

# Combined Removal of H<sub>2</sub>S and Toluene in a Single-Stage Biotrickling Filter

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## ABSTRACT

Most off-gases from POTWs contain H<sub>2</sub>S and a wide range of VOCs. Hence the objective of this work was to determine the effectiveness of co-treatment of H<sub>2</sub>S and toluene (as the model VOC) in single-stage biotrickling filters. The experimental setup included two identical biotrickling filters, but with operation at pH 4.5 or 7.0. High concentrations of H<sub>2</sub>S (up to 170 ppm) and toluene (up to 2.2 g/m<sup>3</sup>) were supplied to investigate the influence of the pH on the maximum performance. A rapid startup (a few days) was observed for both toluene and H<sub>2</sub>S removal in the neutral pH biotrickling filter. In the acidic biotrickling filter, toluene degradation started also immediately but at a lower rate. However, after several weeks of operation the toluene elimination capacity at low pH reached a steady value identical to this found in the neutral biotrickling filter. Once steady states were obtained, the performance of the biotrickling filters was similar. H<sub>2</sub>S did not affect toluene degradation at concentrations up to 170 ppm at either pH. At a volumetric load of 100 m<sup>3</sup>/m<sup>3</sup>.h, maximum elimination capacities of 70 g toluene/m<sup>3</sup>.h (at 1.7 g/m<sup>3</sup> toluene) and 20 g H<sub>2</sub>S/m<sup>3</sup>.h (at 170 ppm H<sub>2</sub>S, the highest concentration tested) were observed. Microbial counting and activity measurements indicated the development of different microbial populations. In the neutral 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<sub>2</sub>S and toluene. Overall, the results presented indicated that effective co-treatment of H<sub>2</sub>S and VOCs can be obtained in a single-stage biotrickling filter.

## KEYWORDS:

Biofilter, biotrickling filter, odor, H<sub>2</sub>S, VOC, POTW

## INTRODUCTION

H<sub>2</sub>S is the principal, polluting component in off-gases from publicly owned treatment works (POTWs), causing odor nuisance at concentration as low as about 8 ppb<sup>8</sup> and corrosion problems in the sewer systems.<sup>6</sup> POTW off-gases also contain a wide range of volatile organic compounds (VOCs),<sup>9,11</sup> of which toluene is a major component. Odor nuisance and regulations concerning the emission of VOCs require POTWs to treat their off-gases.

Many studies have explored the use of biofilters and biotrickling filters for the removal of H<sub>2</sub>S or VOCs as single pollutants. VOCs such as toluene can be effectively removed at rates up to 100 g/m<sup>3</sup>.h.<sup>2,7</sup> Also H<sub>2</sub>S is rapidly removed in biofilters and biotrickling filters,<sup>8</sup> although acidification of the filter medium and accumulation of H<sub>2</sub>S oxidation products may cause poor performance of biofilters in the long run.<sup>12,13</sup>

Relatively little is known on the treatment of off-gases that contain both H<sub>2</sub>S and VOCs. H<sub>2</sub>S in biofilters and biotrickling filters is generally oxidized by *Thiobacillus* species that show optimal activity at acidic pH. However, most *Thiobacillus* species are autotrophic organisms and thus they do not use VOCs as a carbon source for growth. VOCs have therefore to be 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<sub>2</sub>S and VOCs.

One solution is treatment in a two-stage process as proposed by Deviny et al.<sup>3</sup> In the first stage, H<sub>2</sub>S is oxidized in an acidic biotrickling filter. The off-gas is then passed through a neutral pH biofilter for removal of VOCs. Considerable savings can be obtained if H<sub>2</sub>S and VOC removal is combined in one reactor. Recent research at POTWs has shown that H<sub>2</sub>S and low concentrations of VOCs can be co-treated in biofilters without pH control and letting the pH decline.<sup>4,9,11</sup> Experiments with a pilot-scale biotrickling filter were less successful.<sup>9</sup> In particular the removal of the VOCs was poor although the biotrickling filter was operated at a neutral pH.

We investigated the use of biotrickling filters for the co-treatment of high loads of H<sub>2</sub>S and toluene. As pH was expected to be the most critical parameter, two identical biotrickling filters were operated but at different pH. The experiments reported here describe the influence of the pH on the performance of co-treatment of H<sub>2</sub>S and toluene in biotrickling filters.

## MATERIALS AND METHODS

### 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). Details of the design have been presented earlier.<sup>5</sup> Construction and standard operating parameters of the biotrickling filters are summarized in Table 1. The pH was maintained within  $\pm 0.3$  units by a Cole-Parmer pH controller, which regulated the automatic addition of 0.5 M NaOH. Each biotrickling filter was filled with 1 kg of 1" polypropylene Pall rings, resulting in a bed volume of 10 L. Gas flow at a rate of 1 m<sup>3</sup>/h was cocurrent with the recycle liquid. Toluene was introduced into the gas stream by saturating a side airstream by sparging into a bottle with pure toluene. H<sub>2</sub>S was introduced by passing the gas stream over a HCl solution into which a solution of Na<sub>2</sub>S was dripped. H<sub>2</sub>S concentrations ranging from 0 to 170 ppm were obtained by changing the Na<sub>2</sub>S 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. Details on the performance of specific experiments are presented with the results.

**Table 1.** Design and operational parameters of biotrickling filters for removal of H<sub>2</sub>S and toluene.

Design	
Bed height and internal diameter	55 x 15.2 cm
Bed volume	10 L
Packing	1 kg polypropylene 1” 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 <sup>a</sup>	1 m <sup>3</sup> /h, 36 s
Toluene inlet concentration	Variable, up to 2.25 g/m <sup>3</sup>
H <sub>2</sub> S inlet concentration	Variable, up to 170 ppm
Superficial liquid velocity	5.6 m/h
Recycle liquid pH	Reactor 1: 7.0 Reactor 2: 4.5
Medium feed rate	100 mL/h
Medium composition	Reactor 1 (per L): 0.54 g KH <sub>2</sub> PO <sub>4</sub> , 1.05 g K <sub>2</sub> HPO <sub>4</sub> , 0.5 g NH <sub>4</sub> NO <sub>3</sub> , 1 g NaCl, 0.26 g MgSO <sub>4</sub> , 0.025 g CaCl <sub>2</sub> ·2H <sub>2</sub> O, 1 mL trace elements solution  Reactor 2 (per L): same as reactor 1, but with 1.25 g KH <sub>2</sub> PO <sub>4</sub> and no K <sub>2</sub> HPO <sub>4</sub>

<sup>a</sup> EBRT = empty bed retention time = bed volume / gas flow rate

**Table 2.** Experimental design.

Day	Experiment
0-22	Startup with toluene as the sole pollutant (reactors controlled at pH 4.5 and 7.0 resp.)
15	Response to a sudden increase of the toluene inlet concentration
18-19	Performance versus load curve, toluene sole pollutant
22-42	Introduction of 7.7 ppm H <sub>2</sub> S while maintaining toluene at 0.3-0.5 g/m <sup>3</sup>
57	Response to re-introduction of H <sub>2</sub> S after a 7 day break
69-110	Steady state performance with 1 g/m <sup>3</sup> toluene and 0-170 ppm H <sub>2</sub> S
139-140	Microbial counting and characterization of the recycle liquid and biofilm
151	OUR <sup>a</sup> experiments with the biofilm
162	Reactor cleaning; restart with toluene and H <sub>2</sub> S (reactors controlled at pH 4.5 and 7.0 resp.)
169-210	Steady state performance experiments with adaptation to changing pH
210	Reactor cleaning; restart with toluene and H <sub>2</sub> S (reactors controlled at pH 4.5 and 7.0 resp.)
236	Response of the performance to a sudden change of the pH
272-273	Measurement of sulfide in the recycle liquid at standard operation

<sup>a</sup> OUR = oxygen uptake rate

## Analytical Methods

Toluene and CO<sub>2</sub> were analyzed by injecting grab samples into a GC equipped with a FID and TCD.<sup>2</sup> H<sub>2</sub>S was determined with a Jerome 631-X hydrogen sulfide analyzer. Microbial counts were done by serial ten-fold dilutions of recycle liquid and biofilm samples in 8.5 g/L NaCl, and subsequent plating on various media. Heterotrophs were counted on Plate Count Agar (Difco), yeasts and fungi on Oxytetracycline Glucose Yeast Extract Agar (resp. 0.1, 20, 5 and 20 g/L), toluene-degraders on mineral medium solidified with 8 g/L agarose (toluene supplied to the gas phase during incubation), and autotrophic sulfur-oxidizers on Thiosulphate Agar<sup>1</sup> (no C-source other than atmospheric CO<sub>2</sub> 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 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 was placed in 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<sub>2</sub>S, or Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, to reach a final concentration of 0.19 mM toluene, 0.27 mM Na<sub>2</sub>S or 0.14 mM Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in the vessel. OUR values were corrected

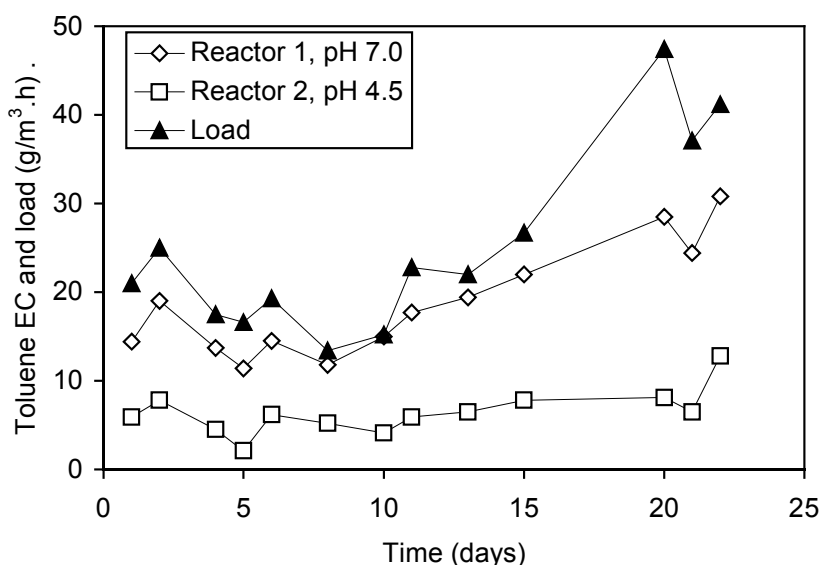
for the endogenous respiration. Sulfide concentrations in the recycle liquid were determined in duplicate with an assay-kit from CHEMetrics (Calverton, VA).

## RESULTS AND DISCUSSION

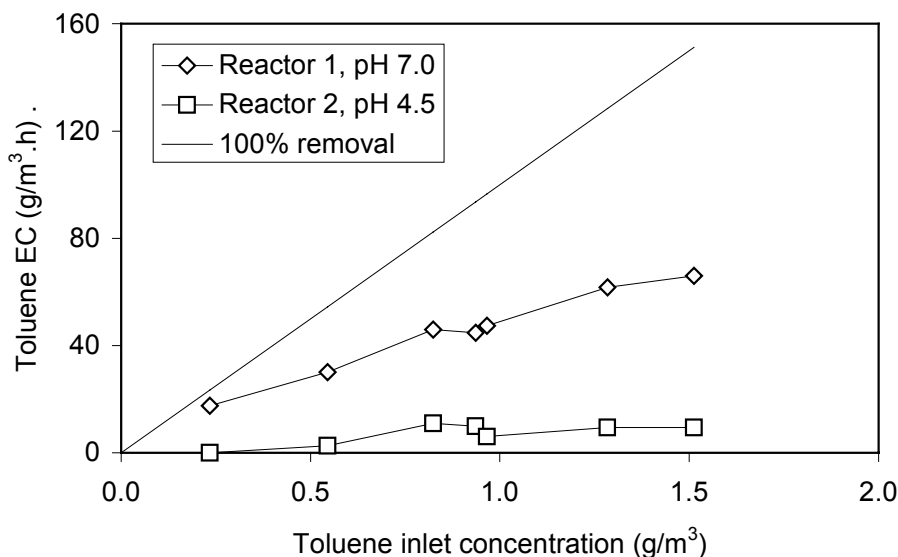
### Start-Up with Toluene as Only Pollutant

On the first day of operation, the biotrickling filters were inoculated with biomass from a toluene-degrading biotrickling filter<sup>2</sup> and toluene as sole pollutant was passed through the reactors. Figure 1 shows the startup at the two different pH. Both biotrickling filters started to degrade toluene within one day, but the elimination capacity at pH of 4.5 was only about 30% of the elimination capacity at pH 7.0. Microscopic investigation of the recycle liquid showed rapid 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 (Figure 2), were determined on day 15-18 during the start-up by stepwise increasing the toluene concentration while maintaining a constant volumetric loading. Clearly, low pH severely inhibited toluene degradation in reactor 2, which reached only a maximum elimination capacity of about 10 g/m<sup>3</sup>.h, even at very high toluene loadings. The maximum toluene degradation in the reactor 1 (pH of 7.0) was up to 70 g/m<sup>3</sup>.h, which is comparable to the rates observed in many other biotrickling filter studies. At the time of this experiment, reactor 1 contained about twice as much biomass as reactor 2 (335 and 155 g wet biomass, respectively). Both amounts are theoretically sufficient for achieving high removal rates, if one assumes that a minimum biofilm thickness of about 75-100 μm is required for effective treatment. Hence, the low toluene degradation rate at pH 4.5 was probably not caused by a limiting amount of biomass, but rather by low specific microbial activity at pH 4.5. It should however be noted that the performance of reactor 2 increased with time, as will be shown in the next sections.



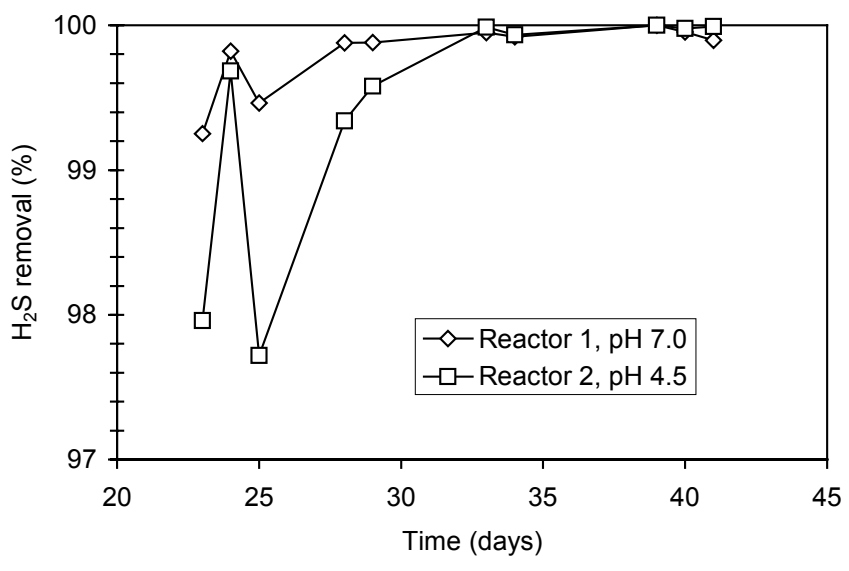
**Figure 1.** Toluene loading and elimination capacity during the startup of the two biotrickling filters (toluene as the single pollutant, inlet concentration was 0.13-0.47 g/m<sup>3</sup>, on average 0.25 g/m<sup>3</sup>, volumetric loading: 100 m<sup>3</sup>/m<sup>3</sup>.h).



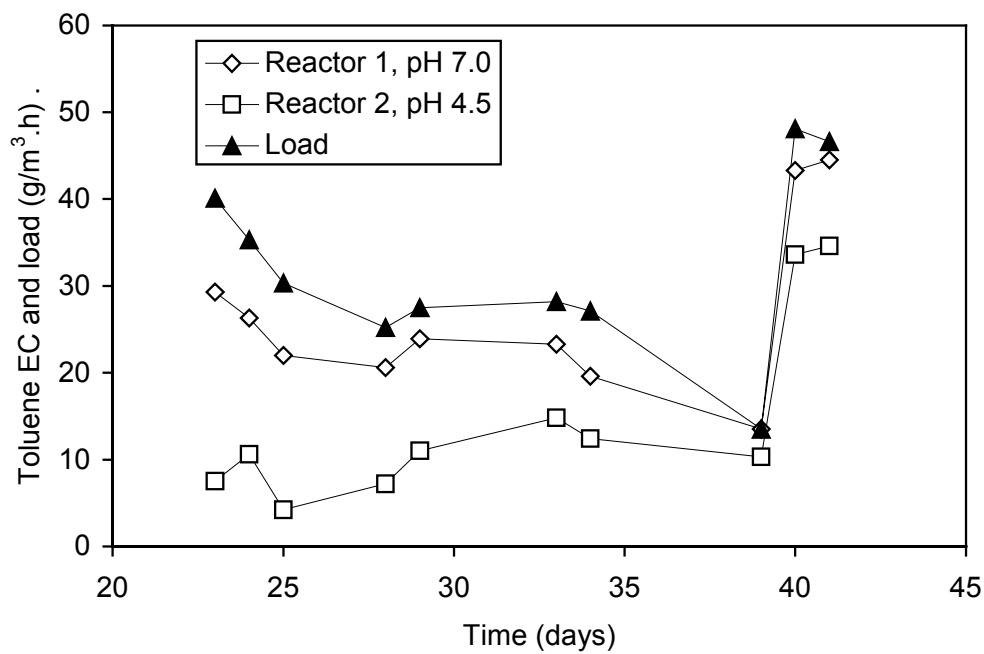
**Figure 2.** Influence of the toluene inlet concentration on the elimination capacity during the startup with toluene as the single pollutant (volumetric gas load 100 m<sup>3</sup>/m<sup>3</sup>.h). The solid line represent 100% removal of the toluene feed.

## Introduction of Low H<sub>2</sub>S Concentration to Toluene-Degrading Biotrickling Filters

On day 22, supply of on average 7.7 ppm H<sub>2</sub>S was started while maintaining a toluene concentration of 0.3-0.5 g/m<sup>3</sup> and removal of toluene and H<sub>2</sub>S was monitored over a period of 20 days. This concentration of H<sub>2</sub>S is representative of POTW off-gas, while the toluene concentration is probably 2-3 times higher than the total VOC concentration in POTW off-gas. Figure 3 shows that removal of H<sub>2</sub>S started immediately and was close to 100%. As *Thiobacillus* and other H<sub>2</sub>S oxidizing species are ubiquitous, inoculation of biotrickling filters was apparently not required for a rapid startup of H<sub>2</sub>S removal. Inoculation will still be required when hydrogen sulfide is the sole pollutant, and probably for very high load applications. The pH did not affect H<sub>2</sub>S removal, but it should be noted that the H<sub>2</sub>S load during this experiment (about 1 g/m<sup>3</sup>.h) was far less than the maximum elimination capacity 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 H<sub>2</sub>S, as shown in Figure 4; the elimination capacities remained virtually the same as during startup with toluene only (Figure 1).



**Figure 3.** H<sub>2</sub>S removal efficiency in the presence of toluene. H<sub>2</sub>S (7.7 ppm) was started on day 22 in toluene-degrading biotrickling filters. Toluene concentration was 0.3-0.5 g/m<sup>3</sup>

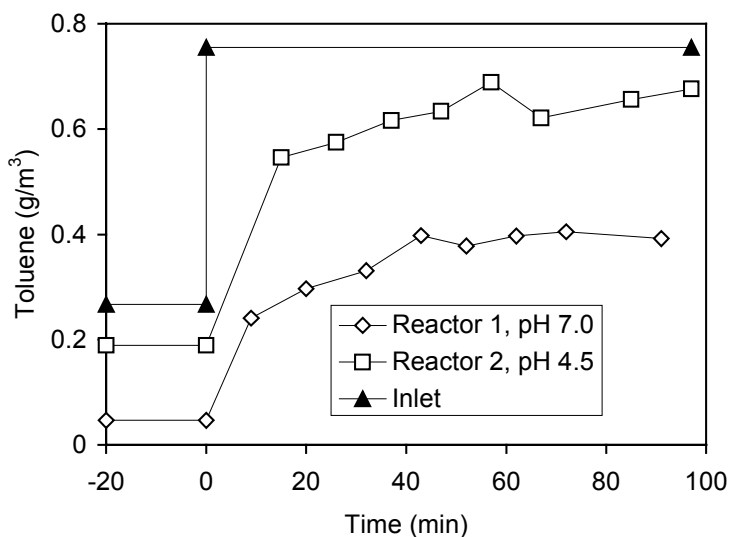


**Figure 4.** Toluene removal after the introduction of 7.7 ppm H<sub>2</sub>S on day 22.

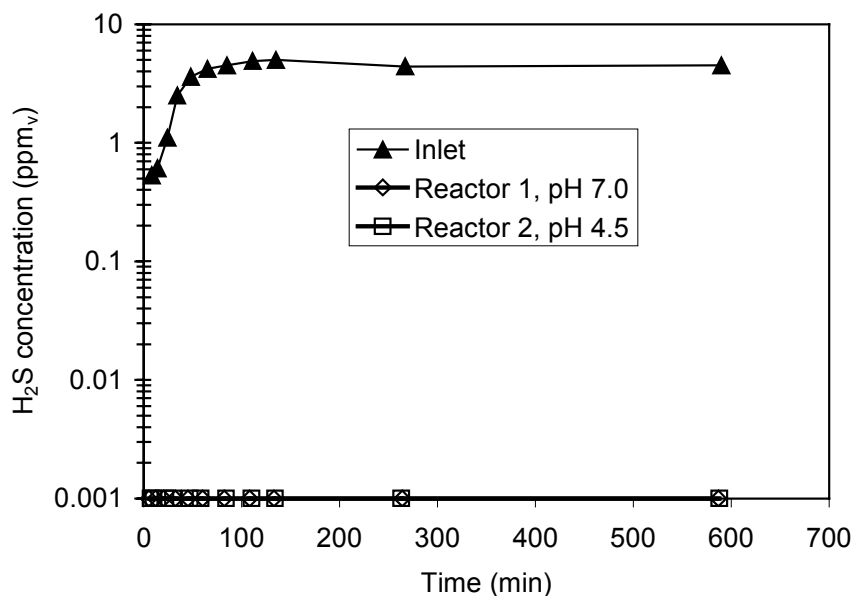
**Dynamic Performance**

At a volumetric load of 100 m<sup>3</sup>/m<sup>3</sup>.h, the toluene concentration was increased from 0.27 to 0.76 g/m<sup>3</sup> and the response of the biotrickling filters was determined by regularly analyzing the outlet

gas (Figure 5). The toluene concentration in the outlet gas of both biotrickling filters rapidly increased to reach a constant value after about 1 hour. In a second experiment, H<sub>2</sub>S removal was investigated after the supply of H<sub>2</sub>S was interrupted for 7 days. After restarting the generation of H<sub>2</sub>S, it took about 100 min before a constant H<sub>2</sub>S inlet concentration was obtained (Figure 6). This was probably due to initial absorption of H<sub>2</sub>S in the (fresh) HCl solution for generation of H<sub>2</sub>S. Even so, H<sub>2</sub>S removal in both reactors was 100% immediately after restart. The relatively low H<sub>2</sub>S load may however have helped; a slower response at higher H<sub>2</sub>S loads can not be excluded as found by Wani et al.<sup>10</sup> for biofilters degrading H<sub>2</sub>S and methyl mercaptan. Overall, the present results indicate that the biotrickling filters respond rapidly to changes in the waste gas.



**Figure 5.** Response of the toluene outlet concentration to an increase of the inlet concentration at time zero.



**Figure 6.** Response of the two biotrickling filters to re-introduction of H<sub>2</sub>S into the waste gas after 7 days without H<sub>2</sub>S. Outlet concentration always remained below the detection limit (1 ppb<sub>v</sub>).

### Steady State Performance at High Loads of Toluene and H<sub>2</sub>S

Since no crossed effect of H<sub>2</sub>S and toluene were observed at low concentrations, toluene and H<sub>2</sub>S concentrations were increased. The objective was to compare maximum performances and to determine possible toxic effects of high H<sub>2</sub>S concentrations on toluene removal. Toluene concentration was maintained at 1 g/m<sup>3</sup>, whereas the H<sub>2</sub>S concentration was gradually increased from 0 to 170 ppm. It should be stressed that these operating conditions were carefully chosen so that only partial removal of toluene (about 30%) occurred. Thus, if H<sub>2</sub>S had any effect (positive or negative) on the biodegradation of toluene, it would have been detected. This would not necessarily be the case if the experiment had been performed at 99+% removal of toluene. Each operating condition was kept constant for at least 3 days to ensure steady state, and pollutant removal and NaOH consumption rates were determined.

Figure 7 presents the data on H<sub>2</sub>S removal. No effect of the recycle liquid pH was observed. H<sub>2</sub>S removal at a volumetric loading of 100 m<sup>3</sup>/m<sup>3</sup>.h was complete in both biotrickling filters up to an inlet concentration of about 50 ppm. This corresponds to a H<sub>2</sub>S elimination capacity of 7 g/m<sup>3</sup>.h. The elimination capacity increased to 20 g/m<sup>3</sup>.h at an inlet concentration of 170 ppm, 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<sub>2</sub>S inlet concentration had been performed. A survey of literature data on H<sub>2</sub>S removal in biofilters and biotrickling filters indicate that elimination capacities vary greatly and range from 8 to 140 g H<sub>2</sub>S/m<sup>3</sup>.h.<sup>8</sup>

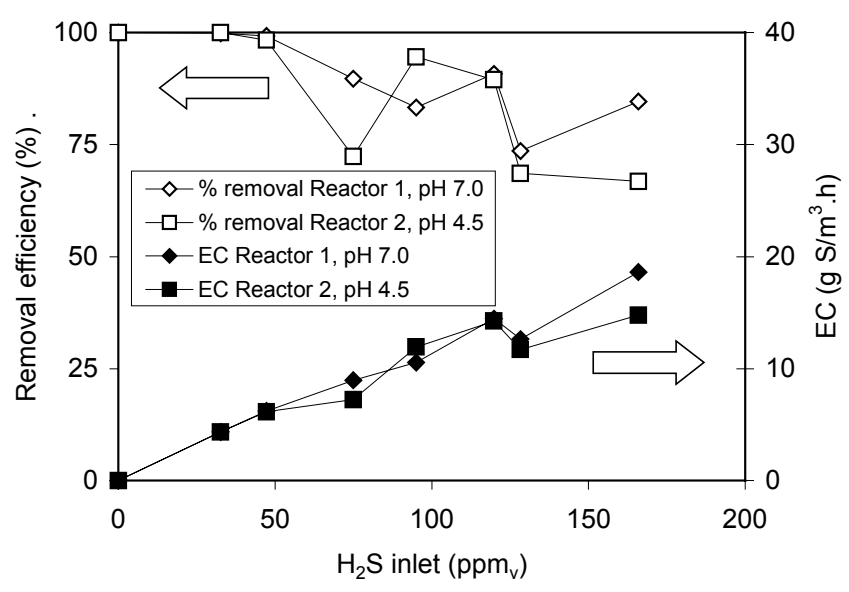
Sulfide concentrations in the recycle liquid remained below 0.10 ppm at H<sub>2</sub>S inlet concentrations of 20 and 70 ppm (Table 3). The amount of H<sub>2</sub>S removed via the liquid purge was insignificant to the total amount removed from the waste gas, indicating that biological oxidation of H<sub>2</sub>S is the only route of removal. It also indicates that H<sub>2</sub>S in the liquid purge is not a point of concern.

Data on the consumption of NaOH are presented in Figure 8. As expected, alkali consumption increased at higher H<sub>2</sub>S inlet concentrations and higher degradation rates. The Figure also compares the amount of NaOH consumed with the calculated amount needed for neutralization in case all the H<sub>2</sub>S removed is completely oxidized to sulfuric acid. In both reactors, this ratio is close to 100% and it strongly suggests that H<sub>2</sub>S is completely oxidized to sulfuric acid both at pH 4.5 and 7.0.

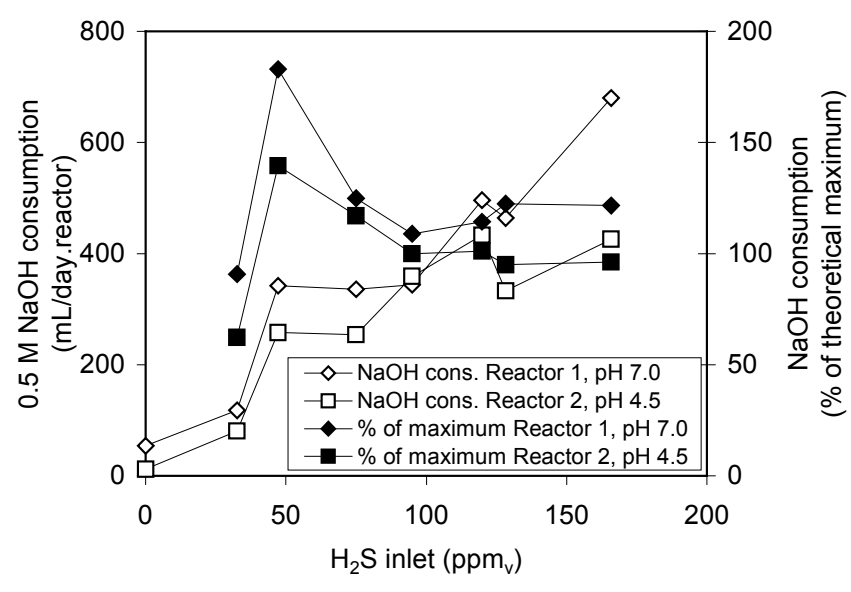
Toluene degradation was not affected by H<sub>2</sub>S up to a concentration of at least 170 ppm (Figure 9). Hence, it can be concluded that co-treatment of H<sub>2</sub>S and VOCs such as toluene in a biotrickling filter is a feasible option. A remarkable finding in Figure 9 is that toluene removal was higher at acidic pH than at neutral pH. The average toluene elimination capacity of reactor 2 was 45 g/m<sup>3</sup>.h, which is 3-5 times higher than found during the startup (Figures 1 and 2). The most likely explanation for this is that slow adaptation of an acid-tolerant toluene-degrading culture occurred in reactor 2. Apart from this, these experiments also show that strict control of the pH at a near neutral value is not required for efficient removal of VOCs such as toluene in biotrickling filters.

**Table 3.** H<sub>2</sub>S removal by biological oxidation and via the liquid purge.

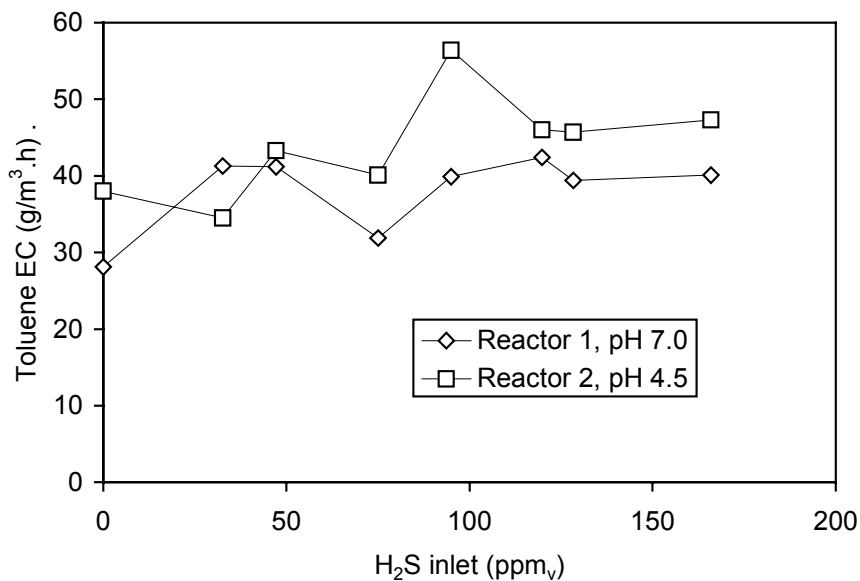
Parameter	Reactor 1, operated at neutral pH		Reactor 2, operated at pH 4.5	
	12-29-99	12-30-99	12-29-99	12-30-99
H <sub>2</sub> S in inlet air (ppm)	20	70	20	70
H <sub>2</sub> S in outlet air (ppm)	0.003	8.1	0.002	3.1
H <sub>2</sub> S in recycle liquid (ppm)	0.10	0.045	0.09	0.06
H <sub>2</sub> S load (g/m <sup>3</sup> .h)	2.83	9.92	2.83	9.92
H <sub>2</sub> S elimination capacity (g/m <sup>3</sup> .h)	2.83	8.77	2.83	9.48
H <sub>2</sub> S removed via liquid purge (g/m <sup>3</sup> .h)	0.001	0.00045	0.0009	0.0006



**Figure 7.** H<sub>2</sub>S removal efficiency and elimination capacity as function of the inlet concentration and during co-treatment with 1 g/m<sup>3</sup> toluene.



**Figure 8.** Influence of H<sub>2</sub>S concentration on NaOH consumption. Full symbols represent the ratio of the actual NaOH consumption to the theoretical consumption if removed H<sub>2</sub>S is completely oxidized to sulfuric acid.



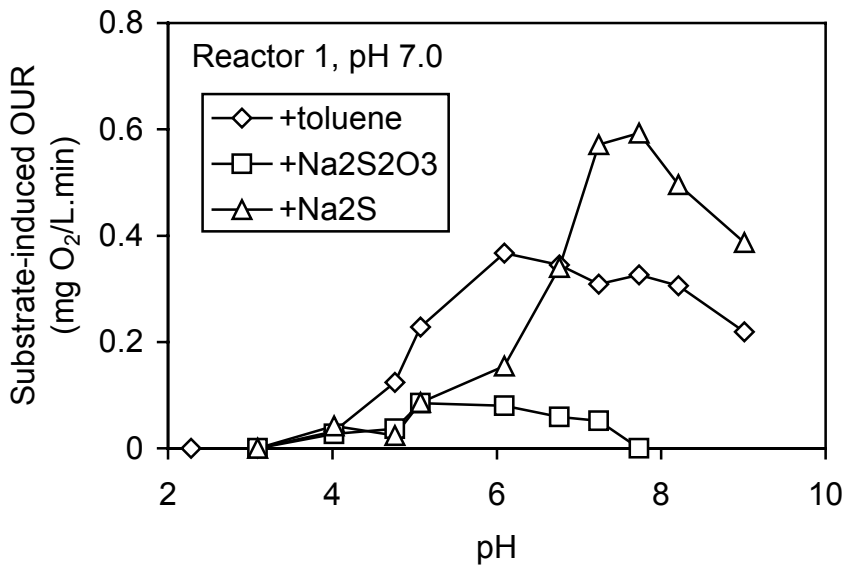
**Figure 9.** Influence of the H<sub>2</sub>S concentration on toluene removal (inlet 1 g/m<sup>3</sup> toluene, toluene loading 100 g/m<sup>3</sup>.h).

### Characterization of Microbial Populations and Activity Measurements

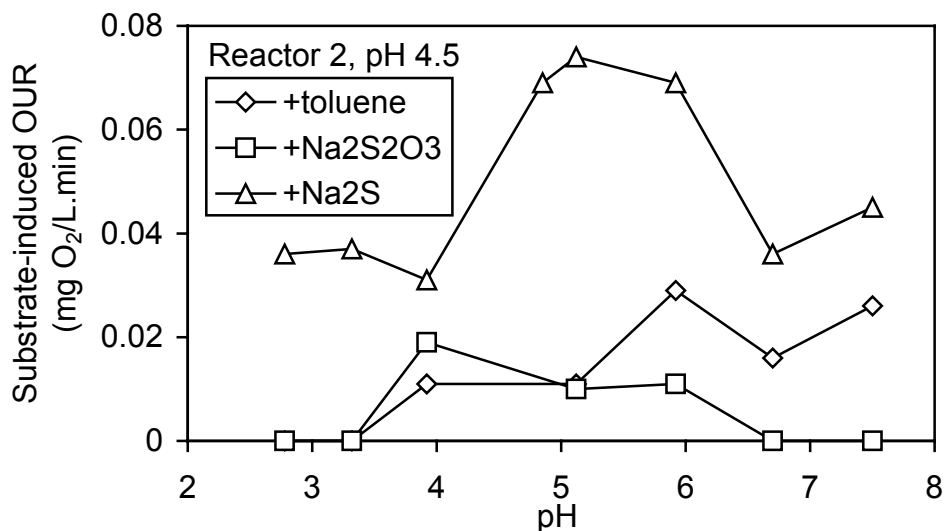
In order to explain some of the observed phenomena, a basic characterization of the process culture was attempted using simple plating techniques. Plate counts on solid media has the limitation that only viable cells capable of growth on the selected media will be counted. These may only constitute a minor fraction of the total population present in the biotrickling filter. Nevertheless, plate counting allows for a rapid assessment of the biodegradation potential 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 neutral media. This suggests 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<sub>2</sub>S and toluene. This was confirmed by activity measurements of the biofilm in OUR experiments. Biofilm from reactor 1 oxidized toluene, Na<sub>2</sub>S and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> with maximum activity at pH 6-8, whereas at pH 4.5 microbial activity was very low (Figure 10). Biofilm from reactor 2 showed a broader pH range for microbial activity (Figure 11). It should be noted that the absolute values of OUR of Figure 10 and 11 are quite different. This is in part because of different specific activities for the two biofilms and because different concentrations of biofilm were suspended for OUR measurement.

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

Population	Reactor 1, operated at pH 7.0				Reactor 2, operated at pH 4.5			
	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



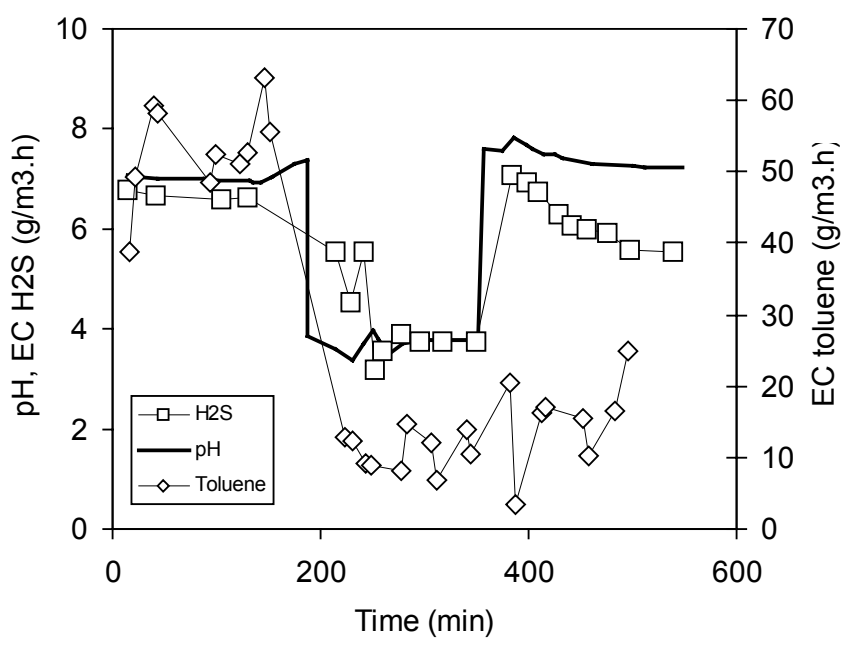
**Figure 10.** Influence of the pH on the substrate-induced oxygen uptake rates by suspended biofilm from reactor 1 operated at neutral pH.



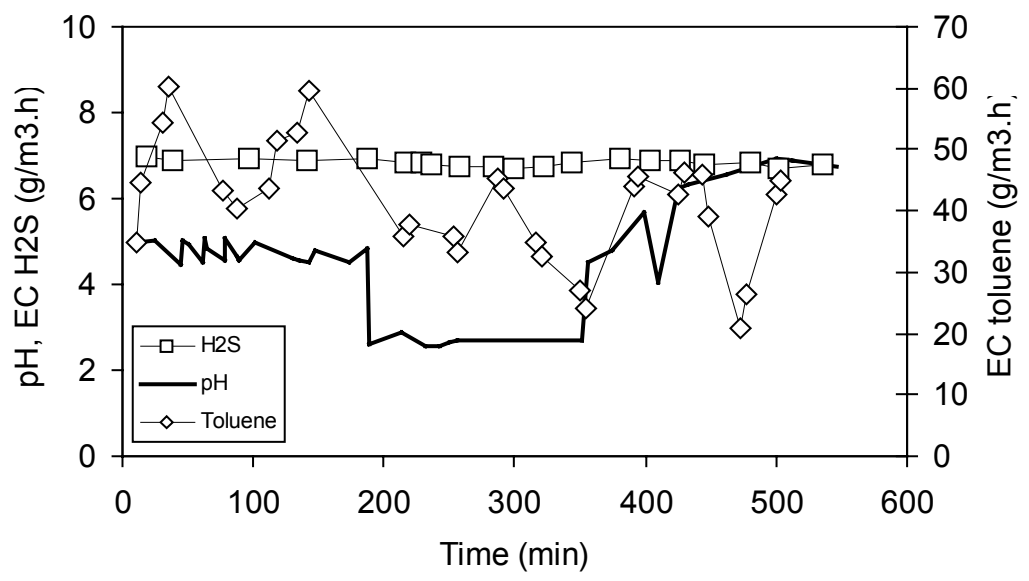
**Figure 11.** Influence of the pH on the substrate-induced oxygen uptake rate by suspended biofilm from reactor 2 operated at pH 4.5.

### Short-Term Sensitivity to a Change of the pH

To simulate a breakdown of the pH control and/or NaOH supply, the pH in the recycle liquid of reactors 1 (pH 7.0) and 2 (pH 4.5) was temporarily lowered to the 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 Figure 12, reactor 1 operated at a neutral pH showed a drastic decrease of the removal rate of both H<sub>2</sub>S and toluene when the pH was lowered to 3.8. Such a response was expected, since the number of acid-tolerant microorganisms in this reactor was low (Table 4). Readjustment of the pH to its original value immediately restored H<sub>2</sub>S removal, but toluene removal remained low (Figure 12). Apparently, temporarily low pH has a different effect on the toluene and H<sub>2</sub>S degrading microorganisms in reactor 1. Reactor 2 operated at pH 4.5 was much less sensitive to a pH change. Even when the pH was lowered to 2.6, removal of H<sub>2</sub>S and toluene was relatively unaffected (Figure 13). Thus operation at low pH results in biotrickling filters with a fast and more stable response to a change of the pH.



**Figure 12.** Effect of a temporary decrease of the pH (set values 7.0 -> 3.8 -> 7.0) on H<sub>2</sub>S and toluene removal in reactor 1, normally operated at pH 7.0.

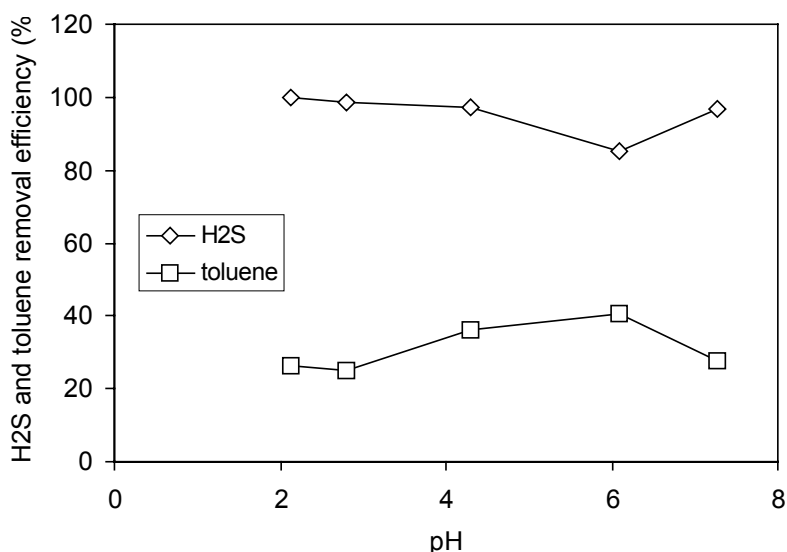


**Figure 13.** Effect of a temporary decrease of the pH (set values 4.5 -> 2.6 -> 4.5) on H<sub>2</sub>S and toluene removal in reactor, normally operated at pH 4.5.

## Long-Term Adaptation to Changing pH

Long-term-adaptation of reactor 1 to low pH operation was investigated by step-wise decreasing the pH with 1-1.5 units once every 5 to 12 days while measuring the performance once every day. Change of the operational pH was as in chronological order as follows: after startup 14 days operation at pH 7.0, followed by 6 days at pH 6.1, 5 days at pH 4.3, 12 days at pH 2.8 and 10 days at pH 2.1. In general, steady state with constant H<sub>2</sub>S and toluene degradation rates was observed within one day after each pH change. As can be seen from Figure 14, the pH did not significantly affect and H<sub>2</sub>S and toluene degradation and removal efficiencies remained relatively constant between pH 2.1 and 7.0. Similar results were observed when the pH in reactor 2 was gradually increased from 4.3 to 7.9 (not shown).

Although the performance of reactor 1 decreases drastically immediately after a drop of the pH (Figure 12), performance is relatively stable when the pH is gradually decreased and the reactor is allowed to reach a new steady state. It was not investigated whether the increased tolerance to low pH was due to adaptation of the population already present and enriched at neutral pH or to growth of new, acid-tolerant species.



**Figure 14.** Steady state H<sub>2</sub>S and toluene removal efficiencies in reactor 1 vs. pH after slow adaptation to low pH.

## CONCLUSIONS

The results discussed herein demonstrate that H<sub>2</sub>S 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<sub>2</sub>S 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 temporarily poor removal of H<sub>2</sub>S and toluene.

Most probably, microbial populations in biotrickling filters will adapt to the environmental conditions present in the reactor. Once an adequate population has established, our results show that high pollutant removal rates can be obtained, even at conditions that first seemed unfavorable for biodegradation.

Biotrickling filters reactors do not need to be complex, thus they may become the preferred technique for treatment of the complex off-gases at POTWs. The specific conditions at each POTW will dictate the design criteria for the biotrickling filter. But in most cases, because of the large volume of off-gases requiring treatment at POTWs, the deployment of biotrickling filters will require designing biotrickling filters with a short gas residence time and capable to achieve H<sub>2</sub>S removal down to very low levels (ppb). This will require further careful evaluation of the rate limiting step in the process, i.e., mass transfer of the contaminants, or biodegradation in the biofilm. Further, 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 should be factored in.

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