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Treatment of benzene-contaminated airstreams in laboratory-scale biofilters packed with raw and sieved sugarcane bagasse and with peat

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Abstract

Three identical upflow laboratory-scale biofilters, inoculated with the benzene-degrading strain *Pseudomonas* sp. NCIMB 9688 but filled up with different packing media (PM), specifically raw sugarcane bagasse, sieved sugarcane bagasse and peat, were employed to eliminate benzene from waste air. Biofilters performances were evaluated by continuous runs in parallel at different influent benzene concentrations, sequentially stepped up through three different superficial gas velocities (31, 61, and 122 m h^{-1}). The peat-packed biofilter exhibited the best performances over the whole experimentation, ensuring removal efficiency of 100% for influent benzene concentrations $\leq$0.05 g m^{-3}, regardless of the superficial gas velocity, and up to 0.4 g m^{-3} at 31 m h^{-1}. Maximum elimination capacities of biofilters packed with raw and sieved sugarcane bagasse and with peat were 3.2, 6.4 and 26 g $m_{PM}{}^{-3}$ h^{-1} at 6.1, 12 and 31 g $m_{PM}{}^{-3}$ h^{-1} loading rates, resulting in 52, 53 and 84% removals, respectively. The bacterial concentration distribution along the medium was shown to depend on the benzene loading rate and a correlation between specific benzene elimination rate and biomass concentration was established for biofilters packed with sieved sugarcane bagasse and peat. The macrokinetics of the process were also studied using the profiles of benzene and biomass concentrations, collected under different conditions over the height of both biofilters, and a zeroth-order kinetic model was shown to describe successfully the degradation process.

Abbreviations: Biofilter A – biofilter packed with raw sugarcane bagasse; Biofilter B – biofilter packed with sieved sugarcane bagasse; Biofilter C – biofilter packed with peat; BLR – benzene loading rate, g $m_{PM}{}^{-3}$ h^{-1}; CFU – colony-forming-units; C_g, C_{ge}, C_{go} – benzene concentrations in the gaseous phase along the packing medium, in the outlet gas and in the inlet gas, g m^{-3}; η – removal efficiency (%); EC – elimination capacity, g $m_{PM}{}^{-3}$ h^{-1}; h – height of a bed section, m; H – total packing medium height, m; k_o – volumetric benzene degradation rate, g $m_{biofilm}{}^{-3}$ h^{-1}; PM – packing medium; U_g – superficial gas velocity, m h^{-1}.

Introduction

Microorganisms are the workhorses in biofiltration systems; therefore, maintenance of suited conditions within the package is essential for long-term biofilter operation. Properly controlled biofilters proved to be effective in the removal of a broad range of gaseous contaminants, among which volatile aromatic compounds. Their efficiency can be affected significantly by various factors including moisture content, pH, temperature, microflora, nutrient availability, accessibility to the target contaminants, pressure drop, gas residence time, and packing medium (Zilli & Converti 1999; Auria et al. 2000; Veiga & Kennes 2001).

The packing medium (PM) plays an important role on the biofilters performance in that it must: (a) guarantee living conditions for the microflora; (b) immobilize the cells to prevent washout; (c) behave as

nutrients and humidity reserve as well as mechanical support; (d) ensure bed stability; (e) minimize reactor volume, energy consumption and maintenance, and (f) allow for satisfactory removal efficiency. Special care should be taken in filling up the biofilter to prevent excess pressure drop and flow channeling (Abumaizar et al. 1998).

The most common packing media are natural organic materials of vegetable origin such as peat, compost, soil, or mixtures of these with bark, leaves, wood chips, etc., which provide high specific surface area, high retention capacities of water and mineral nutrients, and effective biomass immobilization (Zilli & Converti 1999). Sugarcane bagasse, an agricultural residue from industrial sugar extraction, was used in a preliminary study to treat a benzene-polluted air stream (Sene et al. 2002). Although used in sugar factories as fuel for boilers, large quantities of this material are accumulated in the mills, bringing forth environmental problems. Being an inexpensive raw material, it can also be used as a solid support in several bioprocesses (Pandey et al. 2000). In addition, the possibility of using a waste as packing material in biofilters is particularly attractive from the environmental point of view.

Benzene is classified as hazardous substance on the EPA list of priority pollutants (EPA 1996) because of its confirmed carcinogenic properties (Zhu et al. 1998; Yeom & Daugulis 2001). Owing to its high volatility (distribution coefficient of 0.229 at 25 °C), higher water solubility with respect to other aromatics (0.174–0.187%), and high mobility, benzene is a widespread environmental contaminant, commonly found in soils, aquifers, and in the atmosphere (Mackay & Shiu 1981; Zhou et al. 1998; Yeom & Daugulis 2001). For these reasons, strict regulations and air quality standards came into force to drive us to reduce its emissions. The development of effective biofilters could contribute significantly to the elimination of this pollutant, large amounts of which are discharged into the atmosphere.

The objectives of this experimental study were to: (a) evaluate the effects of the packing medium on the removal of benzene vapors; (b) investigate the influence of benzene loading on total bacterial concentration distribution along the filter bed; (c) find a correlation between bacterial concentration and specific benzene elimination rate; and (d) describe the macrokinetics of the process with a model based on zeroth-order kinetics.

Materials and methods

Inoculum preparation

Cells of *Pseudomonas* sp. NCIMB 9688 were grown at 25 °C and 150 rpm in 250-ml Erlenmeyer flasks containing 100 ml of sterilized medium (1.0 g l^{-1} Lab-Lemco beef extract; 2.0 g l^{-1} yeast extract; 5.0 g l^{-1} peptone, and 5.0 g l^{-1} NaCl) at pH 6.8 $\pm$ 0.2. After 24 to 48 h, cells were centrifuged and resuspended in fresh medium to be used for the inoculum.

Packing media

Raw and sieved sugarcane bagasse as well as peat were mixed with glass beads (5-mm diameter) in 4:1 volume proportion. Sieved sugarcane bagasse was the intermediate size fraction obtained by dry sieving the raw material through sieves of 2.38 and 4.76 mm. Peat, having initial pH 4, contained 90% of organic substance (dry weight), of which 52% and 1.0% were organic carbon and nitrogen. Total porosities of raw and sieved bagasse and peat were 83, 98 and 59%, and their relative densities 40.8, 48.0 and 320 kg m^{-3}, respectively.

Biofilters design

Continuous runs were carried out in parallel at 20–22 °C using three identical laboratory-scale biofilters with 0.05 m internal diameter, 0.65 m total height and 0.50 m packed bed height (Zilli et al. 2001). Columns were provided with four sampling ports placed, along both sides, at 0.125, 0.250, 0.375, and 0.510 m from the bottom, for gas and packing medium sampling.

The three biofilters, identified as A (raw sugarcane bagasse), B (sieved sugarcane bagasse), and C (peat), were fed under non-sterile conditions by upflowing benzene-containing air (Sene et al. 2002). Beds were supported at the bottom by punched ceramic sieve plates covered by gravel. Moisture content was kept at 60–70% for raw bagasse and 50–60% for sieved bagasse and peat (Sene et al. 2002). Inlet gas relative humidity was >95%.

Biofilters start-up and operation

The selected amounts of packing media (40.8, 48.0 and 320 g for biofilters A, B and C, respectively) were mixed with 200 ml of a thick cell suspension (about 6 g dry weight l^{-1}) and charged into the biofilters.

The settled cells were recovered three times and recirculated at the top to improve immobilization. The biofilters were started up at the lowest inlet benzene concentration ($C_{go} = 0.010$ g m^{-3}) and superficial gas velocity ($U_g = 31$ m h^{-1}) to prevent shock and acclimatize the microflora. After about 20 days, U_g was progressively increased up to 122 m h^{-1}. Once completed the first cycle, the same schedule was repeated at increasing C_{go} values. Each test under given operating conditions lasted 12 to 15 days, during which pseudo-steady-state conditions were normally achieved within 3 days.

Analytical procedures

Benzene gas-phase concentration was determined by a Carlo Erba gas chromatograph (Electrometer, Model 200, Milan, Italy) equipped with capillary column, flame ionization detector (FID) and computing integrator. Gas-phase samples (0.5 ml) taken from the biofilter ports were injected immediately to the GC/FID unit operated at 160 °C using nitrogen as a carrier gas. Benzene concentration was determined in four replicates using a calibration curve (Lodge 1989). The standard deviation varied in the range 2.1–7.9%.

Moisture content was determined by dry weight (APHA 1995) on wet medium samples (0.50 g) taken from each port and mixed with demineralized water. Total porosity was measured (Converti et al. 1997) by a Carlo Erba mercury porosimeter (Model Unit 120, Milan, Italy), while the mean particle diameter (d_P) was determined by standard sieves. The interfacial area per unit volume (a) was estimated from d_P assuming cylindrical pore geometry and an external void fraction (ϵ) of 0.5 (Ottengraf 1986).

Quantitative determination of bacterial distribution

Moist peat and sieved sugarcane bagasse samples (0.50 g), withdrawn under pseudo-steady state and uniform humidity conditions, were diluted 1:10, mixed for 3 min in 4.5 ml of physiological salt solution (NaCl 0.9%), and then subjected to serial decimal dilutions in 9.0 ml of the same solution. Aliquots of these (100 μl) were spread onto the surface of Petri plates up to complete absorption of the liquid phase. Plates were prepared using a sterilized Plate Count Agar medium (Merck, Cat. 1.05463, Milan, Italy) containing: 5.0 g l^{-1} peptone from casein, 2.5 g l^{-1} yeast extract, 1.0 g l^{-1} D (+) glucose and 14 g l^{-1} agar-agar. After inoculation, the plates were incubated at 30 °C for 36 to 48 h and the number of colonies was counted. The benzene-degrading bacteria concentration was reported as the mean of four determinations of the number of colony-forming-units per gram of moist packing medium (CFU $g_{PM}{}^{-1}$). Standard deviations from average values ranged from 4.5 to 28% (mean value 13%) for peat and from 3.5% to 22 (mean value 13%) for sieved sugarcane bagasse.

Results and discussion

Preliminary tests and start-up

A preliminary experiment was carried out to evaluate the abiotic removal time due to physical adsorption or absorption by the packing media in the absence of any inoculum. Benzene breakthrough occurred after 1.0 and 2.5 h with biofilters A and B, containing raw and sieved sugarcane bagasse, respectively, both working at 50% moisture content, demonstrating the lower water retention capacity of raw bagasse. When the raw sugarcane bagasse water content was increased up to 70%, benzene breakthrough lasted 2.0 h; therefore this condition was selected for continuous tests to carry out with this material. Consistently with the high water retention capacity of peat, peat-packed biofilter C showed a benzene breakthrough after 3.5 h.

After benzene abiotic removal experiments, the biofilters were started-up. During this time period microbial population progressively adapted to the specific environment and biodegradation started after about 7 to 8 h. Complete removal of the pollutant was reached after about 2 days with biofilter C and 3 days with biofilter B. In biofilter A, it started more slowly and was only partial, reaching a maximum value of 97% on the 5th day of operation.

Benzene removal efficiency

The experimental data of the removal efficiency (η) obtained with all three biofilters are reported in Figure 1, each value corresponding to the average of steady-state data collected for each condition tested. Since the biofilters were run under identical conditions, the different performances can reasonably be ascribed to the different packing media.

A gradual decrease in the removal efficiency with increasing either the inlet benzene concentration (C_{go}) or the specific gas velocity (U_g) can be observed for all three biofilters, as a consequence of an increased benzene loading rate (BLR). In particular, it can be observed that 100% removal was never achieved with

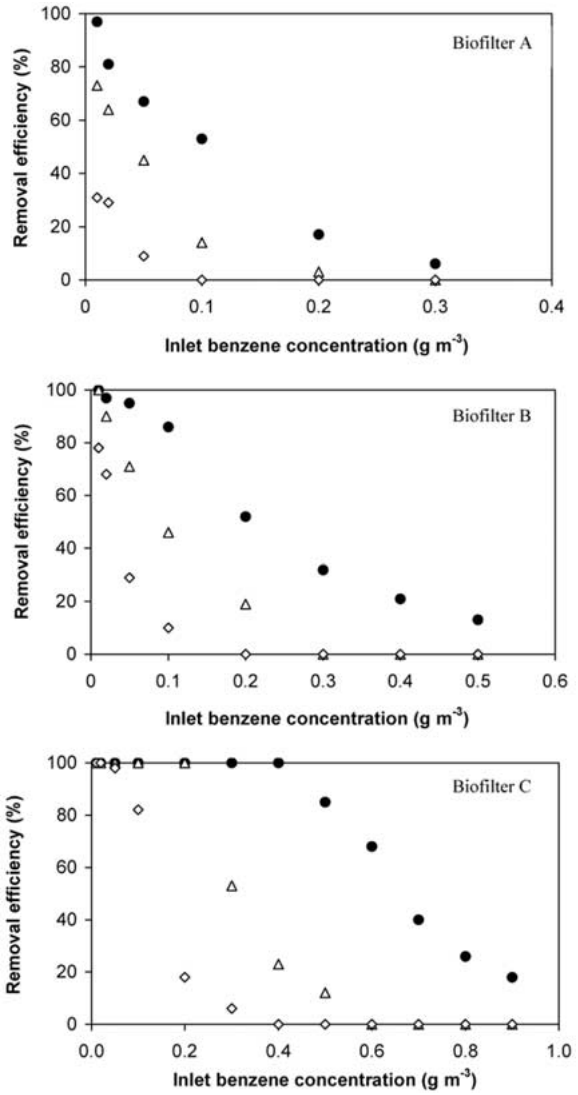

Figure 1. Relationship between removal efficiency and inlet benzene concentration, at different superficial gas velocities (m h^{-1}): (●) 31; (△) 61; (◇) 122.

biofilter A under any operating condition tested, likely due to the fibrous structure of the raw bagasse and consequent low moisture retention capacity. This forced us to operate at higher moisture content (70%).

The higher removal efficiencies provided by biofilter B with respect to biofilter A suggest that dry sieving, besides increasing bagasse density, homogeneity and specific surface area, could have improved the medium structure, enhancing the biofilter performance. The high efficiency of biofilter C provided evidence that peat was the most suitable medium. Removal yields close to 100% were achieved at C_{go} up to 0.050 g m^{-3}, regardless of the superficial gas velocity, and up to 0.40 g m^{-3} operating at $U_g = 31$ m h^{-1}. In comparison with sieved bagasse, peat allowed running at $C_{go} > 0.50$ g m^{-3} at Ug = 31 m h^{-1}. As the biofilters only differed from one another in packing medium, such a performance with peat can reasonably be ascribed to its high moisture retention capacity, specific surface area, microbial immobilizing capacity, and density, which came out to be about 7-fold that of sieved bagasse.

Elimination capacity of biofilters

Figure 2 shows the behavior of benzene elimination capacity (EC) obtained with all three biofilters versus BLR, which was changed alternately varying U_g and C_{go}. This parameter increased regularly with BLR up to maximum thresholds beyond which it decreased, likely due to some inhibition exerted by excess benzene on the microbial activity (Ottengraf 1986; Sene et al. 2002). EC achieved maximum values of 3.2 g $m_{PM}{}^{-3}$ h^{-1} at $C_{go} = 0.10$ g m^{-3} with biofilter A, 6.4 g $m_{PM}{}^{-3}$ h^{-1} at $C_{go} = 0.20$ g m^{-3} with biofilter B, and 26 g $m_{PM}{}^{-3}$ h^{-1} at $C_{go} = 0.50$ g m^{-3} with biofilter C, operating at the same superficial gas velocity ($U_g = 31$ m h^{-1}).

It is noteworthy that there was scarce relevance whether the EC variations observed with biofilter C were due to an increase in C_{go} or a decrease in τ. In contrast, a certain worsening of performances was evident with biofilters A and B when progressively decreasing C_{go} at a given BRL value. That was likely due to a decrease in both the driving force for diffusion into the biofilm and biodegradation kinetics as well as to an U_g increase, which caused lower time for diffusion to occur. These phenomena as well could have contributed to the different BRL thresholds at which maximum ECs were obtained with the different packing media.

Finally, the higher maximum EC obtained with biofilter B with respect to biofilter A is consistent with the earlier-mentioned positive effects of sieving on sugarcane bagasse immobilization capacity and suggests that the good performance of the peat-packed biofilter could be ascribed to the same reason as well as to a much greater medium density.

The maximum EC achieved with peat was found to be higher than that obtained by other authors. Zhu et al. (1998) reported on the biofiltration of benzene contaminated air streams using three biofilter columns packed with a compost-granular activated carbon

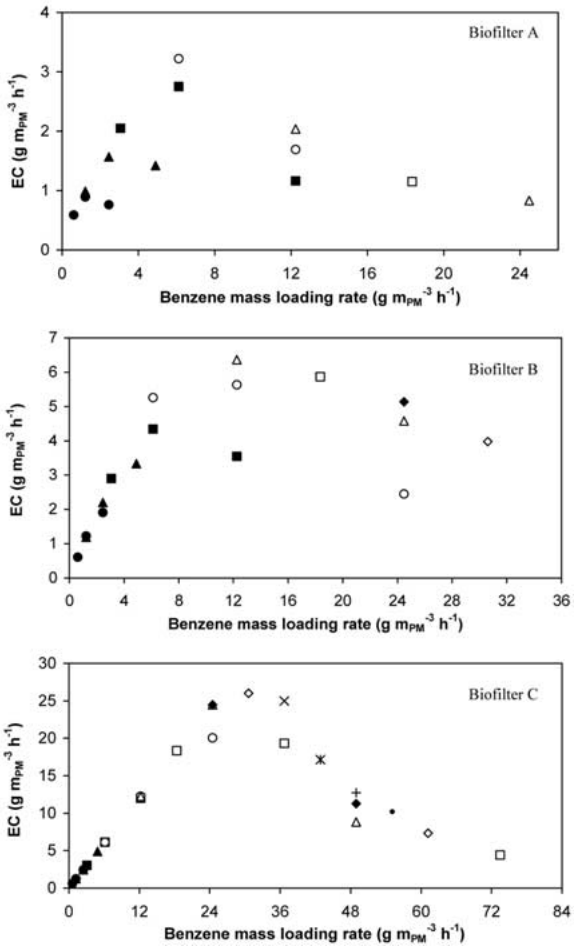

Figure 2. Elimination capacity as a function of the benzene mass loading rate, at different inlet benzene concentrations (g m^{-3}): (●) 0.010; (▲) 0.020; (■) 0.050; (○) 0.10; (△) 0.20; (□) 0.30; (⧫) 0.40; (◇) 0.50; (×) 0.60; (∗) 0.70; (+) 0.80; (•) 0.90. Data were collected at different U_g values with all the three biofilters.

mixture. More than 90% removal efficiency and a maximum EC close to 9.0 g m_{PM}^{-3} h^{-1} were observed for C_{go} = 0.26 g m^{-3} and U_g = 9.0 m h^{-1}, corresponding to τ = 5 min. A similar study described the performance of a trickling fibrous-bed bioreactor inoculated with a coculture of *Pseudomonas putida* and *Pseudomonas fluorescens* (Zhou et al. 1998). When C_{go} was 0.37 g m^{-3}, η and maximum EC were > 90% and 11.5 g m_{PM}^{-3} h^{-1}, respectively, at an empty-bed residence time of 8 min. Better results (EC = 196 g m_{PM}^{-3} h^{-1} at τ = 0.76 min) were obtained using a hybrid bioreactor (Yeom & Yoo 1999) or a continuous system combining absorption and degradation sections (Yeom & Daugulis 2001), both inoculated with Alcaligenes xylosoxidans Y234.

Influence of BLR on biomass distribution along the biofilters

One of the objectives of this research was to investigate the effect of BLR on the distribution of bacterial concentration (expressed as CFU g_{PM}^{-1}) along the best performing biofilters (B and C) and to correlate the specific benzene elimination rate, normalized with respect to the column section area (g m^{-2} h^{-1}) as is usual in biofiltration, with the biomass concentration determined over the height of the columns.

The data of bacterial concentration and specific benzene elimination rate, listed in Tables 1 and 2 for biofilter B and in Tables 3 and 4 for biofilter C, evidenced that these parameters depended directly upon U_g and C_{go}, i.e. upon BLR. In general, operating at low inlet benzene concentrations, one can observe, regardless of the superficial gas velocity adopted, a non-homogeneous distribution of the bacterial concentration that decreased from the bottom to the top of the columns. This trend occurred with biofilter B at C_{go} up to 0.10, 0.050 and 0.020 g m^{-3} and at U_g of 31, 61, and 122 m h^{-1}, respectively, and with biofilter C under harder conditions (C_{go} up to 0.40, 0.10 and 0.050 g m^{-3}, at the same U_g values). This progressive decrease in biomass concentration over the column height was due to the higher BLR in the inlet zone that intensified the biological oxidation and, consequently, the bacterial growth.

Increasing C_{go} and regardless of U_g, a change in biomass distribution took place, which became relatively uniform along the beds, due to the progressive involvement of biomass of the upper column sections in benzene degradation. This situation, which occurred with biofilter B at C_{go} = 0.20, 0.10 and 0.050 g m^{-3} and at U_g = 31, 61 and 122 m h^{-1}, respectively (corresponding in all cases to BLR = 6.1 g m_{PM}^{-3} h^{-1}), and with biofilter C at C_{go} = 0.50, 0.20 and 0.10 g m^{-3} and at U_g = 31, 61 and 122 m h^{-1} (BLR = 31, 24, and 24 g m_{PM}^{-3} h^{-1}), indicated these conditions as the best ones and that the biofilters worked uniformly and were adequately designed. The data of specific benzene elimination rate, measured with biofilters B and C at different heights (Tables 2 and 4), showed a behavior similar to that of biomass (Tables 1 and 3), suggesting the existence of a close relationship between these parameters; for this reason, maximum ECs were achieved just under these optimum uniformity conditions.

Increasing further on C_{go}, the opposite trend was observed for both bacterial concentration and specific

Table 1. Distribution of the bacterial concentration (CFU $\times$ 10^9 g^{-1} of moist sieved bagasse) along Biofilter B at different superficial gas velocities, U_g, and inlet benzene concentrations, C_{go}

C_{go} (g m^{-3})	0.010	0.020	0.050	0.10	0.20	0.30	0.40	0.50
$U_g = 31$ m h^{-1}								
h/H								
0.25	0.928	1.69	3.06	3.82	3.60	3.11	2.76	1.95
0.50	0.334	0.590	1.76	3.15	3.65	3.12	2.81	1.96
0.75	0.287	0.335	0.990	3.11	3.93	3.13	2.83	1.99
1.00	0.117	0.126	0.460	1.75	3.90	3.16	2.88	2.06
$U_g = 61$ m h^{-1}								
h/H								
0.25	1.07	1.80	3.12	3.02	2.62			
0.50	0.932	1.59	2.92	3.06	3.61			
0.75	0.290	0.936	1.83	3.09	2.63			
1.00	0.170	0.410	1.78	3.13	2.65			
$U_g = 122$ m h^{-1}								
h/H								
0.25	1.15	2.09	1.85	1.32				
0.50	0.950	1.88	1.82	1.35				
0.75	0.921	1.64	1.90	1.42				
1.00	0.859	1.56	1.99	1.48				

Table 2. Behavior of the specific benzene elimination rate (g m^{-2} h^{-1}) along Biofilter B at different superficial gas velocities, U_g, and inlet benzene concentrations, C_{go}

C_{go} (g m^{-3})	0.010	0.020	0.050	0.10	0.20	0.30	0.40	0.50
$U_g = 31$ m h^{-1}								
h/H								
0.25	0.230	0.378	0.702	0.810	0.781	0.712	0.630	0.504
0.50	0.0501	0.143	0.386	0.751	0.785	0.723	0.641	0.506
0.75	0.0262	0.0519	0.245	0.710	0.825	0.740	0.647	0.513
1.00	nd[a]	0.0210	0.118	0.379	0.820	0.754	0.656	0.517
$U_g = 61$ m h^{-1}								
h/H								
0.25	0.265	0.397	0.730	0.691	0.595			
0.50	0.232	0.352	0.670	0.700	0.595			
0.75	0.0718	0.238	0.402	0.708	0.599			
1.00	0.0429	0.115	0.387	0.719	0.603			
$U_g = 122$ m h^{-1}								
h/H								
0.25	0.282	0.525	0.419	0.298				
0.50	0.240	0.450	0.435	0.305				
0.75	0.223	0.356	0.448	0.311				
1.0	0.210	0.337	0.477	0.315				

[a]Value below the detection limit of the instrumentation.

Table 3. Distribution of the bacterial concentration (CFU $\times 10^9$ g^{-1} of moist peat) along Biofilter C at different superficial gas velocities, U_g, and inlet benzene concentrations, C_{go}

C_{go} (g m^{-3})	0.010	0.020	0.050	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
$U_g = 31$ m h^{-1}												
h/H												
0.25	0.185	0.329	1.05	2.12	2.29	2.56	2.69	2.41	1.74	1.20	1.03	0.834
0.50	0.0760	0.0761	0.0762	0.0820	1.97	2.03	2.43	2.56	2.02	1.36	1.03	0.858
0.75	0.0758	0.0760	0.0762	0.0763	0.0785	1.89	1.92	2.17	2.56	1.58	1.17	0.892
1.00	0.0761	0.0760	0.0761	0.0762	0.0763	0.0764	1.69	1.91	2.54	2.04	1.31	0.957
$U_g = 61$ m h^{-1}												
h/H												
0.25	0.331	0.845	1.98	2.16	2.39	1.27	0.859	0.477				
0.50	0.0759	0.0762	0.128	1.92	2.16	1.43	0.982	0.478				
0.75	0.0760	0.0762	0.0763	0.152	2.02	1.84	1.02	0.499				
1.00	0.0761	0.0763	0.0762	0.0765	1.97	2.30	1.05	0.535				
$U_g = 122$ m h^{-1}												
h/H												
0.25	0.449	1.18	1.92	1.73	0.551	0.245						
0.50	0.155	0.298	1.69	1.88	0.709	0.253						
0.75	0.110	0.104	0.456	1.97	0.778	0.270						
1.0	0.0762	0.0764	0.153	1.74	0.835	0.315						

Table 4. Behavior of the specific benzene elimination rate (g m^{-2} h^{-1}) along Biofilter C at different superficial gas velocities, U_g, and inlet benzene concentrations, C_{go}

C_{go} (g m^{-3})	0.010	0.020	0.050	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
$U_g = 31$ m h^{-1}												
h/H												
0.25	0.306	0.612	1.53	3.01	3.30	3.58	3.71	3.45	2.47	1.70	1.46	1.22
0.50	nd[a]	nd	nd	0.060	2.80	2.91	3.46	3.69	2.88	1.93	1.50	1.25
0.75	nd	nd	nd	nd	0.020	2.69	2.75	3.18	3.58	2.05	1.67	1.30
1.00	nd	nd	nd	nd	nd	nd	2.32	2.70	3.57	2.90	1.88	1.35
$U_g = 61$ m h^{-1}												
h/H												
0.25	0.612	1.22	2.82	3.11	3.39	1.80	1.25	0.891				
0.50	nd	nd	0.239	2.74	3.17	1.96	1.38	0.888				
0.75	nd	nd	nd	0.272	2.88	2.58	1.49	0.912				
1.00	nd	nd	nd	nd	2.80	3.31	1.53	0.919				
$U_g = 122$ m h^{-1}												
h/H												
0.25	0.843	1.67	2.73	2.20	0.970	0.522						
0.50	0.278	0.588	2.17	2.68	1.03	0.528						
0.75	0.104	0.190	0.854	2.80	1.14	0.536						
1.00	nd	nd	0.268	2.39	1.22	0.552						

[a]Value below the detection limit of the instrumentation.

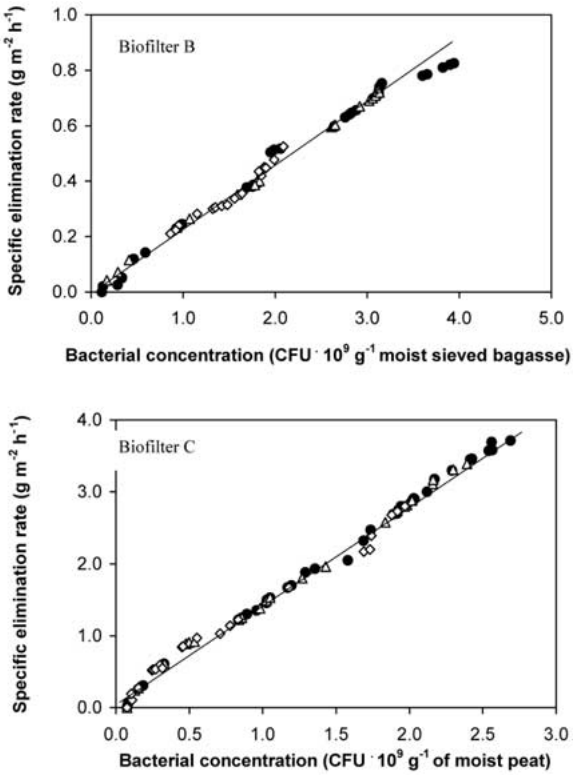

Figure 3. Correlation between the specific benzene elimination rate and the bacterial concentration in biofilters B and C, at different superficial gas velocities (m h^{-1}): (●) 31; (△) 61; (◇) 122.

benzene elimination rate that progressively increased along the biofilters, likely due to excess benzene inhibition. This phenomenon was evident with biofilter B at $C_{go} \geq 0.30$ and 0.10 g m^{-3} and at $U_g \geq 31$ and 122 m h^{-1}, respectively, and with biofilter C at $C_{go} \geq 0.60$, 0.30 and 0.20 g m^{-3} and at $U_g \geq 31$, 61 and 122 m h^{-1}, respectively.

Figure 3 shows the existence for biofilters B and C of a linear relationship between bacterial concentration and specific benzene elimination rate, on which the following macrokinetic modeling is based.

Finally, it is noteworthy that the use of a starting pure culture in this work was not suggested by any claim to maintain sterility inside the biofilter, but only to accelerate acclimation, as suggested by Swanson & Loehr (1997). Other bacteria, either present in the original media or not, mainly actinomycetes, sporeformers, proteobacteria and high G +C Gram positives, appeared throughout the experimentation, most of them entering the biofilters through the non-sterile influent air streams. Species diversity of benzene-degrading strains contained in the biofilters will be investigated in future work by the Ribosomal Intergenic Spacer Analysis and the presence in their genome of specific genes for benzene degradation checked by PCR and Southern hybridization.

Macrokinetics of the process

The experimental data of benzene removal under variable operating conditions, collected using the most effective two media (sieved sugarcane bagasse and peat), were then utilized to check a model already presented by Ottengraf (1986) to describe the macrokinetics of organic pollutant degradation in biofilters and to estimate the kinetic parameters of the model.

Two different situations may occur when the biofilter exhibits zeroth-order macrokinetics, as in the present study. If the reaction is the limiting step of the process, the ratio of the outlet to inlet pollutant concentration (C_g/C_{go}) is described by the equation:

$$\frac{C_g}{C_{go}} = 1 - \frac{K_o H}{U_g C_{go}}, \tag{1}$$

where K_o is the apparent zeroth-order kinetic parameter, H is the total height of the packing material and U_g the superficial gas velocity.

In contrast, when diffusion is the limiting step:

$$\frac{C_g}{C_{go}} = \left(1 - \frac{H}{U_g}\sqrt{\frac{K_o D_e a}{2 m_i C_{go} \delta}}\right)^2, \tag{2}$$

where D_e is the effective benzene diffusivity in the biofilm, m_i the distribution coefficient of benzene, a the interfacial area per unit volume, and δ the biolayer thickness, respectively.

The apparent zeroth-order kinetic parameter is linked to the volumetric rate of benzene degradation, k_o, by the relationship:

$$K_o = k_o a \delta. \tag{3}$$

While the parameter a can be experimentally determined, as described in the Materials and Methods section from the mean particle diameter of the medium, the biolayer thickness can be estimated, under conditions of transition from one regime to the other, by the relationship:

$$\delta = \frac{2a D_e C_{go}}{K_o m_i}. \tag{4}$$

Ottengraf (1986) proposed that k_o is a simple linear function of biomass concentration, X. However, two

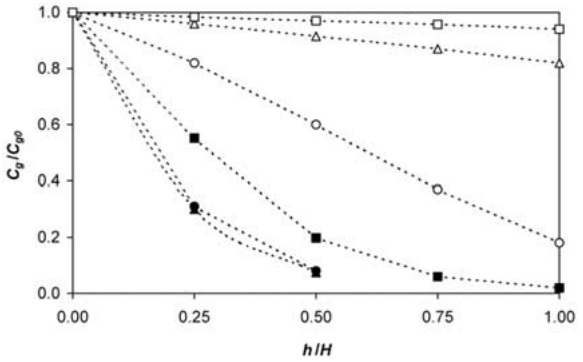

Figure 4. Dependence of the ratio of outlet to inlet benzene concentrations, C_g/C_{go},on the dimensionless height, h/H, of the peat-packed biofilter, at $U_g = 122$ m h^{-1} and different C_{go} values. C_{go} (g m^{-3}): (●) 0.010, (▲) 0.020, (■) 0.050, (○) 0.10, (△) 0.20, (□) 0.30.

contributions can be distinguished in this parameter, the one associated to the growth ($\mu X/Y_{X/S}$) and the other to the consumption of substrate needed to sustain maintenance processes ($m_s X$) (Roels 1983):

$$k_o = \frac{\mu}{Y_{X/S}} X + m_s X. \qquad (5)$$

Analysis of the experimental data of removal efficiency (Figure 1) evidenced that C_g/C_{go} could be described either by Equation (1) or by Equation (2), depending on the working conditions. It is evident from Figure 4, which shows such a typical behavior for $U_g = 122$ m h^{-1} with the peat-packed biofilter as an example, that decreasing the inlet benzene concentration the system shifted from a condition of reaction limitation to that of diffusion limitation. Analogous trends for all tested U_g and C_{go} values were observed (results not shown).

The data collected under reaction limitation conditions, exhibiting nearly constant X values along the columns (Tables 1 and 3), were then used in Equation (1) to calculate, case by case, first K_o and then, by Equation (3), k_o. To this purpose, the constants a and δ appearing in Equation (3) had to be preliminarily estimated for each material. The values of these parameters as well as those of properties of benzene and each support utilized for their calculation are listed in Table 5.

Figure 5 shows that k_o increased linearly with biomass concentration regardless of the packing medium used. From these data it was also possible, by Equation (5), to estimate with excellent correlation ($r^2 = 0.994$) the overall rate of benzene consumption for both maintenance and growth per CFU ($m_s + \mu/Y_{X/S} = 30.1 \times$

Table 5. Parameters used in the model describing benzene degradation in biofilters packed with peat and sieved sugarcane bagasse. Benzene effective diffusivity (De) = 9.07×10^{-10} m^2 s^{-1}; Benzene distribution coefficient (m_i) = 0.229

Package material	Peat	Sieved sugarcane bagasse
a (m^{-1})[a]	5,000	560
δ (mm)[b]	0.262	0.125
d_P (mm)[c]	0.40	3.57
ϵ[d]	0.5	0.5

[a]Interfacial area per unit volume.
[b]Biolayer thickness including biomass grown within the interstices.
[c]Mean particle diameter.
[d]External void fraction of the package (Ottengraf 1986).

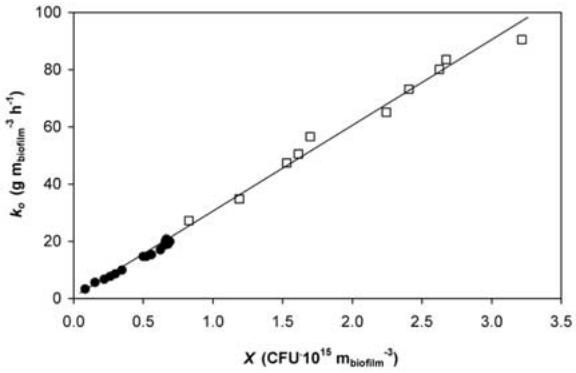

Figure 5. Linear dependence of the volumetric benzene degradation rate, k_o (g $m_{biofilm}^{-3}$ h^{-1}), on biomass concentration, X (CFU $m_{biofilm}^{-3}$), in the biofilters packed with peat (●) and with sieved sugarcane bagasse (□).

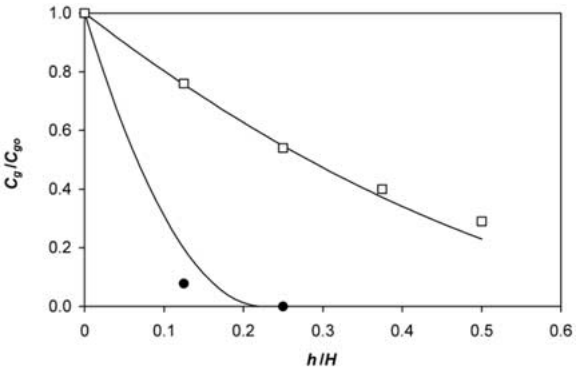

Figure 6. Experimental and theoretical (predicted by Equation (2)) behaviors of the ratio of outlet to inlet benzene concentrations, C_g/C_{go}, versus the dimensionless height, h/H, under conditions of high benzene loads: $U_g = 61$ m h^{-1}; $C_{go} = 0.05$ g m^{-3}. (●) Peat-packed biofilter; (□) Sieved bagasse-packed biofilter.

10^{-15} g CFU^{-1} h^{-1}). Since biomass reaches very high concentrations and grows very slowly in immobilized cell systems under steady-state conditions (Zilli et al. 2003), most of benzene uptake can be ascribed to maintenance rather than to growth; therefore, the term used by Ottengraf (1986) in Equation (5) should include both growth and maintenance, the latter being the most significant in our opinion.

These results suggest that the biofilm grown on sieved sugarcane bagasse could be more effective than that grown on peat, as it allowed for higher biomass concentration. Nevertheless, they must not lead to wrong conclusion, since the performance of peat-packed column was notably higher than that of an equal volume of sieved bagasse (Figure 1). This behavior can be ascribed to the higher density and water retention capacity of peat with respect to bagasse, which allowed for the development of a greater total biofilm amount.

The calculated values of k_o were then used to verify by Equation (2) the macrokinetic behavior of both biofilters under conditions of diffusion limitation. As shown in Figure 6, the predicted curves chosen as examples follow closely the experimental behaviors of both biofilters and similar results were obtained from all experimental data (results not shown). The better performances of peat, obtained under the same conditions as those tested with sieved bagasse, are confirmed in this figure by the lower C_g/C_{go} values at different bed heights.

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