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Toluene and styrene removal from air in biofilters

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Abstract

Two identical sized laboratory-scale biofilters, filled with the same type of packing material, consisting of a mixture of peat and glass beads in a 4:1 volume ratio, are investigated for the purification of toluene and styrene-containing off-gas streams. One of the biofilters was inoculated with a toluene-degrading strain of *Acinetobacter* sp. NCIMB 9689, and the other with a styrene-degrading strain of *Rhodococcus rhodochrous AL* NCIMB 13259. For both pollutants, different sets of continuous experiments were conducted in the biofilter columns, varying both the inlet pollutant concentration and the superficial gas velocity. Maximum elimination capacities of 242 and 63 g $m^{-3}_{\text{packing material}}$ h^{-1} packing material were recorded for toluene and styrene, respectively. Furthermore, the deodorization (defined as the achievement of a pollutant concentration in the effluent gas below the pollutant olfactory threshold value) of toluene and styrene-containing waste-gases was also considered. This was achieved, operating at maximum inlet concentrations of 1.99 and 0.20 g m^{-3} and at superficial gas velocities of 17.8 and 122 m h^{-1}, respectively.

Keywords: Toluene; Styrene; Biofiltration; Deodorization; *Acinetobacter sp*; *Rhodococcus rhodochrous*

Nomenclature

C_{ge}	pollutant concentration in the effluent gas (g m^{-3})
C_{go}	pollutant concentration in the influent gas (g m^{-3})
EC	elimination capacity (g $m^{-3}_{\text{packing material}}$ h^{-1})
U_g	superficial gas velocity (m h^{-1})
X	biomass concentration in the culture medium (g l^{-1})
η	degree of conversion (dimensionless)

Subscript

max	maximum value
0	influent value referred to waste gas

1. Introduction

Benzene, toluene, ethylbenzene and the isomers of xylene (BTEX) and styrene are among the 50 largest-volume industrial chemicals produced in the world. Each of these compounds is produced at a rate of

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millions of tons per year [1,2]. They are widely used as fuels and solvents and provide starting materials for the production of resins, polymers, plastics, explosives, agrochemicals, and pharmaceuticals.

Due to their natural ubiquitous presence in the environment and their widespread release through industrial and agricultural activities, the biodegradation of these compounds has been widely studied. These compounds are quoted by the US Environmental Protection Agency (EPA) as priority environmental toxic pollutants, due to their substantial toxicity and their carcinogenic potential, even at low concentrations.

The control of volatile organic air toxic emissions from industrial facilities has become critical and expensive to the chemical industries, particularly the small sized ones, in order to meet the more and more severe quality standards. The biotechnological approach to air pollution is now a promising field of research which can supply reliable, simple and cheap technologies for the prevention of air contamination.

The reliability of biological processes and, in particular, of biofiltration for the treatment of waste gas streams containing volatile organic compounds has been demonstrated in a very large number of experimental studies [1,3–7]. Biofiltration is particularly suited and cost-effective for the treatment of high volumes of waste gases containing low volatile organic compounds (VOCs) concentrations. Furthermore, it is environmentally friendly because the contaminants are completely converted at low temperature into non-hazardous final products.

Compared with the other biological systems, biofilters have been shown to be more effective for treating some poorly-water-soluble compounds thanks to the high superficial area available for mass transfer. Optimal removal of aromatic hydrocarbons air contaminants can best be reached using biofilters rather than bioscrubbers or biotrickling filters [8]. Provided comparable performance can be obtained with similarly sized biofilters and biotrickling filters, both the simplicity and the easy operation of biofilters will favour their selection for the treatment of waste gases.

The aim of this study is to investigate the ability of the selected strains to remove toluene and styrene vapours in biofilters to get sufficient data for a future macro-kinetic study as well as useful information for industrial application.

2. Materials and methods

2.1. Microorganisms and culture conditions

The Toluene-degrading strain of *Acinetobacter* sp. NCIMB 9689 and a styrene-degrading strain of *Rhodococcus rhodochrous AL* NCIMB 13259 used in this work were obtained from the National Collection of Industrial and Marine Bacteria LTD, Aberdeen, Scotland. Both strains were grown on a nutrient medium containing the following chemicals, per litre of tap water: 1.0 g Lab-Lemco beef extract, 2.0 g yeast extract, 5.0 g peptone, and 5.0 g NaCl. The medium was sterilized by autoclaving for 15 min at 121 °C. Cultivations were performed in 250-ml Erlenmeyer flasks containing 150 ml of medium at pH 6.8. The cultures were then incubated at 25 °C with rotary shaking and aerated with sterile air. After 24–48 h of growth, cells were harvested by centrifugation at 5000 rpm for 20 min and re-suspended in fresh nutrient medium to be used as an inoculum for biodegradation experiments. Stock cultures of the strains were maintained by periodic subculture on the same nutrient medium and stored at 4 °C. The mineral salts solution used for continuous degradation experiments had the following composition per litre of tap water, 5.8 g KH_2PO_4, 4.5 g K_2HPO_4, 2.0 g $(NH_4)_2SO_4$, 0.34 g $MgCl_2 \cdot 6H_2O$, 0.20 g $CaCl_2 \cdot 6H_2O$, 0.002 g $FeSO_4 \cdot 7H_2O$, and 0.0016 g $MnCl_2 \cdot 4H_2O$.

2.2. Analytical procedures

Toluene and styrene gaseous samples were analyzed with a Carlo Erba Model HRGC 5160 gas chromatograph equipped with a capillary column (25 m × 0.32 mm, Mega Laboratory) and a flame ionization detector connected with a computing integrator. The temperatures of injector and detector were 150 and 200 °C, respectively. Oven temperature was initially maintained at 50 °C for 2 min and then increased at a rate of 40 °C min^{-1} up to 250 °C, where it remained constant for 5 min. Nitrogen was used as carrier gas. Vapour phase pollutant standard curves were obtained by injecting a known amount of the selected compound in calibrated glass bottles, following the procedure described by Shareefdeen and Baltzis [9].

Biomass concentration in the culture broth was determined by filtering 10 ml of culture broth through tared 0.45 μm pore size 47 ± 3 mm diameter cellulose nitrate membrane filters (Sartorius AG. 37070 Goettingen, Germany). After washing with 10 ml 0.9% NaCl solution, the filters were dried at 105 °C to constant weight and cooled in a desiccator prior to re-weighting.

The moisture content of the filter bed was determined by the dried weight method [10].

2.3. Apparatuses for continuous experiments

Experiments were carried out in two identical continuously operating bench-scale biofilters, schematically shown in Fig. 1. The apparatus consisted of 0.65 m long cylindrical glass columns with an inner diameter of 0.05 m, provided with sampling ports, located at 0.12, 0.25, 0.37, and 0.52 m from the bottom of the

filter. The height of the filter bed was 0.50 m in both cases.

The filter packing material, in both biofilter columns, was a mixture of sterilized peat (with a specific surface area of 1.6 $m^2\ g^{-1}$) and glass beads (diameter 5 mm) in a 4:1 volume ratio, which was supported by a fine perforated plate of ceramic, placed at the bottom of the column. The moisture content of the packing material was kept between 50 and 60%, either by bubbling the influent synthetic waste air in a humidification unit, or by periodically distributing via nozzle at the top of the packing material a mineral salts solution, flowing counter currently with the gas upward through the column.

The biofilter columns were operated at room temperature (20–21 °C). The pH of the packing material was maintained around neutrality as previously described [11]. Biofilters were inoculated with a cell suspension of the selected strain. The suspension was mixed with dry packing material, previously sterilized by autoclaving at 120 °C for 20 min, in the proportion of 25% by volume. The cell density in the inoculum was 6.0 $g\ l^{-1}$. During the experiments, an inoculum of 50 ml of cells suspension was provided every 2 months to each column, in order to guarantee the predominance of the selected strain within the biofilter.

The synthetic waste gas was generated by injecting a low flow laboratory air stream into a liquid pollutant reservoir, the stream becoming polluted by the contaminant evaporation. The air containing pollutant vapour was then adequately mixed with a high-flow rate air stream previously humidified by bubbling it in a water-containing vessel to obtain the desired concentration of contaminant in the air stream, before entering the base

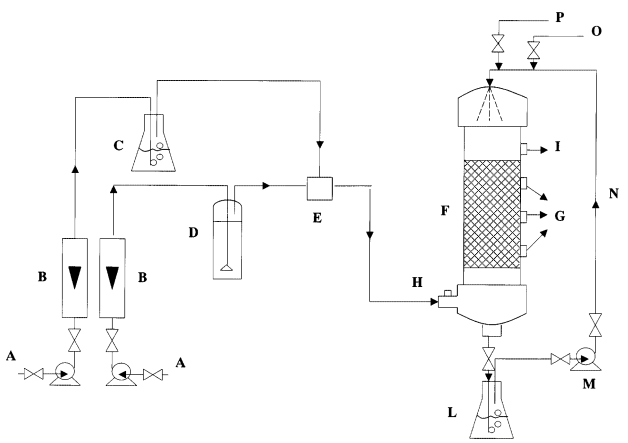

Fig. 1. Schematic representation of the experimental apparatus. (A) compressed air; (B) air flow-meters; (C) pollutant vessel; (D) humidifier; (E) mixing chamber; (F) peat/glass beads packing; (G) sampling ports; (H) influent waste gas; (I) effluent gas; (L) leachate vessel; (M) peristaltic pump; (N) liquid recirculation circuit; (O) water supply; (P) mineral salts solution.

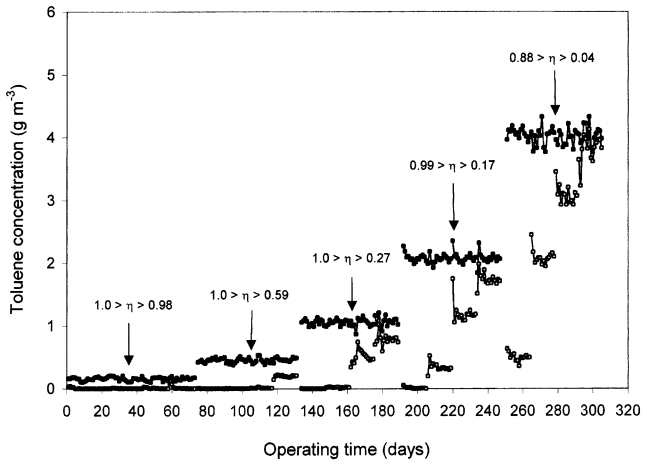

Fig. 2. Experimental results of continuous tests of toluene removal from air stream ($g\ m^{-3}$), (●) inlet toluene concentration; (○) outlet toluene concentration.

of the biofilter. The system was provided with two flow-meters which allowed the measurement of the total air flow and the streams flowing in the vessels. The pollutant concentration in the influent gas was varied by regulating, by means of the flow-meters, the flows of both contaminated and laboratory air streams in a mixing chamber.

3. Results

3.1. Continuous tests of toluene biofiltration

In order to test the toluene elimination capacity of the lab-scale biofilter, different sets of continuous experiments were performed over a period of 10 months by changing both the superficial gas velocity and the toluene concentration in the influent air stream. In particular, four series of experiments were performed at superficial gas velocities of 17.8, 35.7, 127.5, and 255 $m\ h^{-1}$ (corresponding to apparent gas residence times of 101, 50, 14 and 7 s, respectively), and testing, for each given superficial gas velocity, five different inlet toluene concentrations, namely 0.1–0.2, 0.4–0.5, 1.0, 2.0, and 4.0 $g\ m^{-3}$. All experiments were conducted under non-sterile conditions. During the start-up phase, a control column was used in order to determine the starting abiotic removal due to the physical adsorption by the packing material. Toluene breakthrough occurred after 3 h of operation.

Fig. 2 shows the experimental results of continuous tests carried out during the whole experimental investigation. Each test, under a given set of operative conditions, lasted a period of about 10–12 days. In order to prevent a shock to the microorganisms due to excess substrate, the first set of experiments was performed at

the lowest superficial gas velocity (17.8 m h^{-1}) as well as at the lowest range of inlet toluene concentration (0.1–0.2 g m^{-3}). During this period, a removal efficiency close to 100% was initially observed, which was followed by a gradual decrease and a final restoration of the high starting values. This behaviour is the result of the preliminary adsorption of the pollutant by the filter bed and of the subsequent biological action of the microbial cells.

Nearly constant values of degradation efficiency were reached after about 3 days of continuous operation at the lowest concentration range and the highest residence time. This short start-up period was likely due to the inoculation of the biofilter with a specific and adapted microorganism. A final average degree of conversion close to 100% has been assured, which indicated biofiltration is a really efficient technique in the control of waste gases containing toluene at low concentrations.

After the efficiency of the system had been tested at low pollutant levels, the inlet toluene concentration was progressively increased to 0.4–0.5, 1.0, 2.0, and 4.0 g m^{-3}, while the apparent gas residence time was decreased from 101 to 7 s, with the aim of evaluating the actual possibility of employing this system in the presence of relatively high toluene loads, with respect to those usually applied in biofilters.

The average degree of conversion calculated in these subsequent phases were surprisingly high and the system proved very stable during the whole continuous experimentation. This indicates the high capacity of the cells to adapt themselves to large variations of pollutant concentrations as well as an unexpected ability to survive concentrations higher than 3.5 g m^{-3}.

3.2. Continuous tests of styrene biofiltration

The laboratory-scale biofilter used for styrene vapours removal was run for a period of 6 months with styrene volumetric loading rates varying from 6.14–588 g m^{-3} of packing material per hour, corresponding to superficial gas velocities of 61.2–245 m h^{-1} and influent styrene concentrations of 0.05–1.2 g m^{-3}, which approximately, corresponds to the concentration range of styrene in industrial emissions [12].

The experimental procedure followed for the continuous tests of styrene removal was similar to that followed for toluene. In order to prevent a shock to the microorganism (*R. rhodochrous*), the first series of runs was also conducted at the lowest superficial gas velocity (61.2 m h^{-1}), corresponding to an apparent gas residence time of 30 s, as well as at the lowest styrene concentration in the influent gas (0.05 g m^{-3}). The adaptation period of the biofilter lasted 2 days, during which the styrene removal reached an efficiency close to 100%, evidencing the achievement of the system stabilization.

After 20 days of operation, the superficial gas velocity was progressively increased to 122 and 245 m h^{-1} (corresponding to apparent gas residence times of 15 and 7 s, respectively), while the inlet styrene concentration (0.05 g m^{-3}) was kept constant. Every tests lasted 10 days, during which a pseudo-steady state conditions were normally achieved within 10 h.

The same experimental procedure was followed for the other influent styrene concentrations investigated (0.2, 0.4, 0.8 and 1.2 g m^{-3}), in order to study the influence of both parameters on the elimination capacity. The performance of the bench-scale biofilter over a period of 6 months is reported in Fig. 3.

3.3. Deodorization tests

In the last part of this study, the deodorization of both toluene and styrene waste-gases was considered. Deodorization is defined as the achievement of a pollutant concentration in the effluent gas below the pollutant olfactory threshold values, that are 8.8×10^{-3} and 0.2×10^{-3} g m^{-3} for toluene and styrene, respectively. In particular, the influence of the superficial gas velocity on the biofilters deodorization capacity was investigated. In both cases, tests were performed changing the influent pollutant concentration as well as the superficial gas velocity.

4. Discussion

4.1. Continuous tests of toluene and styrene biofiltration

The combined effects of the superficial gas velocity and the inlet pollutant concentration on the biofilter

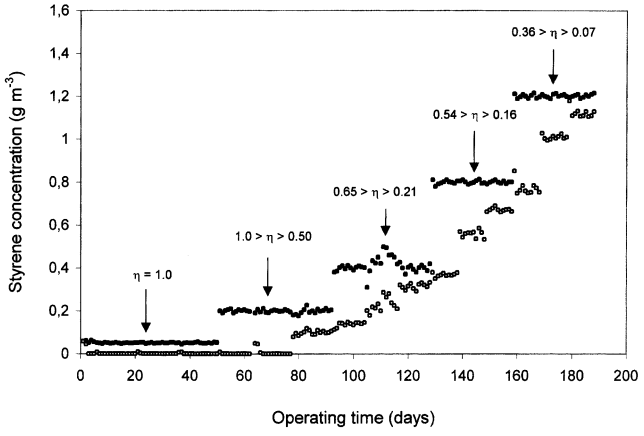

Fig. 3. Experimental results of continuous tests of styrene removal from air stream (g m^{-3}), (●) inlet styrene concentration; (○) outlet styrene concentration.

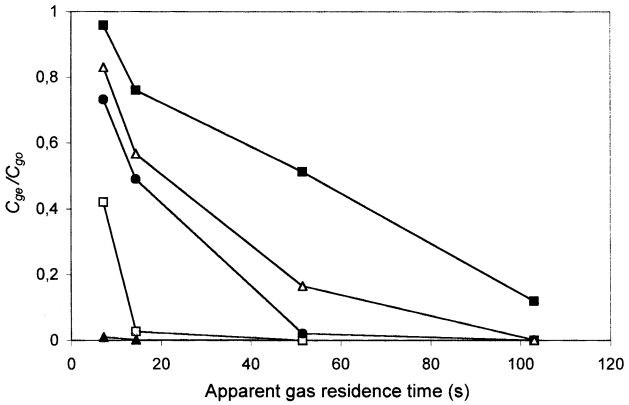

Fig. 4. Toluene gas concentration profiles as a function of the apparent gas residence time (s), obtained at different inlet toluene concentrations, C_{go} (g m^{-3}), (▲) 0.1–0.2; (□) 0.4–0.5; (●) 1.0; (△) 2.0; (■) 4.0.

removal efficiency are evident in Figs. 4 and 5 for both toluene and styrene degradation. The ratio between the outlet and inlet pollutant concentrations is reported, for different ranges of inlet concentrations, as a function of the apparent gas residence time. Each experimental value corresponds to the average of about 10 experimental runs with inlet concentration equal to the reported nominal value $\pm 5\%$. As expected, these results on the whole clearly show that the biofilter removal efficiency ($1 - C_{ge}/C_{go}$) decreases with increasing either C_{go} or U_g (and thus with decreasing apparent gas residence time).

The satisfactory removal capacity of the biofilter is demonstrated in Figs. 6 and 7, where the elimination capacity of toluene and styrene, respectively, are plotted versus the organic load at different inlet concentrations of these pollutants. From these results, it is evident that this parameter increases regularly with the organic load, with scarce relevance whether such a dependence is the result of an increase in C_{go} or of a decrease in residence time. In particular, a gradual and

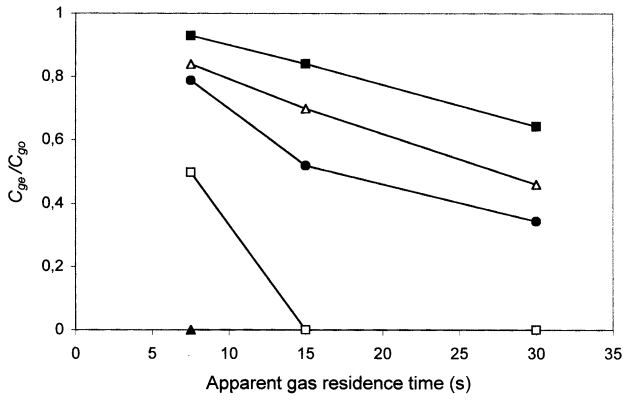

Fig. 5. Styrene gas concentration profiles as a function of the apparent gas residence time (s), obtained at different inlet styrene concentrations, C_{go} (g m^{-3}), (▲) 0.05; (□) 0.2; (●) 0.4; (△) 0.8; (■) 1.2.

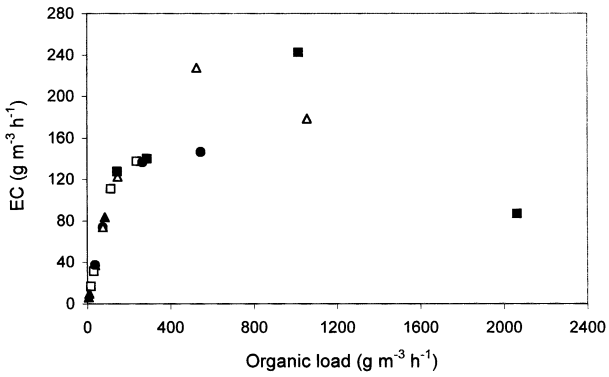

Fig. 6. Toluene elimination capacity of the biofilter versus the organic load, C_{go} (g m^{-3}), (▲) 0.1–0.2; (□) 0.4–0.5; (●) 1.0; (△) 2.0; (■) 4.0.

linear increase of the elimination capacity occurs up to a value of the organic load corresponding to about 100 g m^{-3} h^{-1} for toluene and 50 g m^{-3} h^{-1} for styrene. Beyond these values, the elimination capacity increases more slowly and reaches maximum values of 242 and 63 g $m^{-3}_{\text{packing material}}$ h^{-1} for toluene and styrene, respectively. These thresholds were obtained for toluene at an inlet concentration of 4.0 g m^{-3} and at a superficial gas velocity of 127.5 m h^{-1}, and for styrene at 0.8 g m^{-3} and 245.0 m h^{-1}.

Such a behaviour of the elimination capacity indicates that, at low loading rates, there is a linear relationship between the removal rate and the inlet load, and that the pollutants are nearly completely removed. In this range of organic load, the system performance is only limited by the pollutant availability, that is by the diffusion. With further increase of the load, on the contrary, the elimination rate increases more slowly up to a critical load (characteristic for each pollutant) at which it keeps constant, indicating that the maximum elimination capacity of the biofilter is achieved. Under these last conditions, the limiting step of the process is

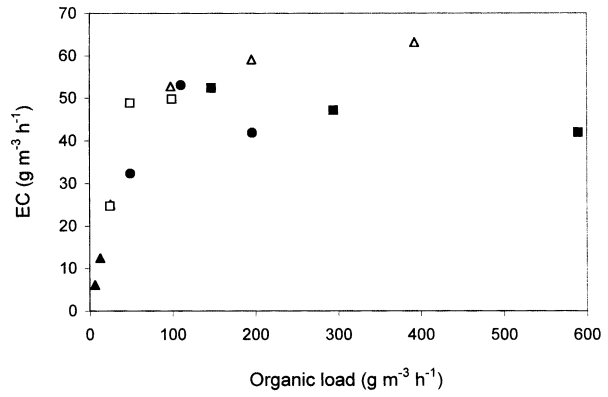

Fig. 7. Styrene elimination capacity of the biofilter versus the organic load, C_{go} (g m^{-3}): (▲) 0.05; (□) 0.2; (●) 0.4; (△) 0.8; (■) 1.2.

Table 1
Operating conditions at which the deodorization of toluene and styrene-containing waste-gases was obtained

C_{go} (g m^{-3})	U_g (m h^{-1})	Loading rate (g m^{-3} h^{-1})	Removal rate (g m^{-3} h^{-1})
Toluene deodorization			
1.99	17.8	70.8	70.5
1.02	35.7	72.8	72.2
0.31	127.5	79.0	76.8
0.25	255.0	127.5	123.0
Styrene deodorization			
0.05	245.0	24.5	24.5
0.20	122.0	48.8	48.8

the biological reaction, the elimination rate being lower than the pollutant feed rate. At loads higher than 1000 g m^{-3} h^{-1} for toluene and 400 g m^{-3} h^{-1} for styrene, the pollutant becomes inhibitory and the elimination capacity falls down.

The maximum toluene elimination capacity obtained in this work through continuous tests in biofilter is about 10% higher than the best values reported in the literature (190–215 g m^{-3} h^{-1}) [13,14]. A higher toluene elimination capacity (275 g m^{-3} h^{-1}) was obtained in a biotrickling filter [15]. The good results obtained in this work could be due to an excellent capability of *Acinetobacter* sp. to predominate in heterogeneous consortia, as the result of its peculiar adaptability to the conditions present within the biofilter, which would be the object of a future work.

As far as the styrene degradation ability of *R. rhodochrous* in biofilter is concerned, the elimination capacity obtained in this work is about 100% higher than that reported (30 g m^{-3} h^{-1}) by Arnold et al. [16] for a peat biofilter inoculated with activated sludge and nearly coincident with that (62 g m^{-3} h^{-1}) observed by Cox et al. [17] for a biofilter operated in a down-flow mode inoculated with the yeast *Exophiala jeanselmei*.

4.2. Deodorization tests

The average results of toluene and styrene deodorization obtained under different conditions are summarized in Table 1, where the effect of superficial gas velocity on the maximum inlet pollutant concentration, at which the gas deodorization is obtained, is shown together with the pollutant removal rates, calculated at the different superficial gas velocities. It can be observed that the value of the maximum inlet pollutant concentration, at which the deodorization of the gas is ensured, sharply decreases with increasing superficial gas velocity, as a consequence of the decrease of the removal efficiency of the biofilter with decreasing apparent gas residence time. The maximum concentrations at which the outlet pollutant concentration was reduced below the olfactory threshold values (8.8×10^{-3} g m^{-3} for toluene and 0.2×10^{-3} g m^{-3} for styrene) were 1.99 and 0.2 g m^{-3}, and were obtained at a superficial gas velocity of 17.8 m h^{-1} for toluene and 122.0 m h^{-1} for styrene, respectively. These seem to be interesting results if one consider that biofiltration is usually considered a particularly effective technique for treating gaseous emissions containing contaminants only in relatively low concentrations (< 1.0 g m^{-3}).

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