



Co-treatment of H₂S and toluene in a biotrickling filter

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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 H₂S 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 H₂S 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 H₂S (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 H₂S 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 biotrickling filter. H₂S did not affect toluene degradation at concentrations up to 170 ppm_v at either pH. At a volumetric load of 100 m³ m⁻³ h⁻¹, maximum elimination capacities of 70 g toluene m⁻³ h⁻¹ (at 1.7 g m³ toluene) and 20 g H₂S m⁻³ h⁻¹ (at 170 ppm_v H₂S, 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 H₂S and toluene. Overall, the results presented indicated that effective co-treatment of H₂S and VOCs can be obtained in a single-stage biotrickling filter. © 2001 Published by Elsevier Science B.V.

Keywords: Waste air treatment; Biotrickling filter; Odor; H₂S; VOC; POTW; Biofilter

1. Introduction

Hydrogen sulfide (H₂S) 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 is 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 H₂S. 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 H₂S 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]. H₂S is also rapidly degraded in biofilters and in biotrickling filters [1]. However, in biofilters, accumulation of sulfate from the oxidation of H₂S often

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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 ($1 \text{ m}^3 \text{ h}^{-1}$) 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 in-

Table 1
Experimental setup and operating parameters of the biotrickling filters

<i>Design</i>	
Bed height and internal diameter	$55 \times 15.2 \text{ cm}^2$
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
<i>Operation</i>	
Gas flow rate (EBRT ^a)	$1 \text{ m}^3 \text{ h}^{-1}$ (36 s)
Volumetric loading ^b	$100 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$
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 $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 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.

roduced 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.

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 liq-

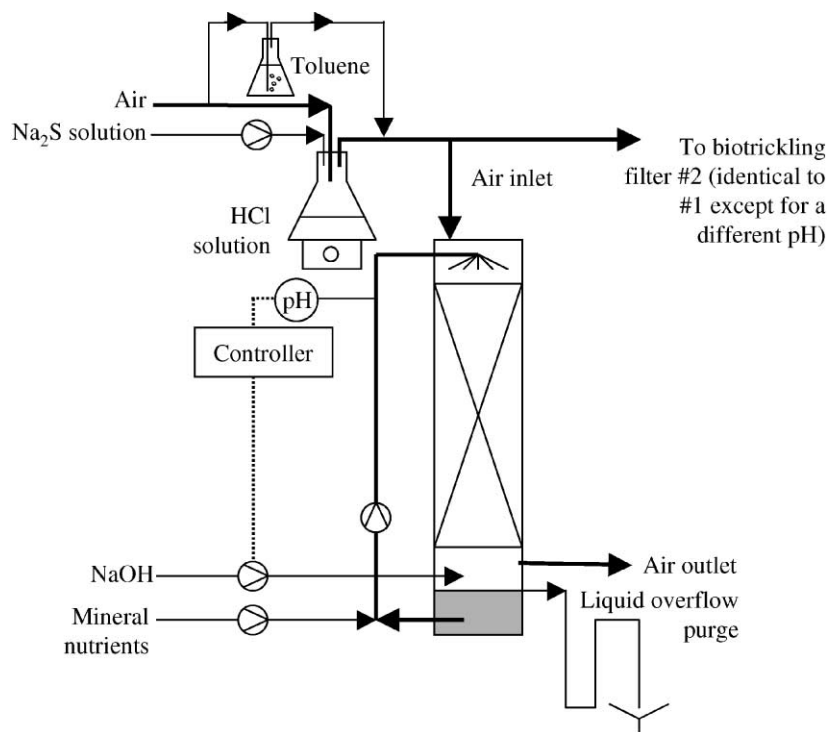


Fig. 1. Schematic representation of the experimental setup (only one biotrickling filter is shown).

145 uid and analyzed for substrate-induced oxygen uptake rates
 146 (OURs) at various pH. After adjustment of the pH with
 147 HCl or NaOH, 2.5 ml sample were placed in custom-made
 148 vessel fitted with an oxygen electrode (YSI, Yellow
 149 Springs, OH) and saturated with air at room temperature.
 150 Substrate-induced OURs were measured after the addition
 151 of aqueous solutions of toluene, Na_2S or $\text{Na}_2\text{S}_2\text{O}_3$. The initial
 152 concentrations for OUR determinations were 0.19 mM
 153 toluene, 0.27 mM Na_2S or 0.14 mM $\text{Na}_2\text{S}_2\text{O}_3$. OUR values
 154 were corrected for the endogenous respiration. Sulfide con-
 155 centration in the recycle liquid was determined in duplicate
 156 with an assay-kit from CHEMetrics (Calverton, VA).

3. Results and discussion

3.1. Startup with toluene as only pollutant

157 On the first day of operation, both biotrickling filters
 158 were inoculated with biomass from a toluene-degrading
 159 biotrickling filter [9] and toluene as sole pollutant was
 160 passed through the reactors. Fig. 2 shows the startup at the
 161 two different pHs. In both biotrickling filters, biodegrada-
 162 tion of toluene started within 1 day, but toluene removal
 163 at pH 4.5 was only about 30% of the rate at pH 7.0. Mi-
 164 croscopic examination of the recycle liquid showed rapid
 165
 166

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)
15	Response to a sudden increase of the toluene inlet concentration
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.

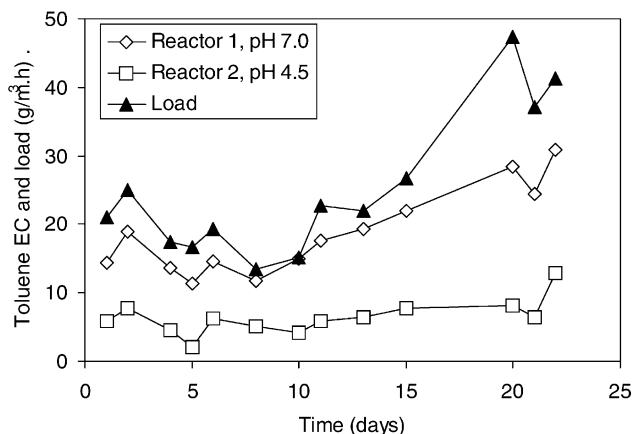


Fig. 2. Toluene loading and EC (= air flow \times (inlet – outlet concentration)/bed volume) during the startup phase of the two biotrickling filters at a constant empty bed retention time (EBRT) of 36 s. Toluene (sole pollutant) inlet concentration fluctuated between 0.13 and 0.47 g m^{-3} .

167 development of a very diverse microbial population at pH
168 7.0, including various protozoa. The microbial population
169 at pH 4.5 was less diverse, but not unexpectedly, contained
170 a relatively high concentration of yeasts.

171 Performance versus load curves (Fig. 3), were deter-
172 mined on days 16–19, i.e., before complete acclimation,
173 by stepwise increasing the toluene concentration while
174 maintaining a constant volumetric loading. Clearly, the low
175 pH severely inhibited toluene degradation in Reactor 2,
176 which only reached a maximum elimination capacity (EC)
177 of about 10 $\text{g m}^{-3} \text{h}^{-1}$, even at very high toluene loadings
178 ($>100 \text{ g m}^{-3} \text{h}^{-1}$). The maximum toluene degradation in
179 Reactor 1 (pH of 7.0) was about 70 $\text{g m}^{-3} \text{h}^{-1}$, which is
180 comparable to the rates observed in several other biotrick-
181 ling filter studies. It is worth mentioning that at the time of
182 this experiment, Reactor 1 contained about twice as much

183 biomass as Reactor 2 (335 and 155 g wet biomass, respec-
184 tively). Assuming uniform coverage of the packing, these
185 amounts correspond to biofilm thicknesses of about 150
186 and 70 μm , respectively. This is expected to be sufficient
187 for achieving high removal rates. Hence, the low toluene
188 degradation rate at pH 4.5 was probably not caused by a
189 limiting amount of biomass, but rather by a low specific
190 microbial activity at pH 4.5. As discussed further in the
191 paper, as acclimation of the process culture proceeded, the
192 performance of Reactor 2 increased significantly over time
193 until it equaled this of Reactor 1.

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

196 On day 22, supply of H_2S was started at an average con-
197 centration of 7.7 ppm_v , while maintaining an inlet toluene
198 concentration of 0.3–0.5 g m^{-3} and the removal of toluene
199 and H_2S was monitored over a period of 20 days. The H_2S
200 concentration selected is representative of POTW off-gas,
201 while the toluene concentration is 2–20 times higher than the
202 total VOC concentration in POTW off-gas. These operating
203 conditions were carefully chosen. Toluene was deliberately
204 supplied in great excess to allow for the determination of a
205 possible effect (positive or negative) of H_2S on toluene re-
206 moval. This would not necessarily be possible if the exper-
207 iment was performed at 99+% removal of the contaminants.
208 Fig. 4 shows that removal of H_2S started immediately and
209 was close to 100% in both reactors less than 5 days after H_2S
210 introduction. Inoculation of biotrickling filters was appar-
211 ently not required for a rapid startup of H_2S removal, prob-
212 ably because *Thiobacillus* and other H_2S oxidizing species
213 are quite ubiquitous. Although inoculation was not required,
214 the startup time of 5 days (Fig. 4) indicates that some adap-
215 tation towards H_2S degradation was required. This was ei-
216 ther growth of the specific H_2S oxidizers, or acclimation of

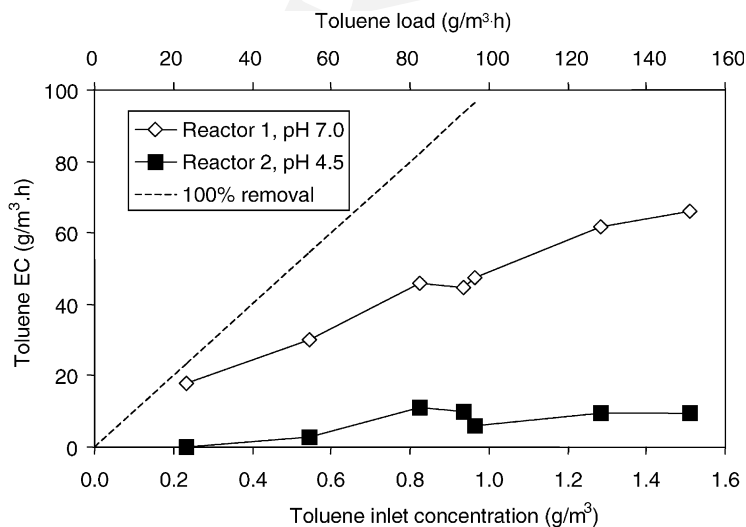


Fig. 3. Influence of the toluene inlet concentration on the EC during the startup phase, with toluene as the single pollutant (volumetric gas load $100 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$). The dashed line represent 100% removal of the toluene feed.

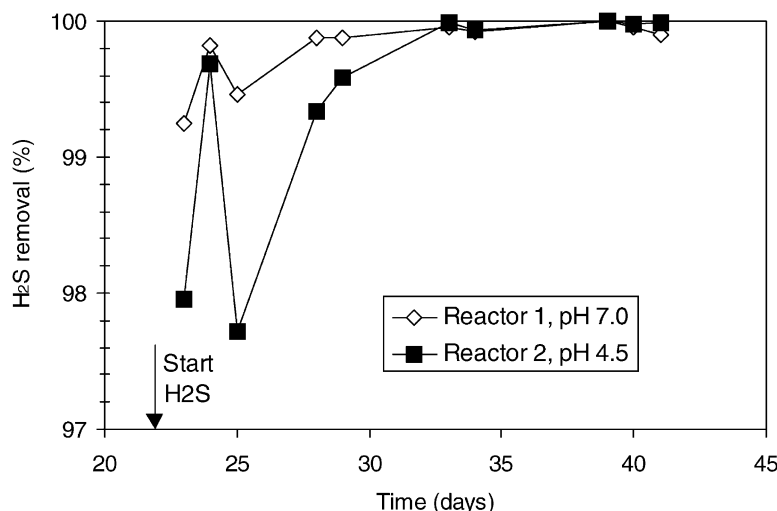


Fig. 4. H₂S removal efficiency in the presence of toluene. H₂S (7.7 ppm_v) was started on day 22 (arrow) in toluene-degrading biotrickling filters. Toluene concentration was 0.3–0.5 g m⁻³, EBRT was 36 s.

217 the existing population. Such adaptation was not observed
 218 in an experiment performed 1 month later under similar
 219 conditions (inlet concentration: 8 ppm_v, same conditions as
 220 above). The removal of H₂S was monitored upon restarting
 221 the system after 7 days without H₂S. In that experiment, no
 222 breakthrough of H₂S was observed and the outlet concentra-
 223 tion always remained under the detection limit [16]. While
 224 inoculation of the biotrickling filter was not needed here, in-
 225 oculation is recommended when H₂S is the sole pollutant, or
 226 for very high load applications. Under the conditions tested
 227 herein, removal of H₂S was not affected by the pH once a
 228 steady state was reached. However, it should be noted that
 229 the H₂S loading during this experiment (about 1 g m⁻³ h⁻¹)
 230 was far less than the maximum EC in either reactors (see
 231 next sections). Hence, possible effects of the pH may have
 232 remained undetected since only the outlet gas was moni-
 233 tored. Toluene removal was not affected by the presence of
 234 H₂S (not shown). Toluene elimination capacities remained
 235 virtually the same as during startup with toluene only.

236 3.3. Steady-state performance at high loads 237 of toluene and H₂S

238 Since no cross-inhibition effect of H₂S and toluene was
 239 observed at low concentrations, toluene and H₂S concentra-
 240 tions were increased. The objective was to evaluate the max-
 241 imum performance of the systems and to determine possible
 242 toxic effects of high H₂S concentrations on toluene removal.
 243 The toluene concentration was set to 1 g m⁻³, and H₂S con-
 244 centrations were gradually increased from 0 to 170 ppm_v.
 245 As explained in the previous section, these conditions were
 246 specifically chosen to allow for a positive identification of
 247 possible pollutant interactions. Besides varying the H₂S con-
 248 centration, all other operating conditions were kept constant
 249 for at least 3 days to ensure steady state, and pollutant re-

250 moval and NaOH consumption rates were determined. The
 251 results are presented in Figs. 5 and 6 and in Table 3.

252 In Fig. 5, the EC of toluene is plotted as a function of
 253 the inlet concentration of H₂S for both the low-pH and the
 254 neutral-pH biotrickling filters. Clearly, toluene degradation
 255 was not affected by H₂S up to a concentration of at least
 256 170 ppm_v. A remarkable finding illustrated in Fig. 5 is that
 257 the low-pH biotrickling filter exhibited a markedly higher
 258 toluene elimination than during the startup phase (compared
 259 to Fig. 3). The most probable explanation for this is that
 260 slow adaptation of an acid-tolerant toluene-degrading cul-
 261 ture occurred in the reactor. Once this population reached a
 262 sufficient density, effective removal of toluene occurred. In
 263 fact, toluene elimination was about 15% higher at low pH
 264 than at neutral pH. This finding suggest that a strict control
 265 of the pH at a near neutral value is not necessarily required
 266 for efficient removal of easily biodegradable VOCs such as
 267 toluene in biotrickling filters.

268 Fig. 6 presents the data on H₂S removal in the two
 269 biotrickling filters. They were not statistically different. At
 270 a volumetric loading of 100 m³ m⁻³ h⁻¹, H₂S removal was
 271 complete up to an inlet concentration of about 50 ppm_v in
 272 both reactors. This corresponds to a H₂S EC of 7 g m⁻³ h⁻¹.
 273 The EC increased to 20 g m⁻³ h⁻¹ at an inlet concentra-
 274 tion of 170 ppm_v, but the removal efficiency decreased
 275 to 70–80%. Higher elimination capacities (but lower re-
 276 moval percentages) would probably have been obtained if
 277 further increases in the H₂S inlet concentration had been
 278 performed. For comparison, a survey of literature data on
 279 H₂S removal in biofilters and biotrickling filters indicates
 280 that elimination capacities vary greatly with reported values
 281 ranging from 8 to 140 g H₂S m⁻³ h⁻¹ [1].

282 The fate of H₂S was further investigated. Sulfide concen-
 283 trations in the recycle liquid was measured at the two oper-
 284 ating conditions. The analysis revealed that dissolved sulfide

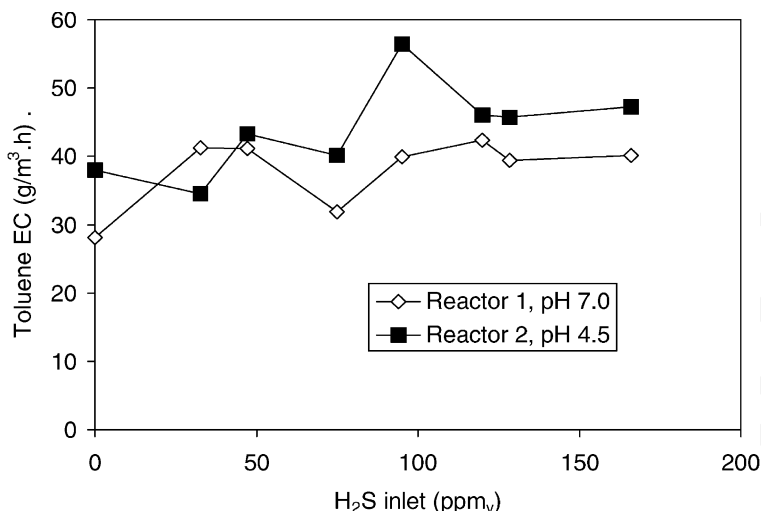


Fig. 5. Influence of the H₂S concentration on toluene removal (inlet 1 g m⁻³ toluene, toluene loading 100 g m⁻³ h⁻¹).

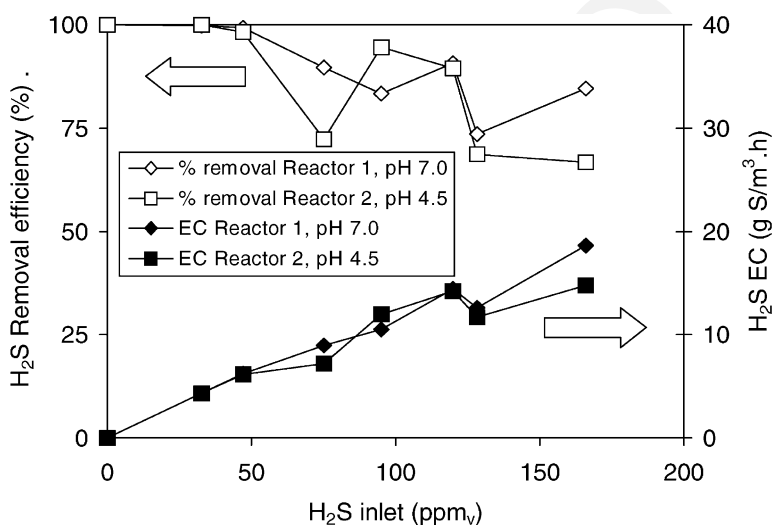


Fig. 6. H₂S removal efficiency and EC as a function of the inlet concentration and during co-treatment with 1 g m⁻³ toluene.

285 remained below 0.10 ppm at H₂S inlet concentrations of 20
 286 and 70 ppm_v (Table 3). Hence, the amount of H₂S removed
 287 via the liquid purge was insignificant compared to the total
 288 amount removed from the waste gas and should not be a
 289 concern for industrial application. Data on the consumption
 290 of NaOH (Fig. 7) provided further insight as to the fate of

sulfide. As expected, alkali consumption increased at higher
 291 H₂S inlet concentrations and higher degradation rates. Fig. 7
 292 also compares the amount of NaOH consumed with the calcu-
 293 lated amount needed for neutralization in case all the H₂S
 294 removed is completely oxidized to sulfuric acid. In both re-
 295 actors, this ratio is close to 100% which strongly suggests
 296

Table 3
 H₂S 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 ₂ S in inlet air (ppm _v)	20	70	20	70
H ₂ S in outlet air (ppm _v)	0.003	8.1	0.002	3.1
H ₂ S in recycle liquid (ppm)	0.10	0.045	0.09	0.06
H ₂ S load (g m ⁻³ h ⁻¹)	2.83	9.92	2.83	9.92
H ₂ S EC (g m ⁻³ h ⁻¹)	2.83	8.77	2.83	9.48
H ₂ S removed via liquid purge (g m ⁻³ h ⁻¹)	0.001	0.00045	0.0009	0.0006

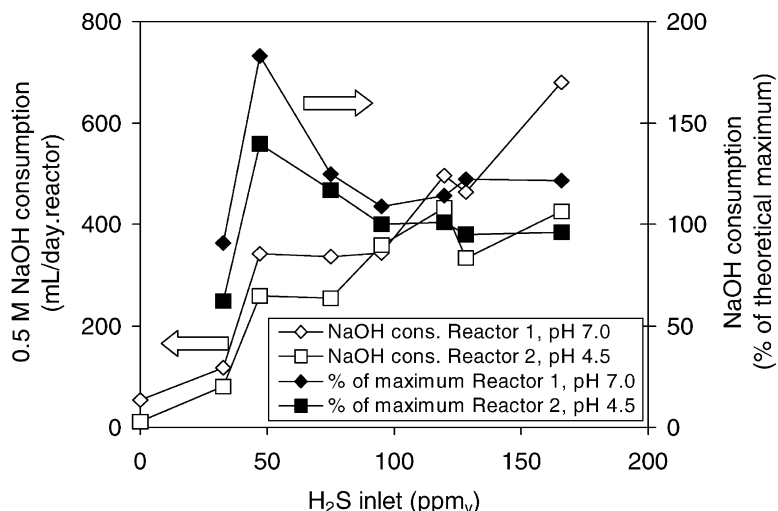


Fig. 7. Influence of H₂S concentration on NaOH consumption. Full symbols represent the ratio of the actual NaOH consumption to the theoretical consumption if removed H₂S is completely oxidized to sulfuric acid.

297 that H₂S is completely oxidized to sulfuric acid both at pH
298 4.5 and 7.0.

299 3.4. Characterization of microbial populations
300 and activity measurements

301 In order to develop an explanation to some of the ob-
302 served phenomena, a basic characterization of the process
303 culture was attempted using simple plating techniques. Plate
304 counting on solid media has the limitation that only vi-
305 able cells capable of growth on the selected media will be
306 counted. These may only constitute a minor fraction of the
307 total population present in the biotrickling filter. Neverthe-
308 less, plate counting allows one to rapidly assess the micro-
309 biota of biotrickling filters. The results in Table 4 indicate
310 that Reactor 1 operated at neutral pH contained a micro-
311 bial population with a strong preference for a neutral pH.
312 Counts on pH 4.5 media were several orders of magnitude
313 lower than on neutral media. This is an indication that op-
314 eration of biotrickling filters at neutral pH caused selec-
315 tive enrichment of species capable of growing only at neu-
316 tral pH. On the other hand, Reactor 2 operated at low pH
317 contained relatively similar proportions of acid-tolerant and

pH-neutral microorganisms, indicating that this reactor may
318 have broader pH range for degradation of H₂S and toluene.
319 This was confirmed by activity measurements of the biofilm
320 in OUR experiments (Figs. 8 and 9). The biofilm from Reactor
321 1 oxidized toluene, Na₂S and Na₂S₂O₃ with maximum
322 activity at pH 6–8, whereas at pH 4.5 microbial activity was
323

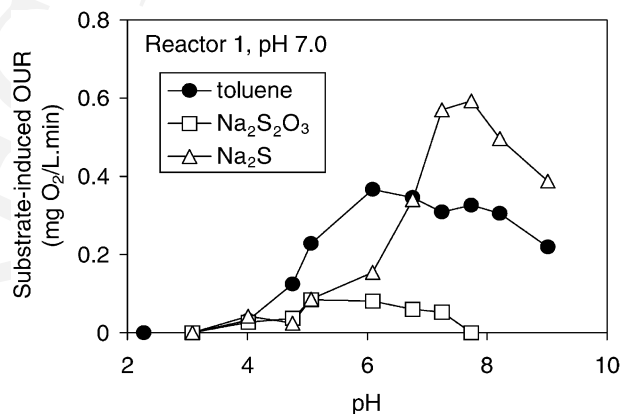


Fig. 8. Influence of the pH on the substrate-induced OURs by suspended biofilm from Reactor 1 operated at neutral pH.

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

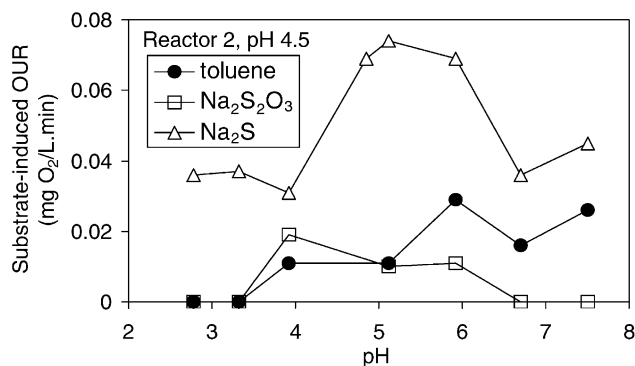


Fig. 9. Influence of the pH on the substrate-induced OUR by suspended biofilm from Reactor 2 operated at pH 4.5.

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

330 3.5. Short-term sensitivity to a change of the pH

331 The effect of pH was further investigated in pH shock ex-
 332 periments. The pH of the recycle liquid of the neutral-pH
 333 reactor and of the low-pH reactor was temporarily lowered
 334 to set values of 3.8 and 2.6, respectively. Standard operation
 335 was continued throughout the experiment, and the perfor-
 336 mance of biotrickling filters was determined before, during
 337 and after the pH change. As shown in Fig. 10, the reactor pre-
 338 viously operated at a neutral-pH showed a drastic decrease
 339 of the removal rate of both H₂S and toluene when the pH was
 340 lowered to 3.8. Such a response was expected, since plating
 341 experiments had shown that the number of acid-tolerant
 342 microorganisms in this reactor was low (Table 4). Readjust-

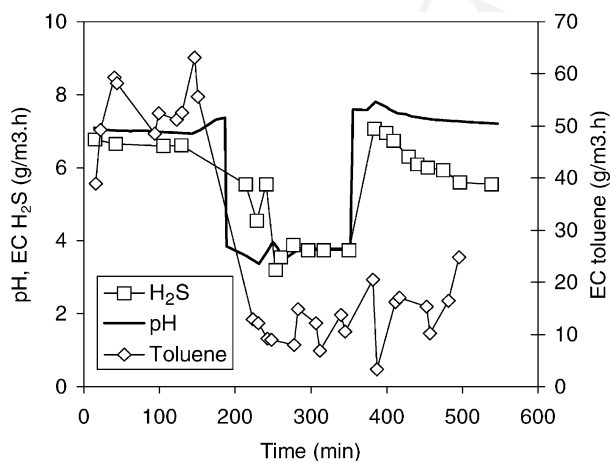


Fig. 10. Effect of a temporary decrease of the pH (set values 7.0 → 3.8 → 7.0) on H₂S and toluene removal in Reactor 1, normally operated at pH 7.0.

343 ment of the pH to its original value immediately restored
 344 H₂S removal, but toluene removal remained low (Fig. 10).
 345 Apparently, the short-term low pH incursion had a different
 346 effect on the toluene and H₂S degrading microorganisms in
 347 Reactor 1. It is interesting to compare this experiment with
 348 another one where the pH of Reactor 1 was gradually de-
 349 creased to a value of 2.1 over 33 days (not shown). Under
 350 these slowly changing conditions, the EC of toluene and H₂S
 351 was not affected, most probably because it allowed time for
 352 pH resistance mechanisms to develop or more likely it al-
 353 lowed sufficient time for acid-tolerant species to grow.

354 The pH shock experiment of Reactor 2 is shown in Fig. 11.
 355 The low-pH reactor was much less sensitive to a pH change,
 356 and the removal of H₂S and toluene was relatively unaf-
 357 fected (Fig. 11). Thus operation at low pH results in the
 358 establishment of biotrickling filters with a faster and more
 359 stable response to a change of the pH.

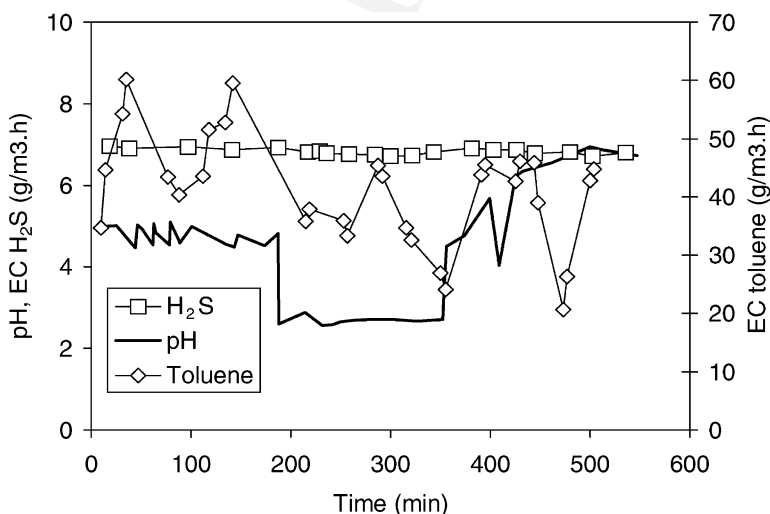


Fig. 11. Effect of a temporary decrease of the pH (set values 4.5 → 2.6 → 4.5) on H₂S and toluene removal in reactor, normally operated at pH 4.5.

360 4. Discussion

361 The results presented herein clearly demonstrate that H₂S
362 and toluene can be effectively treated simultaneously in a
363 single-stage biotrickling filter. Depending on the conditions,
364 high elimination rates or high removal percentages of H₂S
365 and toluene were obtained. H₂S biooxidation resulted in a
366 near stoichiometric production of sulfate which was leached
367 out of the system, while toluene was degraded to CO₂. All
368 the data were consistent with a biological conversion of the
369 pollutants. Toluene and H₂S biodegradation was a parallel
370 process occurring simultaneously with no cross-inhibition.
371 This was not totally unexpected since H₂S degradation is
372 mediated by autotrophic organisms, while toluene degra-
373 dation is mediated by heterotrophic organisms. Apparently,
374 competition for nutrients, oxygen or other potentially limit-
375 ing nutrient did not occur, hence both populations behaved
376 relatively indifferently in the presence of each other. This is
377 clearly different from the competition and cross-inhibition
378 observed by others, especially in cases of pollutants of simi-
379 lar nature that are expected to be degraded by the same group
380 of organisms, possibly even via the same pathway [17–19].

381 The effect of the pH on the biotrickling filtration pro-
382 cess was complex. On the one hand, the reactor operated
383 at a low pH required a 20–40-day startup time for the effi-
384 cient removal of toluene. On the other hand, after startup, its
385 H₂S and toluene removal performance was similar to that
386 of the neutral-pH reactor. This is quite remarkable since the
387 pH influences both the mass transfer of the pollutants (by
388 changing the gas–liquid partition) and the composition and
389 the characteristics of the process culture. Regarding the lat-
390 ter, marked differences were indeed observed in the activity
391 of the biofilm (Figs. 8 and 9) and in the composition of the
392 mixed cultures (Table 4) from the two reactors. These dif-
393 ferences were found to be the result of the slow growth of
394 different populations over time rather than from phenotype
395 changes or stress-related responses. Plating experiments (Ta-
396 ble 4) revealed that a majority of the culturable organisms
397 present in the neutral-pH biotrickling filter could not grow
398 at low pH, while those of the low-pH bioreactor could thrive
399 either at low or at neutral pH. Clearly, the process culture in
400 the low-pH reactor was acid-tolerant rather than acidophilic,
401 as shown by higher plate counts at pH 7 than at pH 4.5. This
402 hypothesis is consistent with the oxygen uptake experiments
403 (Figs. 8 and 9) which revealed a wide window of operating
404 pH for the biomass in the low-pH reactor, and a narrow pH
405 range for the biomass in the neutral-pH reactor. It is further
406 reinforced by the lesser pH sensitivity of the low-pH reactor
407 during the pH shock experiments (Figs. 10 and 11).

408 While the good performance of the low-pH biotrickling
409 filter for the removal of H₂S may not be a surprise in the light
410 of the many studies on H₂S degradation alone [3,6,11,13],
411 the good EC of toluene at low pH is remarkable (Fig. 5). It
412 contrasts with a number of published and unpublished re-
413 ports of biofilter failure due to low pH [6,20], and the large
414 body of papers on the negative effect of low pH in soils. Re-

garding the latter, an interesting common finding in many 415
soil studies is that the specific activity of microorganisms is 416
often reduced under low pH conditions, but that the bacte- 417
ria density may be unaffected by extreme pH. An interest- 418
ing example of this was discussed by Mori et al. [21]. The 419
biodegradation of the fungicide chlorothalonil was compared 420
in four soils subjected to different nutrient and pH condi- 421
tions. Degradation of chlorothalonil was increased by adjust- 422
ing the soil pH to a neutral value, although the most prob- 423
able number of degrading microorganisms remained con- 424
stant. Thus, reduced microbial degradation of chlorothalonil 425
at low pH was due to the decrease in the degrading capacity 426
rather than a decrease in the number of degrading microor- 427
ganisms. The low specific activity at low pH may explain 428
the large differences observed during the oxygen uptake ex- 429
periments (Figs. 8 and 9). 430

431 Overall, the results of this paper suggests that a strict con- 432
trol of the pH at a near neutral value is not required for 433
efficient removal of toluene in biotrickling filters. However, 434
the good performance of toluene degradation at low pH may 435
not necessarily be extrapolated to less biodegradable com- 436
pounds that are degraded by fewer microorganisms. When 437
less functional redundancy exists for degrading the VOC or 438
when VOC concentrations are low enough to prevent effec- 439
tive growth, selective enrichment of acid-tolerant VOC de- 440
grading organisms may not occur. Hence, a pH control may 441
then be desired. Clearly, controlling the pH will influence 442
the treatment costs. Options to control the pH include addi- 443
tion of caustic which can be expensive. At POTWs, where 444
industrial water is available at virtually no cost, increasing 445
the water supply to the reactor may be considered. One will 446
need to keep in mind that the water requirements will in- 447
crease exponentially which each pH unit, hence, this method 448
may be impractical for the treatment of high concentrations 449
of H₂S. For such cases, if a near neutral pH is required for 450
VOC removal, the co-treatment of H₂S and VOC in one 451
reactor will need to be reconsidered. Sequential treatment, 452
i.e., treatment of H₂S in an acidic reactor first followed by 453
VOC treatment in a near neutral bioreactor as proposed by 454
Deviny et al. [3] may well be the method of choice. 455

5. Conclusions

456 The results discussed herein demonstrate that H₂S and 457
toluene can be effectively treated simultaneously in a 458
single-stage biotrickling filter. The pH of operation (4.5 459
and 7.0) did not greatly affect the performance of H₂S and 460
toluene removal, except that at pH 4.5, the startup phase of 461
toluene degradation was relatively long. Also, at pH 7.0, 462
a sudden decline of the pH (e.g., after the failure of the 463
pH control) caused temporary poor removal of H₂S and 464
toluene which contrasts with the robustness of the low-pH 465
biotrickling filter to changes in operating pH.

466 Selective enrichment of suitable microbial populations in 467
biotrickling filters is a key condition for successful treat-

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

475 Biotrickling filters are simple and effective. They may
 476 become the preferred treatment technique for complex
 477 off-gases at POTWs. The specific conditions at each POTW
 478 will dictate the design criteria for each biotrickling filter.
 479 But in most cases, because of the large volume of off-gases
 480 requiring treatment at POTWs, the deployment of biotrick-
 481 ling filters will call for designing biotrickling filters with
 482 a short gas residence time and capable to achieve H₂S
 483 removal down to very low levels (ppb_v), while removing
 484 target VOCs. This will require further careful evaluation
 485 of the rate-limiting step in the process and of the impact
 486 of the operating pH on the cost of the biotrickling filter
 487 equipment and on the costs associated with the operation
 488 and the maintenance of the reactor.

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