Comparison of organic packing materials for toluene biofiltration

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ABSTRACT. The paper focuses on the operation of a pilot plant with four biofilters operated in parallel for determining the suitability of coconut fiber, peat, compost from the digested sludge of a wastewater treatment plant and pine leaves as packing materials for biofiltration of toluene. Physical characteristics of packing materials such as specific surface area, density, pore size and elemental composition were determined for each packing material. Biological activity and packing capabilities related to toluene removal were determined during the startup and operation of the four biofilters under different conditions of nutrients, watering and inlet air relative humidity supply. Nutrient addition was key in improving removal efficiency (RE) and elimination capacity (EC) of biofilters. Feeding of medium with nutrients increased the RE and the EC by a factor of 2 to 4 than these found when supplying only tap water. Additionally, when extra nitrogen was supplied in the medium, RE and EC increased by a factor of 2. Nutrient addition also lead to a microbial population change from bacterial to fungal biofilters. It was denoted that watering control is necessary to improve fungal biofilters performance in terms of ensuring a proper washout of acidic by-products to avoid fungi inhibition and consequent lowered removal capacities.

1 INTRODUCTION

Biofiltration has been used successfully applied to control odours and both organic and inorganic air pollutants that are toxic to humans, as well as volatile organic compounds (VOC). Nowadays, biofiltration is the most commonly used biological gas treatment technology when high gas flow rates are involved. In this technology, the gas to be treated is forced through a bed packed with material on which microorganisms are attached as a biofilm, where biodegradation of the harmful compounds occurs.

Biofilters efficiency is highly dependant on the nature and characteristics of the packing material. Proper packing material selection is a key factor in the reactor performance since biomass development and activity depends on the presence of a suitable support. Various materials have already been studied: *e.g.* compost, soil, peat wood chips, polystyrene spheres (Kennes and Thalasso, 1998). Even though compost is probably the most widely used material, it can develop compaction problems due to over wetting. This drawback can be reduced by mixing the raw compost with structuring materials.

Main characteristics to consider upon the selection of an appropriate packing material are: specific surface area, density, porosity, pH, water holding capacity, buffering capacity and material composition (Bohn, 1996). Physical and chemical parameters determination of packing materials must be accompanied with testing of operational conditions in lab- and pilot-scale reactors before moving to full-scale systems.
Toluene is one of the main pollutants released by the chemical industries and, thus it has been extensively used as a characteristic VOC in previous biofiltration studies (Barona *et al.,* 2004; Delhomenie *et al.,* 2002, 2003; Rene *et al.,* 2005)
This paper focuses on the startup and operation of a pilot plant consisting of four biofilters operated in parallel for determining the suitability of coconut fiber, peat, compost from digested sludge of a WWTP and pine leaves as packing materials for gaseous toluene treatment. Physical and chemical characteristics of packing materials besides the treatment capacity determination for different operating conditions, including the effect of nutrients addition and moisture content, are the main objectives of this study.

2 MATERIALS AND METHODS

2.1 Biofilters pilot plant construction and operation

Experiments were carried out using a lab-scale plant consisting of four PVC columns (8.8 cm ID). Reactors were packed with the four different media (compost, peat, coconut fiber and pine leaves) to a height of 50 cm, that is, giving a total bed volume of 2.9 L each. The top of each biofilter was fitted up with a port and a sprinkler for extra watering of the bioreactors. Each reactor has two sampling ports (see Figure 1) used for toluene concentration measurements. Additionally, two media sampling ports were fitted. An aqueous solution was automatically sprinkled daily over the biofilter beds. The excess of solution (leachate) was manually collected at the bottom section. Pressure drop along the bed in each reactor was also measured by a glass U-tube manometer.
Each biofilter was fed by a measured primary airflow. This stream was previously passed through a water column to increase the inlet air relative humidity. The flow rate of humid air was metered by calibrated rotameters. In addition, another air stream was pumped by a peristaltic pump into a glass bubbler unit containing pure liquid toluene. Both gaseous flowrates are mixed and the resulting gas mixture is fed from the base of the reactor. Throughout this study, the gaseous stream was supplied in up-flow mode. It is noteworthy to point out that the polluted stream was in contact only with polyamide and PVC tubing in order to minimize the sorption of toluene onto pipes and reaction walls. The reactors were inoculated with sewage sludge provided by a WWTP.
A structured control system with a PLC (Siemens, S7-314C-2DP) and a commercial SCADA software (Siemens, WinCC v.5.2) have had been used to automate the pilot-plant (water addition and temperature and inlet gas moisture measurements).

2.1 Analytical Methods

Gas samples were collected from sampling ports using Tedlar® bags. Toluene concentration was measured by using a gas chromatograph (GC) (series 6890N GC, Agilent Technologies) equipped with a capillary column (HP-5, Agilent technologies) and a flame ionization detector (FID).

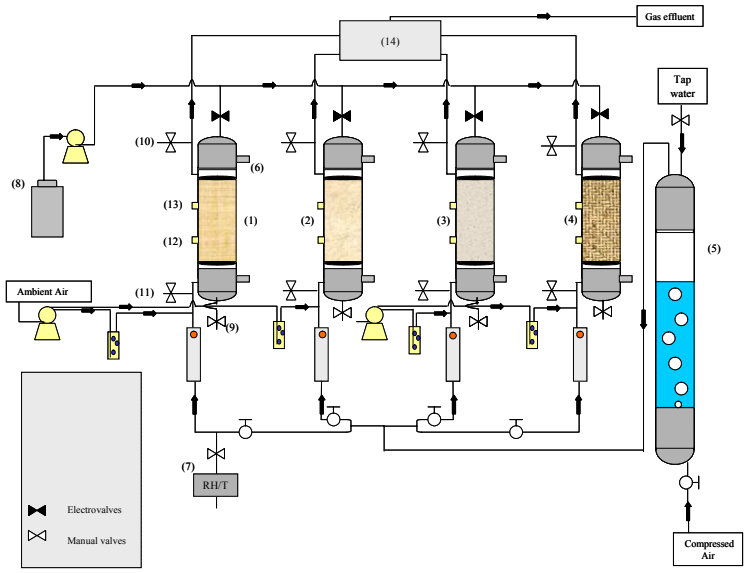

Figure 1. Experimental setup of the lab-scale biofiltration system. 1-R1 Coconut fiber reactor, 2- R2 Compost reactor, 3- R3 Peat reactor, 4- R4 Pine leaves reactor, 5-Humidification column, 6-U-manometer connector, 7-Relative Humidity and temperature sensor, 8-Nutrient reservoir, 9-Leachate collection port, 10-Outlet gas sampling port, 11-Inlet gas sampling port, 12-Low media sampling port, 13-High media sampling port, 14-Granulated active carbon reservoir.

Leachate samples were periodically collected from the bottom of the reactors. From these samples, conductivity and pH were measured with lab probes (Crison, microCM 2100 and MicropH 2001) prior to filtering. Nitrite, nitrate and phosphate were determined by capillary electrophoresis in a Quanta 4000E unit (Waters). Ammonia was measured in a continuous flow analyzer (Baeza *et al.*, 1999).

Packing materials porosity and specific surface area were determined in an external laboratory (Serveis Científico-tècnics, UB) by BET absorption isotherms in a Micromeritics ASAP 2000 porosimeter. Materials density was measured in a helium picnometer (Serveis Científico-tècnics, UB). Elementary analysis for C, N, H, P and S content of the packing material were performed in an external laboratory (Servei Anàlisi, UAB). Periodically, media samples were collected in order to measure water and organic matter content and pH of the biofilter media. pH was measured by stirring the sample in water during 1h in a 1:25 dilution ratio.

3 RESULTS AND DISCUSSION

3.1 Packing materials and biofilters characterization

A complete characterization of the packing materials used in the present study was performed prior to setting up the four biofilters. In addition, the four biofilters were characterized for typical parameters such as bed porosity or water content right before inoculation. Table 1 shows the results obtained.

It must be stressed that some of the parameters determined are inherent to the material such us pore size, specific surface area, material density, CHNSP content and thus

comparable to other materials characterized in the literature (Bohn, 1996). In particular, a high specific surface area of compost was found compared with other materials. In any case, low pore size of the material may lead to biomass growth over the surface of the packing material, thus reducing the specific surface area available for pollutant degradation. Also, highly mineralized materials such as compost and peat showed low organic matter content compared with other packing materials, which may lead to a more resistant material to long-term deterioration.

Table 1. Initial characteristics of biofilters and organic packing materials used in this study. Deviations are reported as the standard deviation of a set of three replicates per sample.

Parameter	Coconut fiber	Compost	Peat	Pine leaves
Water content (%)	78 ± 2	46 ± 0	73 ± 1	68 ± 3
Organic matter (% dry weight)	81 ± 2	38 ± 5	59 ± 5	87 ± 1
Wet bed density (g L^{-1})	720	750	660	310
Bed porosity (--)	0,55	0,43	0,51	0,71
C (% dry weight)	47,32 ± 0,12	28,65 ± 1,51	31,62 ± 5,62	46,42 ± 0,62
H (% dry weight)	5,69 ± 0,12	3,29 ± 0,21	3,38 ± 0,59	5,32 ± 0,05
N (% dry weight)	0,52 ± 0,01	2,87 ± 0,33	1,17 ± 0,13	0,57 ± 0,01
S (% dry weight)	Not detected	0,52 ± 0,01	0,10 ± 0,01	0,11 ± 0,01
P (% dry weight)	0,23	Not analyzed	0,05	0,02
Material pore size (Å)	109 ± 1	213 ± 1	175 ± 1	205 ± 2
Specific surface area ($m^2.g^{-1}$)	0,75 ± 0,10	5,12 ± 0,10	1,21 ± 0,02	0,23 ± 0,01
Material density (g m^{-3})	2,02 ± 0,01	1,79 ± 0,01	1,46 ± 0,01	1,28 ± 0,01

Other parameters shown in Table 1 depend on the operating conditions and on the way the reactor is packed. Pine leaves biofilter was packed with a much lower amount of material than other biofilters, leading to a higher bed porosity and a notably lower wet bed density which implies a lower pressure drop across the bed during normal operation and a better water trickling across the bed during watering periods. The later was especially problematic with the compost, peat and coconut fiber biofilters, which accumulated too much water that lead to compost deterioration and to biofilters overpressure. Thus, coconut fiber was withdrawn from this reactor after the startup period of both biofilters, reaching a wet bed density of 310 g L^{-1} and a bed porosity of 0.89. Similarly, compost of the compost biofilter was mixed in a 3 to 1 ratio with pine leaves. It must be noted that, in all cases, pine leaves were submerged in distilled water for a 24h period prior to setting up the reactor to increase their initial water content.

In any case, analyses were useful in order to gain knowledge prior to setting up the pilot-biofilter. As an example, the low phosphate and nitrogen content in all packing materials indicated that limitation of biomass growth might occur in the biofilters and that phosphate and ammonium addition as nutrients in the watering liquid would help promoting biomass growth.

3.2. Performance of biofilters in biofiltration of toluene

Once biofilters were packed and completely characterized, 350 ml of activated sludge from an urban wastewater treatment plant containing 2,8 g TSS L^{-1} were trickled over the bed of each biofilter as an inoculation step. After biofilters inoculation, empty bed retention time was always kept at 60 seconds at a gas flow rate of 177 L h^{-1}, watering was performed once per day at a water flowrate of 0.2 L·d^{-1} for all biofilters, and inlet air relative humidity was kept at 75%. Biofilters operating temperature ranged from 22 to 29ºC along the period under study.

Four different phases are distinguished during biofilters performance operation (Figures 2a and 2b). In Phase I, corresponding to the start-up of the setup, tap water was added as watering solution. In Phase II, a nutrient solution with macro and micronutrients was used. In Phase III, the ammonium content of the nutrient solution added was incremented by a factor of 15 with respect to this of Phase II. In Phase IV, watering rate was decreased to 0.1 $L \cdot d^{-1}$ and inlet air relative humidity was increased to around 100%.

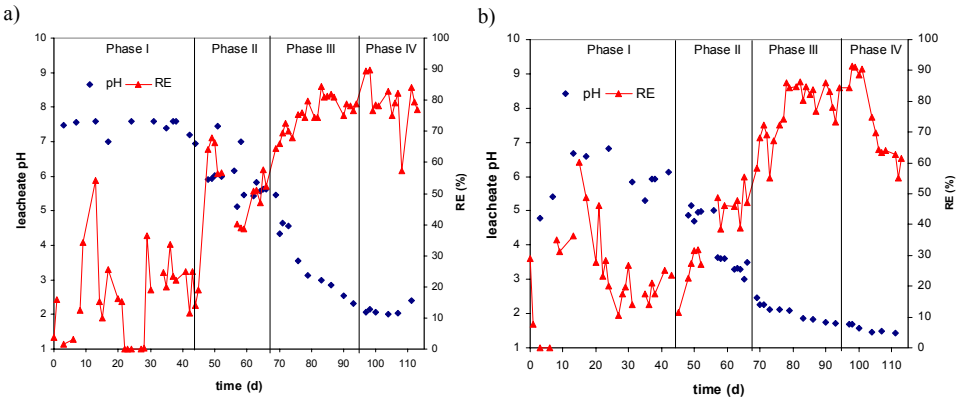

Figure 2. Removal efficiency and leacheate pH profiles for a) pine leaves biofilter, and b) coconut fiber biofilter.

Performance was assessed in terms of $_{EC}$ and $_{RE}$ against the toluene loaded to the reactor (Table 2). The EC is defined as the amount of pollutant removed per unit volume of bed volume per time ($EC= Q \cdot (C_{in}-C_{out})/V$), while the RE is the ratio of pollutant removed to the amount of contaminant fed ($RE=((C_{in}-C_{out})/C_{in}) \cdot 100$) . The mass loading rate (L) is defined as the mass of contaminant fed to the biofilter per unit time and unit volume of carrier material ($L=Q \cdot C_{in}/V$). Average values reported in Table 2 correspond to measures taken once a quasi-steady state was reached at the end of each phase, *i.e.* day 20 to 45 in Phase I, day 45 to 66 in Phase II, day 69 to 94 in Phase III, and day 105 to 113 in Phase IV.

Figure 2a and 2b show a similar performance of pine leaves and coconut fiber biofilters during the four phases. A similar behaviour was found to occur in the compost and the peat biofilter along the four phases of operation (data not shown). In Phase I, several operation problems related with setup startup such as watering tuning or improper toluene and air flow adjustment occurred from day 0 to 20, which lead to a highly variable inlet load and, concurrently, unstable operation. A more uniform and stable period from day 20 to 45 indicated that some kind of limitation was occurring in all four biofilters. Average removal efficiencies were lower than 35% in all cases and maximum elimination capacities achieved were much lower than EC_{max} of 45-100 g m^{-3} h^{-1} for peat and compost-based biofilters reported in the literature (Seed and Corsi, 1994; Don and Feestra, 1996). It was decided to substitute the tap water by a nutrients solution as watering solution on day 45. Even if organic packing materials may provide the necessary nutrients for biomass growth, several authors have found that performance of toluene-degrading biofilters improves when an extra source of ammonium and phosphate is provided to the reactor (Song *et al.*, 2003; Aizpuru *et al.*, 2005).

In period II and III, nutrients were added to the biofilters. The nutrient medium supplied in Phase II was adapted from Trotsenko (Trotsenko, 1976), and contained 1 g L^{-1} of KH_2PO_4, 1 g L^{-1} K_2HPO_4, 1 g L^{-1} NH_4Cl, 1 g L^{-1} NaCl, 0.2 g L^{-1} $MgSO_4$, 0.02 g L^{-1}

Table 2. Performance parameters for the coconut fiber biofilter (R1), compost biofilter (R2), peat biofilter (R3), and pine leaves biofilter (R4). Deviations are reported as the standard deviation of measures taken once a quasi-steady state was reached at the end of each phase.

Phase	Biofilter	EC_{max} (g m^{-3} h^{-1})	Load (g m^{-3} h^{-1})	RE (%)	C_{in} (ppm_v)	pH min	pH max
	R1	17,0 ± 6,6	75,1 ± 18,6	23,6 ± 10,3	330 ± 89	5,3	6,8
	R2	24,6 ± 9,6	73,0 ± 15,0	34,3 ± 12,0	319 ± 70	7,0	7,8
I	R3	6,3 ± 4,7	60,3 ± 14,7	9,9 ± 6,7	261 ± 65	7,2	7,9
	R4	13,3 ± 11,0	73,0 ± 15,0	16,6 ± 12,0	295 ± 94	7,0	7,6
	R1	34,4 ± 5,5	85,2 ± 16,4	46,0 ± 5,4	379 ± 85	3,0	5,2
	R2	46,0 ± 5,7	90,8 ± 15,7	57,1 ± 4,4	415 ± 101	5,7	7,1
II	R3	24,2 ± 7,2	72,7 ± 11,2	35,0 ± 11,1	312 ± 47	6,1	7,6
	R4	35,0 ± 5,7	90,8 ± 15,7	47,1 ± 7,2	369 ± 72	5,1	7,4
	R1	67,9 ± 12,7	88,5 ± 16,5	82,1 ± 4,0	393 ± 73	1,7	2,5
	R2	72,5 ± 14,7	86,2 ± 17,4	87,5 ± 5,1	381 ± 77	5,4	5,9
III	R3	52,7 ± 14,7	78,2 ± 17,8	70,3 ± 10,5	345 ± 79	4,6	5,9
	R4	75,8 ± 11,0	86,2 ± 17,4	78,9 ± 3,1	430 ± 59	2,3	5,5
	R1	65,1 ± 14,4	92,5 ± 28,9	60,9 ± 4,0	409 ± 137	1,4	1,7
	R2	92,3 ± 25,2	102,1 ± 23,3	78,7 ± 8,3	471 ± 138	3,7	5,6
IV	R3	67,0 ± 9,7	85,9 ± 9,3	75,8 ± 7,8	371 ± 48	3,9	5,1
	R4	73,5 ± 20,4	102,1 ± 23,3	74,5 ± 11,8	455 ± 64	2,0	2,4

$CaCl_2$ and 1 ml L^{-1} of a trace elements solution (Pfenning, 1981). The nutrient medium supplied in Phase III was identical except for the N content.15 g L^{-1} NH_4Cl were added instead. A gradual increase in the removal of toluene was observed (Figure 2a and 2b) in both phases and the elimination capacities were notably higher in the hole period than in previous phases (Figure 3a and 3b). A similar behaviour was found as well for compost and peat biofilters to these shown in Figure 3 (data not shown). Concurrently, leachate pH dropped in most of all reactors to acidic pH and some fungal colonies were detected in the internal wall of the biofilters. At similar elimination capacities, coconut fiber and pine leaves biofilters were even more affected by the pH drop, probably due to a lower buffering capacity of the packing material compared with this of compost. Platting on common agar medium revealed qualitatively the increasing presence of fungi, even if yeast and bacterial colonies were also detected. Thus, the initial bacterial population of the activated sludge used for the inoculation progressively switched to a fungi-enriched culture. Pressure drop was around 20 mm of water column per meter of bed height for peat and compost biofilters and around 5 mm of water column per meter of bed height for coconut fiber and pine leaves biofilters, and no significant increase was detected during Phase II and II, even if fungal development can induce clogging problems due to mycelia proliferation (Auria *et al.*, 1993).

Biofilters performance increased notably with nutrient addition, even more when an extra nitrogen amount was supplied to the biofilters during Phase III (Figure 3). Removal efficiencies between 70 and 80% were reached at the end of Phase III (Table 2), with maximum ECs around 70 g m^{-3} h^{-1} for all reactors except for the peat biofilter (R3). A notable water accumulation on top of the bed after watering periods was observed in the peat biofilter that lead to compaction and probably channeling of the top of the bed and a worst irrigation of the bottom part of the reactor, which tended to run

dry at the end of this period. This also occurred in the compost biofilter even if to a minor extent. This correlated well with a notably higher pressure drop in both biofilters. Even if a low water content of the packing material may improve reactor performance in case of hydrophobic compounds treated in fungal reactors (Cox *et al.*, 1993), low pH in local areas of the biofilter due to inefficient by-products removal may lead to a decrease in the treatment capacity of the bioreactor.

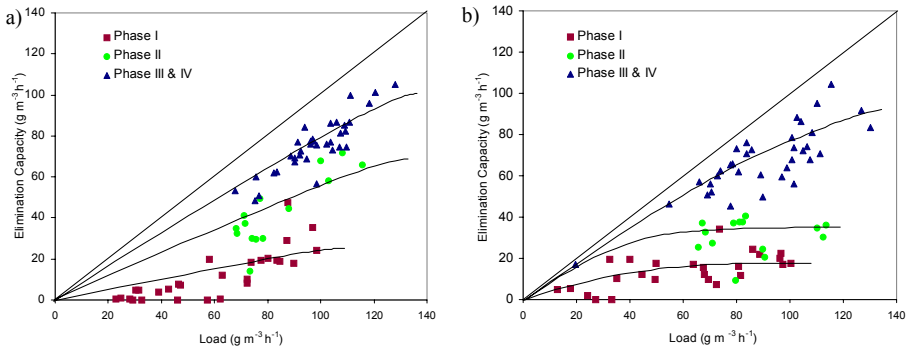

Figure 3. Elimination capacities reached in each phase in the a) pine leaves biofilter, and b) coconut fiber biofilter.

Since drying of the bottom side of all bioreactors was observed, inlet air relative humidity was increased from 75% to 100% in Phase IV. Also, the watering rate was decreased to half the rate maintained in Phases I to III seeking and improvement of the RE by homogenizing the water content of the packed bed of biofilters. As shown in Table 2, no significant improvement was found during Phase IV in the performance but some significant decrease in the removal efficiencies was found, particularly for the coconut fiber biofilter (from 82 to 61%). A sudden drop in the RE occurred on day 104 (Figure 2b) when leachate pH decreased below 1.5. This was attributed to the low pH inhibition of some species present in the biofilter produced by an excessive accumulation of acidic intermediate products of toluene degradation. Thus, a proper washout of toluene degradation by-products is necessary to ensure no inhibition of the process culture.

In general terms, all packing materials offered interesting EC and RE, even if notably lower than this obtained by other authors using inorganic packing materials (Aizpuru *et al.*, 2005). In comparison, coconut fiber and pine leaves as packing materials offer a similar behaviour in terms of toluene degradation capacity, even if this was achieved with biofilters with a much lower pressure drop than compost and peat biofilters, which is critical in terms of process economics. On the other hand, compost and peat present a higher buffering capacity which may be important to avoid an excessive pH drop that may lead to biofilter failure. In any case, further research is warranted to find out the optimum relationship between watering and pressure drop, the later closely related with bed porosity and bed density, to increase long-term operation and performance of fungal biofilters.

4 REFERENCES

Aizpuru, A., Dunat, B., Christen, P., Auria, R., García-Peña, I. and Revah, S. (2005) Fungal biofiltration of toluene on ceramic rings. *J. Environ. Eng.* 131: 396-402.

Auria, R., Morales, M., Villegas, E. and Revah, S. (1993) Influence of mold growth on the pressure drop in aerated solid state fermenters. *Biotechnol. Bioeng.* 41: 1007-1013.

Baeza, J.A., Gabriel, D. and Lafuente, J. (1999) An expert supervisory system for a pilot WWTP. *Environ. Modell. Softw.* 14: 383-390.

Barona, A., Elias, A., Arias, R., Cano, I. and Gonzalez, R. (2004) Biofilter response to gradual and sudden variations in operating conditions. *Biochem. Eng. J.* 22 (1): 25-31.

Bohn, H.L. (1996). Biofilter media. In: Proceedings of the Air & Waste Manage. Assoc. 89th Annual Meeting & Exhibition, Nashville, US.

Cox, H.H.J., Hotman, J.H.M., Doddema, H.J. and Harder, W. (1993) Enrichment of fungi and degradation of styrene in biofilters. *Biotechnol. Lett.* 15: 737–742.

Delhomenie, M.C., Bibeau, L., Bredin, N., Roy, S.,Broussau, S., Brzezinski, R., Kugelmass, J.L. and Heitz, M. (2002) Biofiltration of air contaminated with toluene on a compost-based bed. *Adv. Environ. Res*. 6: 239-254.

Delhomenie, M.C., Bibeau, L., Gendron, J., Brzezinski, R. and Heitz, M. (2003) Degradation of Toluene, xylene and trimethylbenzene vapors by biofiltration: a comparison. *J. Air Waste Manage. Assoc*. 53: 217-226.

Don, J.A. and Feestra, L. (1984) Odor abatement through biofiltration. In: Proceedings of Characterization and control of odoriferous pollutants in process industries, Le Neuve, Belgium.

Kennes, C. and Thalasso, F. (1998) Waste gas biotreatment technology. *J. Chem. Technol. Biotechnol.* 72: 303-319.

Pfenning, N., Widdel, F. and Trüpper, H.G. (1981) The dissimilatory sulfate-reducing bacteria. In (Starr and Schelgel eds.): The Prokariotes, Vol. 1. Springer-Verlag, NY, USA, pp. 926-940.

Rene, E.R., Murthy, D.V.S. and Swaminathan, T. (2005) Performance evaluation of a compost biofilter treating toluene vapours. *Proc. Biochem*. 40 (8): 2771-2779.

Seed, L.P. and Corsi, R.L. (1996). Biofiltration of BTEX contaminated streams: laboratory studies. In: Proceedings of the Air & Waste Manage. Assoc. 87th Annual Meeting & Exhibition, Pittsburgh, US.

Song, J., Ramírez, J. and Kinney K.A. (2003) Nitrogen utilization in a vapor-phase biofilter. *Water Res.* 37: 4497-4505.

Trotsenko, Y.A. (1976) Isolation and characterization of obligate methanotrophic bacteria. In (Schlegel, H.G., Gottschalk, G., and Pfnenning eds): Proceedings of the Symposium on microbial production and utilization of gases (H_2, CH_4, CO). Goettingen, Germany, pp. 329-336