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Biotreatment of ammonia- and butanal-containing waste gases

Received: 12 January 1994 / Received revision: 8 April 1994 / Accepted: 20 April 1994

Abstract The biological removal of ammonia and butanal in contaminated air was investigated by using, respectively, a laboratory-scale filter and a scrubber-filter combination. It was shown that ammonia can be removed with an elimination efficiency of 83% at a volumetric load of $100 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ with 4–16 ppm of ammonia. During the experiment percolates were analysed for nitrate, nitrite, ammonium and pH. It was found that the nitrification in the biofilter could deteriorate due to an inhibition of *Nitrobacter* species, when the free ammonia concentration was rising in the percolate. It should be easy to control such inhibition through periodic analysis of the liquid phase by using a filter-scrubber combination. Such a combination was studied for butanal removal. Butanal was removed with an elimination efficiency of 80% by a scrubber-filter combination at a volumetric load of $100 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and a high butanal input concentration. Mixing the filter material with CaCO_3 and pH control of the liquid in the scrubber resulted in an increase of the elimination efficiency. These results, combined with previous results on the biofiltration of butanal and butyric acid, allow us to discuss the influence of odour compounds on the removal efficiency of such systems and methods for control. The results were used to construct a full-size system, which is described.

Introduction

The process of waste-water purification by biological methods is often accompanied by odour emissions. This may often be considered a major problem, especially

when purification plants operate close to residential areas, although no harmful gases are produced. Thus, it becomes more and more important to complement waste-water treatment plants with odour abatement systems (Weckhuysen et al. 1991, 1993b).

From a large group of commonly produced odorous compounds, ammonia and butanal were chosen to be representative for bio-elimination studies. They present low odour thresholds of $2.7 \text{ mg} \cdot \text{m}^{-3}$ and $13 \text{ mg} \cdot \text{m}^{-3}$ respectively (Gemert and Nettenbreijer 1977) and ammonia emissions are also involved in water and soil acidification (van Breemen et al. 1982), through nitrification processes.

For the reduction of odorous compounds in contaminated air, biological techniques have some potential advantages over other treatments (Ottengraf 1986; Weckhuysen et al. 1993b). They are based on the microbiological degradation of the odorants to water, CO_2 and mineral salts (Brauer 1984; Bardtke unpublished results). In the literature three techniques have been reported: biofiltration, bioscrubbing and biotrickling. These methods can be distinguished by the behaviour of the liquid phase (continuously moving or stationary in the contact reactor) and of the micro-organisms (freely dispersed or immobilized on a carrier material) (Diks and Ottengraf 1991). With respect to ammonia removal it might be expected that it becomes oxidized to nitrate. The removal principles are summarized in Fig. 1. *Nitrosomonas* and *Nitrobacter* are the main autotrophic bacteria involved. Butanal can be completely metabolized, eventually through its oxidation to butyric acid. In both instances the acidification of the medium might become a rate-limiting step. Biofiltration, bioscrubbing and biotrickling may behave differently in that respect.

In this paper we describe experiments with a biofilter, a bioscrubber and a biotrickling filter. In a biofilter the odorous air is forced through a packed bed of materials containing micro-organisms able to degrade the odorants. In a bioscrubber the odorants in the contaminated air are transferred from the air to absorption in a

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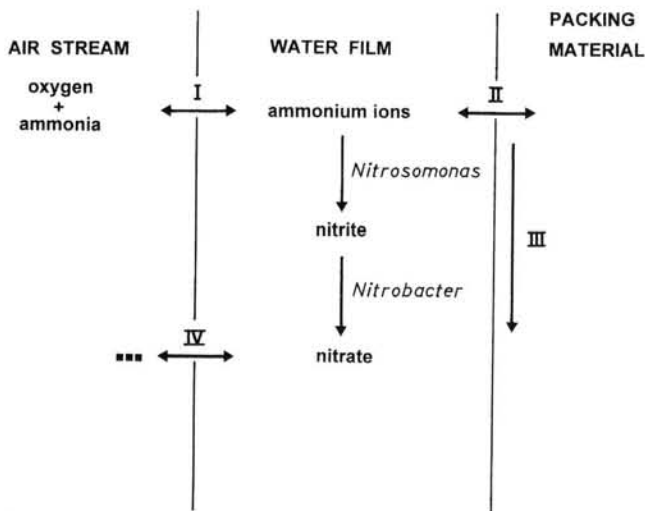


Fig. 1 The successive biofiltration removal phases of ammonia: *I* absorption, *II* adsorption, *III* nitrification, *IV* desorption

water phase, where biodegradation takes place, while in a biotrickling filter a packed bed is continuously sprayed with water (Weckhuysen et al. 1993b).

Materials and methods

Experimental set-up

A scheme of the biofilter set-up is given in Fig. 2. It consists of three plexiglass columns with a diameter of 0.10 m and a height of 0.33 m each, all filled with wood bark and connected with each other. To the total amount of wood bark needed to fill the system 100 g CaCO_3 was eventually added. It was shown previously that CaCO_3 addition is a simple way to avoid over-acidification (Weckhuysen et al. 1993a). Analysis of the air was done at four heights of the column.

The scrubber-filter combination is shown in Fig. 3. It consists of a wash bottle (scrubber) containing 0.5 l liquid medium and a plexiglass filter column 0.5 m high. Analysis of the air was done at three measuring points. Ammonia- or butanal-saturated air were mixed with humidified air and introduced in the systems as shown. The liquid medium of the scrubber section consisted of a nutrient solution (Weckhuysen et al. 1993a) and an inoculum of *P. fluorescens*. This micro-organism was introduced to speed up the aldehyde degradation in the scrubber section. *Pseudomonas fluorescens* was reported to be capable of this reaction (Kirchner et al. 1987). Air flows were measured with a home-made anemometer. The biotrickling-scrubber-filter combination consists of a plexiglass container (0.75 m \times 0.80 m \times 0.80 m) subdivided into three compartments: a biotrickling unit (0.25 m length and 0.9 m bed height), a bioscrubber unit (0.25 m in length and 0.9 m bed height) and a biofilter unit (0.25 m in length and 0.95 m filter-bed-height). A large-scale container system (12.2 m \times 2.4 m \times 2.8 m) was constructed and divided into three compartments: a biotrickling and a bioscrubber unit (each of 1 m length and respectively 1 m and 1.4 m bed height) and a biofilter unit (10 m in length and 1.4 m filter-bed height).

Analytical Methods

The humidity, the pH of the filter material, butanal and butyric acid concentration were determined as described previously (Weckhuysen et al. 1993a). Ammonia, nitrite and nitrate were de-

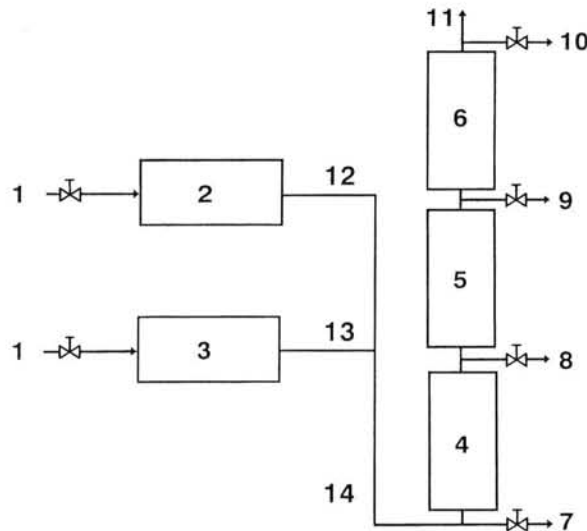


Fig. 2 Experimental set-up of the biofilter: *1* air inlet, *2* humidification unit: wash bottle and a bubble column with water in series, *3* wash bottle with ammonia, *4-6* three biofilter sections filled with wood bark, *7-10* measurement point at filter bed height 0.00 m, 0.33 m; 0.66 m and 0.99 m, *11* air outlet, *12* humidified air, *13* ammonia-saturated air, *14* humidified air polluted with ammonia

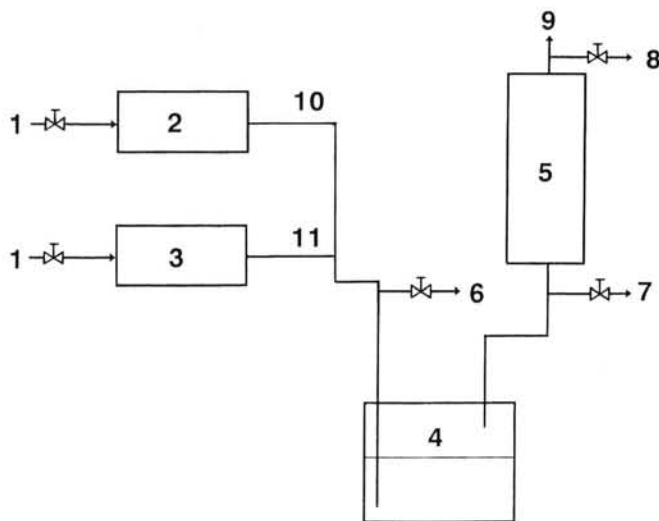


Fig. 3 Experimental set-up of the scrubber-filter combination: *1* air inlet, *2* humidification unit: two wash flasks with water in series, *3* wash flask with butanal, *4* wash flask with 0.5 l nutrient solution, *5* biofilter column, *6-8* measurement points, *9* air outlet, *10* humidified air, *11* butanal-saturated air

termined according to Standard Methods (APHA 1979). Microbial growth was followed by turbidity measurements at 550 nm.

Results

Removal efficiency of ammonia by biofiltration

The biofiltration experiments with wood bark at a pH of 7.2 and 58% humidity were done with a waste

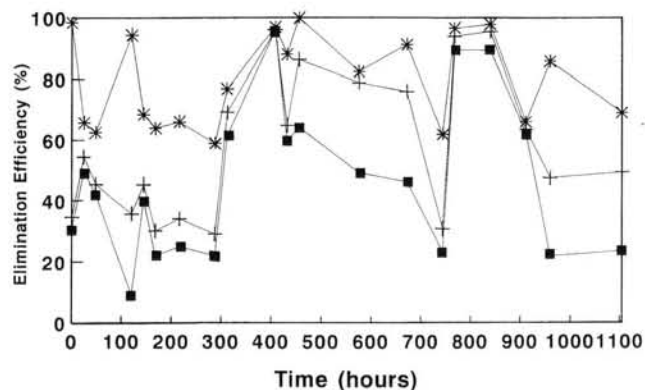


Fig. 4 Ammonia elimination efficiency (%) at different filter-bed heights: 0.33 m (■); 0.66 (+) and 0.99 m (*)

stream containing from 4 to 16.5 ppm (v/v) of ammonia. The volumetric load was $100 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. Ammonia concentrations were measured during a 7-week operation. The results are expressed as elimination efficiencies, η (%):

$$\eta = \left(1 - \frac{C_i}{C_o}\right) \times 100 \quad (1)$$

where C_i is the ammonia concentration measured at height i in the biofilter and C_o is the ammonia input concentration.

The results in Fig. 4 show a mean elimination of 83%. In contrast with the removal of butanal (Weckhuysen et al. 1993a) the first filter section removed only about 20% of the ammonia. The results agree with measurements by Eggels (1986) and Jol (1989). Van Langenhove et al. (1988) reported elimination efficiencies of 90% and more with an optimal humidity and an ammonia input lower than 2 g of Nitrogen (N) $\cdot \text{m}^{-3} \cdot \text{h}^{-1}$. Under optimal conditions we found efficiencies of 95% and more. Another biological method for ammonia removal is a rotating biological contactor. This technique has a removal efficiency of about 60%, much lower than for biofilters (Vis and Rinzema 1991). The limited ammonia absorption is responsible for this low ammonia removal.

Percolate analysis

As can be seen in Fig. 4, there is a fluctuation in the elimination efficiency during the experiment. Accord-

ing to Anthonissen et al. (1976) the nitrification process in waste-water treatment plants can be disturbed by the concentrations of free ammonia (FA) and free nitrous acid (FNA) rather than by the total concentration in ammonia and nitrite. In order to find out whether this phenomenon may be responsible for the fluctuations in ammonia removal, column percolates were analysed at three time periods for FA and FNA concentrations.

The FA and FNA concentrations were calculated using total ammonia and nitrite values and the pH according to Eqs. 2 and 3. Two-liter amounts of percolate were obtained by sprinkling the top of the biofilter with bidistilled water. The results are given in Table 1.

$$\text{FA (ppm)} = \frac{17}{14} \times \frac{\text{total } \text{NH}_4^+ - \text{N} \times 10^{\text{pH}}}{\frac{K_b}{K_w} + 10^{\text{pH}}}$$

$$\text{with } \frac{K_b}{K_w} = e^{\left(\frac{6344}{273+t}\right)} \quad (2)$$

$$\text{FNA (ppm)} = \frac{46}{14} \times \frac{\text{NO}_2 - \text{N}}{K_a \times 10^{\text{pH}}} \quad \text{with } K_a = e^{-\left(\frac{2300}{273+t}\right)} \quad (3)$$

where K_w , K_b and K_a are the ionization constants of water, ammonium and nitrous acid.

When these concentrations are introduced in a figure redrawn from Antonissen et al. (1977) (Fig. 5) the percolates should be fitted in zone 2. This is the zone of observed inhibition of *Nitrobaacter* by FA. This should result in an increase of nitrite and a lowered elimination efficiency. This was indeed found (Table 1) to occur at a time of 1104 h.

Scrubber-biofiltration of butanal-loaded air

In a previous publication we reported an excellent removal of butanal by biofiltration (Weckhuysen et al. 1993a). This was now compared to a scrubber-biofilter combination. The biofilter operated at a pH of 6.5 and a moisture content of 57%. Butanal-loaded air (mean butanal concentration of 27 ppm, v/v) was introduced at a loading of $100 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. The elimination efficiencies during more than 9 weeks are given in Fig. 6. It is interesting to note that periods of low scrubber activity correspond to high filter activity and vice versa, resulting in a combined mean removal of around 80%, a mean removal efficiency for the scrubber of 49% and 31% for the biofilter. Fluctuations may be due to acidification. This is shown in the next section.

Table 1 The pH, nitrate- ($\text{NO}_3^- - \text{N}$), nitrite- ($\text{NO}_2^- - \text{N}$) and ammonium-nitrogen ($\text{NH}_4^+ - \text{N}$) concentrations in the percolates, the free ammonia (FA)- and free nitrous acid (FNA) concentra-

tions, as calculated with Eqs. 2 and 3, together with the corresponding elimination efficiencies (El. Ef.) at the given time x (h)

Percolate after x (h)	pH	$\text{NO}_3^- - \text{N}$ (ppm)	$\text{NO}_2^- - \text{N}$ (ppm)	$\text{NH}_4^+ - \text{N}$ (ppm)	FA (ppm)	FNA (ppm)	El. Ef. (%)
408	7.9	9.0	0.4	121.3	4.5	4.4×10^{-5}	97.0
768	7.8	9.4	0.4	125.9	3.7	5.1×10^{-5}	96.7
1104	8.1	15.9	3.1	130.9	7.5	2.1×10^{-4}	70.0

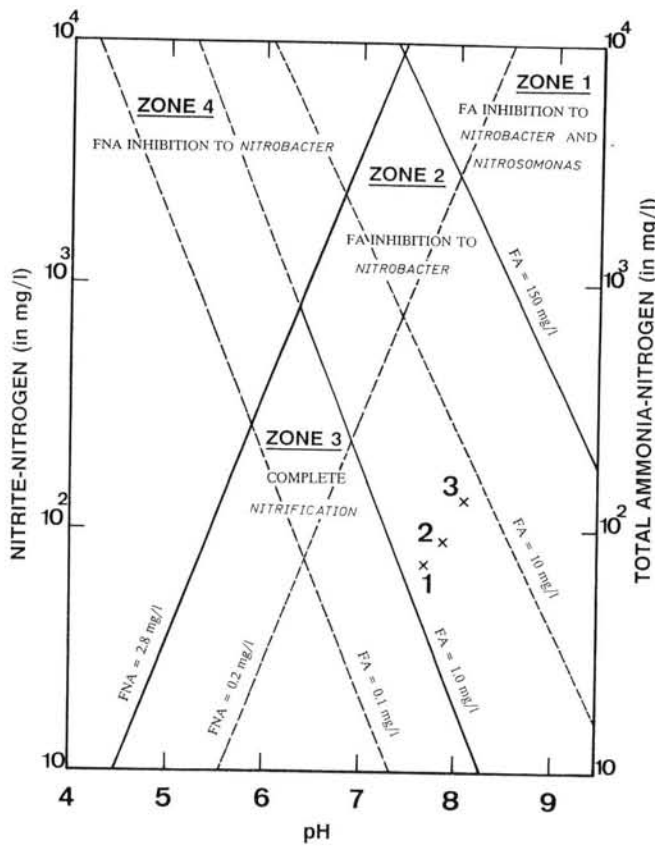


Fig. 5 Influence of pH, free ammonia (FA) and free nitrous acid (FNA) on the nitrification process: measurement point 1 (after 768 h), measurement point 2 (after 408 h) and measurement point 3 (after 1104 h) as calculated by using Eqs. 2 and 3 (see text) using the percolate composition (redrawn from Anthonissen et al. 1976).

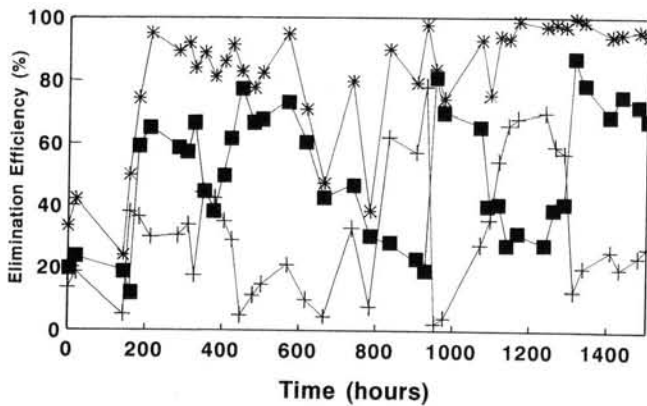


Fig. 6 Butanal elimination efficiency (%) in the filter (+), in the scrubber (■) and in the whole installation (*)

Influence of scrubber pH

Figure 7 shows the relation between the pH of the scrubber solution and its removal efficiency. After a pH drop, the pH was adjusted by adding NaOH to the

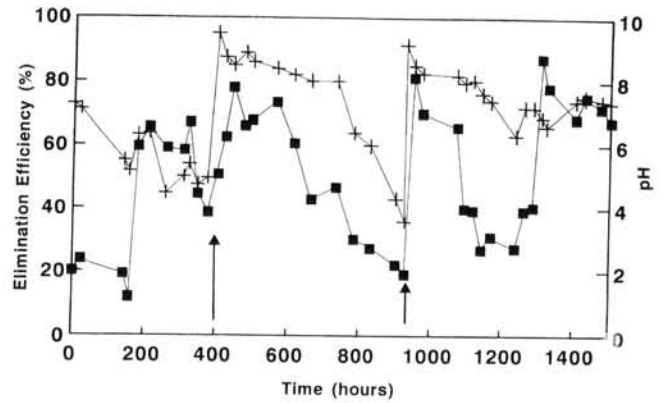


Fig. 7 Relationship between the pH of the scrubber liquid (+) and the elimination efficiency (■): pH adjustments are indicated by arrows

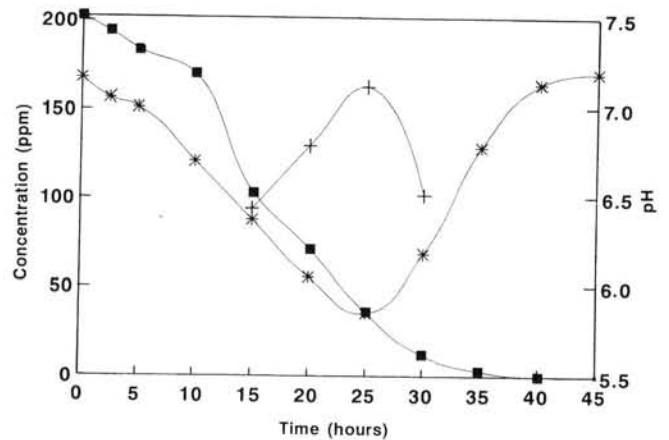


Fig. 8 Batch experiment: relationship between butanal degradation (■), butyric acid formation (+) and pH (*)

scrubber solution (see arrows in Fig. 7). Clearly the elimination drops dramatically whenever the pH shows a tendency to decrease.

Using only biofiltration of butanal we showed (Weckhuysen et al. 1993a) that the intermediate formation of butyric acid is the most likely cause of acidification. To confirm this finding, part of the scrubber solution was at first aerated well for 48 h to obtain the removal of all residual butanal and butyric acid by bio-oxidation. Butanal was then added and butanal and butyric acid concentrations were determined during 45 h. The results in Fig. 8 clearly show the intermediate formation of butyric acid and the corresponding decrease in pH. In this experiment butanal losses due to evaporation were corrected for by running a sterile control under the same conditions.

Construction of a filter-scrubber-trickling system

Based on these results a system as shown in Fig. 9 was constructed. It is a combination of a biofilter, a bio-

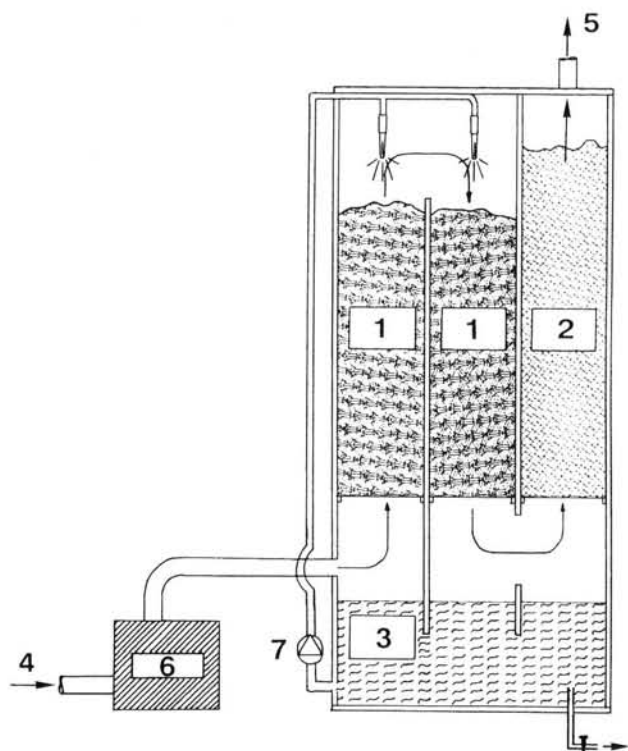


Fig. 9 Biotrickling-scrubber-filter combination for the removal of waste gases from a waste-water treatment plant: 1 packing material, 2 biofilter, 3 wash liquid, 4 air inlet, 5 air outlet, 6 blower, 7 liquid pump

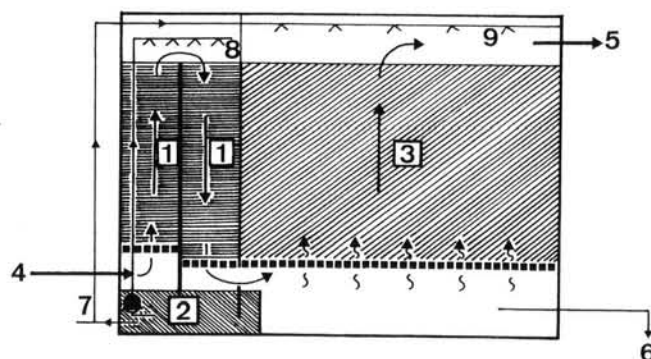


Fig. 10 General design for the removal of odorous compounds in waste gases using a container system: 1 biotrickling and bioscrubber unit, 2 wash basin for regeneration of activated sludge, 3 biofilter unit, 4 waste gases, 5 cleaned air, 6 percolate water, 7 water recycling, eventually with activated sludge for biofilter or water supply, 8 sprinkling system for scrubber units, 9 sprinkling unit for biofilter

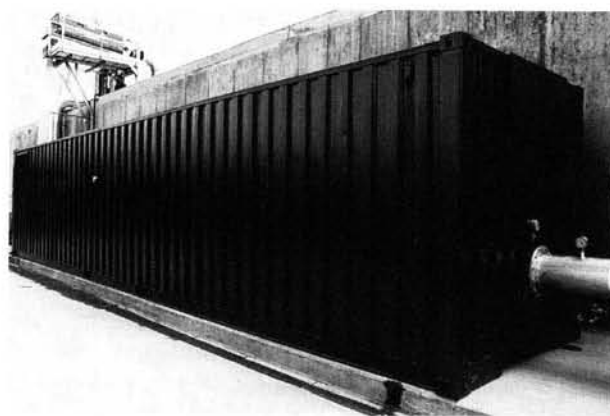


Fig. 11 Container system for a waste water treatment plant of a brewery, based on the principles outlined in Fig. 10

trickling filter and a bioscrubber. In a first step the waste gas is directed through a biotrickling filter (counter-currently). In a second step the waste stream is passing a second bed (direct-currently), while in a last step the gas is directed through a biofilter. In such a system micro-organisms growing on the packing material in the trickling section are continuously reactivated through recycling of a mixed microbial culture developed in the wash liquid (about $5 \text{ g} \cdot \text{l}^{-1}$ of dry matter). With this installation a total removal of odorous compounds, such as butanal and ammonia, in waste gases was obtained ($\eta > 99\%$). The volumetric load was for each compartment $500 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ (residence time of 30 s) and the pH and nutrient control were easily to perform.

Such a system was also constructed on real dimensions to be tested in a waste-water treatment plant for a brewery. Figure 10 shows the general design of the full size odour abatement unit. For scale-up of the filter-scrubber-trickling system, the relative dimensions of the three compartments were changed from 1:1:1 to 1:1:10. With a load varying between 2000 and 5000 $\text{m}^3 \cdot \text{h}^{-1}$, the volumetric load of the biofilter was lowered sufficiently, resulting in a good residence time and consequently excellent performances ($\eta > 99\%$). The trickling-scrubber unit contains water mixed with activated sludge ($5\text{--}8 \text{ g} \cdot \text{l}^{-1}$), while the filter unit contains a mixture of wood bark and polyethylene rings, the latter

to avoid clogging of the filter. After several months of operation in a well-populated area, no odour problems were recorded. Figure 11 shows the location of the container system adjacent to a waste-water treatment plant.

Discussion

The biofiltration removal of some odorous compounds can be inhibited by the accumulation of some biodegradation products. Thus, it was shown previously (Weckhuysen et al. 1993a) that the intermediate formation of butyric acid from butanal may be detrimental. The addition of nutrients and a simple pH control by the addition of CaCO_3 to the filter material highly improved the process performance.

The removal of ammonia, which leads to the formation of nitrate and protons, may present similar problems. In order to study this possibility its removal was studied using biofiltration. However, for ammonia

there are indications that the accumulation of free ammonia rather than the acidification may be a very important process characteristic. Similar to the results obtained for waste-waters by Anthonissen et al. (1976) we found that the elimination efficiency decreased sharply when biofilter percolates showed an increased concentration of free ammonia. This may result in the inhibition of *Nitrobacter* species and the accumulation of nitrite. The FA concentration is dependent on pH and total $\text{NH}_4^+ - \text{N}$ concentration. The continuous determination on column percolates of pH, ammonia and nitrite may be a necessary procedure for overall process control. However, this is not easy as the volumetric load cannot be adapted easily during the process.

The use of a scrubber-filter combination may be the best solution. This was studied with butanal-loaded air. With this compound acidification due to the intermediate formation of butyric acid is responsible for lower performances. Thus the pH control by the addition of NaOH to the scrubber section can be highly beneficial and is easy to perform. It is obvious that the presence of micro-organisms and nutrients, such as phosphate, in the scrubber will enhance the overall performance.

Using a filter-scrubber-trickling system these assumptions were confirmed. In the trickling and scrubber unit water-soluble odorous compounds, such as ammonia and organic acids are degraded by micro-organisms and the process can be easily controlled by pH adjustments and nutrient additions. However, the presence of activated sludge may overcome the need for further additions of nutrients. Hydrophobic odorants, like aldehydes can be efficiently removed from the waste gases in the filter section. Thus, this combination offers the possibility for the total removal of odour compounds in a complex gas mixture, frequently encountered in waste gases of waste water-treatment plants.

Acknowledgement B.W. acknowledges the Belgian National Fund for Scientific Research (N.F.W.O.) for a grant as research assistant.

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