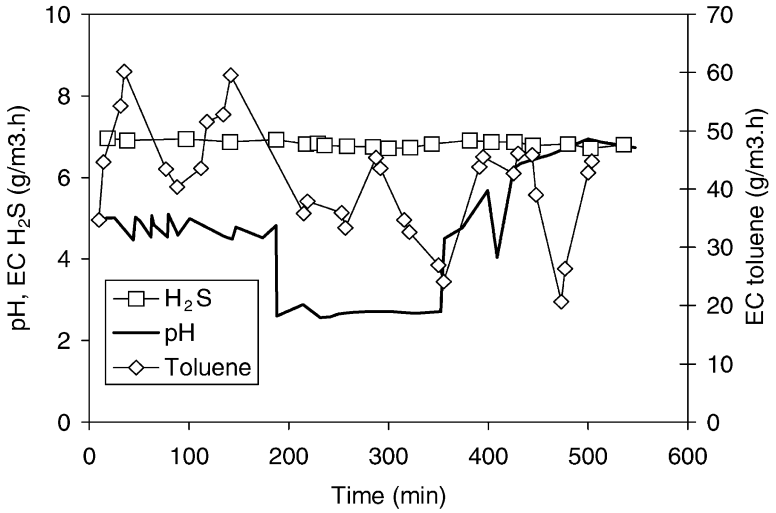

Fig. 11. Effect of a temporary decrease of the pH (set values 4.5 → 2.6 → 4.5) on H_2S and toluene removal in reactor, normally operated at pH 4.5.

4. Discussion

The results presented herein clearly demonstrate that H_2S and toluene can be effectively treated simultaneously in a single-stage biotrickling filter. Depending on the conditions, high elimination rates or high removal percentages of H_2S and toluene were obtained. H_2S biooxidation resulted in a near stoichiometric production of sulfate which was leached out of the system, while toluene was degraded to CO_2. All the data were consistent with a biological conversion of the pollutants. Toluene and H_2S biodegradation was a parallel process occurring simultaneously with no cross-inhibition. This was not totally unexpected since H_2S degradation is mediated by autotrophic organisms, while toluene degradation is mediated by heterotrophic organisms. Apparently, competition for nutrients, oxygen or other potentially limiting nutrient did not occur, hence both populations behaved relatively indifferently in the presence of each other. This is clearly different from the competition and cross-inhibition observed by others, especially in cases of pollutants of similar nature that are expected to be degraded by the same group of organisms, possibly even via the same pathway [17–19].

The effect of the pH on the biotrickling filtration process was complex. On the one hand, the reactor operated at a low pH required a 20–40-day startup time for the efficient removal of toluene. On the other hand, after startup, its H_2S and toluene removal performance was similar to that of the neutral-pH reactor. This is quite remarkable since the pH influences both the mass transfer of the pollutants (by changing the gas–liquid partition) and the composition and the characteristics of the process culture. Regarding the latter, marked differences were indeed observed in the activity of the biofilm (Figs. 8 and 9) and in the composition of the mixed cultures (Table 4) from the two reactors. These differences were found to be the result of the slow growth of different populations over time rather than from phenotype changes or stress-related responses. Plating experiments (Table 4) revealed that a majority of the culturable organisms present in the neutral-pH biotrickling filter could not grow at low pH, while those of the low-pH bioreactor could thrive either at low or at neutral pH. Clearly, the process culture in the low-pH reactor was acid-tolerant rather than acidophilic, as shown by higher plate counts at pH 7 than at pH 4.5. This hypothesis is consistent with the oxygen uptake experiments (Figs. 8 and 9) which revealed a wide window of operating pH for the biomass in the low-pH reactor, and a narrow pH range for the biomass in the neutral-pH reactor. It is further reinforced by the lesser pH sensitivity of the low-pH reactor during the pH shock experiments (Figs. 10 and 11).

While the good performance of the low-pH biotrickling filter for the removal of H_2S may not be a surprise in the light of the many studies on H_2S degradation alone [3,6,11,13], the good EC of toluene at low pH is remarkable (Fig. 5). It contrasts with a number of published and unpublished reports of biofilter failure due to low pH [6,20], and the large body of papers on the negative effect of low pH in soils. Regarding the latter, an interesting common finding in many soil studies is that the specific activity of microorganisms is often reduced under low pH conditions, but that the bacteria density may be unaffected by extreme pH. An interesting example of this was discussed by Mori et al. [21]. The biodegradation of the fungicide chlorothalonil was compared in four soils subjected to different nutrient and pH conditions. Degradation of chlorothalonil was increased by adjusting the soil pH to a neutral value, although the most probable number of degrading microorganisms remained constant. Thus, reduced microbial degradation of chlorothalonil at low pH was due to the decrease in the degrading capacity rather than a decrease in the number of degrading microorganisms. The low specific activity at low pH may explain the large differences observed during the oxygen uptake experiments (Figs. 8 and 9).

Overall, the results of this paper suggests that a strict control of the pH at a near neutral value is not required for efficient removal of toluene in biotrickling filters. However, the good performance of toluene degradation at low pH may not necessarily be extrapolated to less biodegradable compounds that are degraded by fewer microorganisms. When less functional redundancy exists for degrading the VOC or when VOC concentrations are low enough to prevent effective growth, selective enrichment of acid-tolerant VOC degrading organisms may not occur. Hence, a pH control may then be desired. Clearly, controlling the pH will influence the treatment costs. Options to control the pH include addition of caustic which can be expensive. At POTWs, where industrial water is available at virtually no cost, increasing the water supply to the reactor may be considered. One will need to keep in mind that the water requirements will increase exponentially which each pH unit, hence, this method may be impractical for the treatment of high concentrations of H_2S. For such cases, if a near neutral pH is required for VOC removal, the co-treatment of H_2S and VOC in one reactor will need to be reconsidered. Sequential treatment, i.e., treatment of H_2S in an acidic reactor first followed by VOC treatment in a near neutral bioreactor as proposed by Devinny et al. [3] may well be the method of choice.

5. Conclusions

The results discussed herein demonstrate that H_2S and toluene can be effectively treated simultaneously in a single-stage biotrickling filter. The pH of operation (4.5 and 7.0) did not greatly affect the performance of H_2S and toluene removal, except that at pH 4.5, the startup phase of toluene degradation was relatively long. Also, at pH 7.0, a sudden decline of the pH (e.g., after the failure of the pH control) caused temporary poor removal of H_2S and toluene which contrasts with the robustness of the low-pH biotrickling filter to changes in operating pH.

Selective enrichment of suitable microbial populations in biotrickling filters is a key condition for successful treatment.

Clearly the time for such enrichment will depend on the severity of the stress imposed and the diversity of the organisms capable of performing the required degradation. However, once an adequate culture is established, the results of this paper show that high pollutant removal rates can be obtained, even at conditions that first seemed unfavorable for biodegradation.

Biotrickling filters are simple and effective. They may become the preferred treatment technique for complex off-gases at POTWs. The specific conditions at each POTW will dictate the design criteria for each biotrickling filter. But in most cases, because of the large volume of off-gases requiring treatment at POTWs, the deployment of biotrickling filters will call for designing biotrickling filters with a short gas residence time and capable to achieve H_2S removal down to very low levels (ppb_v), while removing target VOCs. This will require further careful evaluation of the rate-limiting step in the process and of the impact of the operating pH on the cost of the biotrickling filter equipment and on the costs associated with the operation and the maintenance of the reactor.

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