Journal of Hazardous Materials 260 (2013) 442–450

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Biological anoxic treatment of O_2-free VOC emissions from the petrochemical industry: A proof of concept study

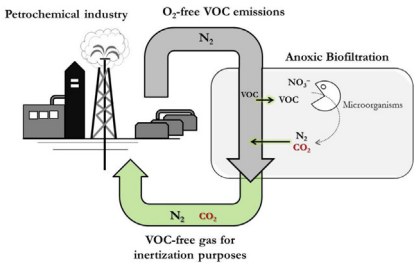
Raúl Muñoz[a], Theo S.O. Souza[a], Lina Glittmann[b], Rebeca Pérez[a], Guillermo Quijano[a,*]

[a] Department of Chemical Engineering and Environmental Technology, University of Valladolid, Dr Mergelina s/n, 47011 Valladolid, Spain
[b] Ostfalia University of Applied Sciences, Department of Supply Engineering, Wolfenbüttel, Germany

HIGHLIGHTS

- The treatment of O_2-free VOC emissions can be done by means of denitrifying processes.
- Toluene vapors were successfully removed under anoxic denitrifying conditions.
- A high bacterial diversity was observed.
- *Actinobacteria* and *Proteobacteria* were the predominant phyla.
- The nature and number of metabolites accumulated varied with the toluene load

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 February 2013
Received in revised form 19 April 2013
Accepted 25 May 2013
Available online xxx

Keywords:
Anoxic VOC removal
Biological gas treatment
Biotrickling filter
Denitrification
O_2-free VOC emissions
Toluene

ABSTRACT

An innovative biofiltration technology based on anoxic biodegradation was proposed in this work for the treatment of inert VOC-laden emissions from the petrochemical industry. Anoxic biofiltration does not require conventional O_2 supply to mineralize VOCs, which increases process safety and allows for the reuse of the residual gas for inertization purposes in plant. The potential of this technology was evaluated in a biotrickling filter using toluene as a model VOC at loads of 3, 5, 12 and 34 g m^{-3} h^{-1} (corresponding to empty bed residence times of 16, 8, 4 and 1.3 min) with a maximum elimination capacity of ~3 g m^{-3} h^{-1}. However, significant differences in the nature and number of metabolites accumulated at each toluene load tested were observed, o- and p-cresol being detected only at 34 g m^{-3} h^{-1}, while benzyl alcohol, benzaldehyde and phenol were detected at lower loads. A complete toluene removal was maintained after increasing the inlet toluene concentration from 0.5 to 1 g m^{-3} (which entailed a loading rate increase from 3 to 6 g m^{-3} h^{-1}), indicating that the system was limited by mass transfer rather than by biological activity. A high bacterial diversity was observed, the predominant phyla being *Actinobacteria* and *Proteobacteria*.

1. Introduction

Petrochemical industrial facilities are nowadays identified as major emission hotspots of volatile organic compounds (VOCs) worldwide [1,2]. Approximately 20% of the total VOC emissions in the USA are emitted by facilities devoted to oil and gas production, bulk fuel/solvent storage and petroleum refining [3]. Likewise, petroleum refining and bulk storage (including storage for energy production and industrial processes) account for approximately 15% of the total non-methane VOC emissions in Europe [4]. Most VOC emissions from the petrochemical industry are characterized by their O_2-free nature and explosion risk when O_2 is present [5]. Explosion risks in petroleum refining and bulk storage tanks are normally controlled by headspace inertization with N_2 or CO_2, leading to VOC emissions when these inert atmospheres are vented [6]. Despite VOC emissions from the petrochemical industry are commonly treated by means of gas flaring (often with the addition of a support fuel), the release of VOC-laden emissions to the

* Corresponding author. Tel.: +34 983186424, fax: +34 983423013.
E-mail address: gquijano@iq.uva.es (G. Quijano).

0304-3894/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2013.05.051

atmosphere without any treatment (gas venting) is still common [5,7]. For instance, in 2004 the World Bank estimated that 1×10^{12} m^3 of gas derived from petrochemical activities were flared or simply vented to the atmosphere worldwide [7]. Moreover, it is worth noting that VOC flaring does not constitute an environmentally friendly practice, with complete combustion in conventional flares being rarely achieved (combustion efficiencies as low as 10–15% being reported at wind speeds higher than 20 km h^{-1}) [8]. Therefore, there is a lack of environmentally friendly, cost-efficient and robust technologies for the treatment of such particular VOC emissions.

Despite biotechnologies constitute a promising off-gas treatment alternative, the O_2-free nature and the explosion risks associated with the presence of O_2 have strongly limited the use of conventional aerobic biofiltration as an end-of-pipe technology for the control of VOC emissions from the petrochemical industry. Nevertheless, although anaerobic biocatalytic processes have not been explored so far in biological gas treatment systems, there is enough empirical evidence to support the fact that VOC biodegradation can also be achieved in the absence of O_2. In this regard, VOCs such as benzene, toluene, ethylbenzene and xylene have been successfully removed under anoxic and iron reducing environments, and particularly high VOC biodegradation rates were recorded under anoxic denitrifying conditions [9,10]. Likewise, anoxic methane mineralization via denitrification has also been reported [11,12]. However, these preliminary studies conducted batchwise in closed bottles were focused on the treatment of pollutants in wastewater, and the feasibility of using denitrification as a core metabolic process for off-gas VOC biodegradation under continuous operation in bioreactors must still be evaluated.

In this work, the potential of an innovative biofiltration technology based on the anoxic biodegradation of VOCs was evaluated. In contrast to the traditional aerobic biofiltration, anoxic biofiltration does not require O_2 to mineralize VOCs, and generates N_2 and CO_2 as innocuous by-products. Thus, besides increasing process safety, this biotechnology would allow the reuse of the residual gas for inertization purposes in petrochemical processes (e.g. blanketing of storage tanks). For this proof of concept, toluene was used as model VOC and the anoxic biofiltration system was implemented in a biotrickling filter.

2. Materials and methods

2.1. Chemicals and mineral salt medium

All chemicals for mineral salt medium (MSM) preparation were purchased from PANREAC (Barcelona, Spain) with a purity of at least 99%. Toluene (99.0% purity) was obtained from Sigma–Aldrich (Madrid, Spain). The MSM was composed of (g L^{-1}): $Na_2HPO_4{\cdot}12H_2O$, 6.15; KH_2PO_4, 1.52; $MgSO_4{\cdot}7H_2O$, 0.2; $CaCl_2$, 0.038; and 10 mL L^{-1} of a trace element solution containing (g L^{-1}): EDTA, 0.5; $FeSO_4{\cdot}7H_2O$, 0.2; $ZnSO_4{\cdot}7H_2O$, 0.01; $MnCl_2{\cdot}4H_2O$, 0.003; H_3BO_3, 0.03; $CoCl_2{\cdot}6H_2O$, 0.02; $CuCl_2{\cdot}2H_2O$, 0.001; $NiCl_2{\cdot}6H_2O$, 0.002; $NaMoO_4{\cdot}2H_2O$, 0.003. A $NaNO_3$ stock solution of 100 g L^{-1} was prepared to supplement the MSM with NO_3^- as electron acceptor for toluene oxidation and as nitrogen source for microbial growth. The final pH of the medium was 7.

2.2. Enrichment of toluene denitrifying microorganisms

Enrichment cultures were performed batchwise in 1.25-L serum bottles to isolate microorganisms able to degrade toluene under anoxic denitrifying conditions from activated sludge (Valladolid wastewater treatment plant, Spain). The bottles, containing 94 mL of MSM, 1 mL of $NaNO_3$ stock solution and 5 mL of fresh activated sludge, were gas-tight closed with butyl septa and plastic caps. Then, the O_2 contained in the headspace was flushed with helium for 5 min and once the bottles were deoxygenated 20 μL of toluene were added. The bottles were incubated at 25 °C and 300 rpm. Toluene and CO_2 concentrations in the headspace, as well as NO_3^- and NO_2^- concentrations in the liquid phase, were periodically measured. Ten cycles of toluene/NO_3^- additions were performed, with a reproducible toluene mineralization being observed from the 5th cycle onwards (overall enrichment period of 30 days). The enriched consortium served as inoculum for the biotrickling filter.

2.3. Toluene biodegradation in a biotrickling filter

Continuous toluene biodegradation under anoxic denitrifying conditions was performed in a biotrickling filter reactor (BTF). The BTF consisted of a cylindrical jacketed PVC column (0.07 m inner diameter, 0.6 m height) with a working packed bed volume of 1.5 L of Kaldnes K1 rings (Evolution Aqua Ltd., UK). The packing material was characterized by: ring diameter 1 cm, density 0.17 g mL^{-1}, void fraction 83%, and water-holding capacity (volume basis) 11% [13]. The bioreactor was operated in countercurrent flow mode at 25 °C throughout the entire experiment.

The O_2-free toluene emission was obtained by mixing a pure and humidified N_2 stream (99.0% purity, Abello Linde, Spain) with a toluene-saturated N_2 stream regulated by a mass flow controller (Aalborg, Denmark). The BTF was operated at 0.5 g toluene m^{-3} and empty bed residence times (EBRT) of 1.3, 4, 8 and 16 min. The nutrients solution (0.5 L of MSM) was continuously agitated at 200 rpm and 25 °C in an external 0.6-L holding tank and recycled at 0.63 m h^{-1}. NO_3^- was supplied by periodically injecting 10 mL of a 100 gNO_3^- L^{-1} stock solution to the holding tank. The NO_3^- supply frequency varied according to the experimental stage in order to avoid NO_3^- limitation in the recycling liquid medium. In addition, to avoid nutrient limitation 25 mL of liquid culture broth were replaced by fresh MSM each 3 days. The pH of the liquid recycling media was daily adjusted to 7. A complete replacement of the recycling nutrient solution by fresh mineral salt medium was conducted at day 22 to assess the role of potentially accumulated metabolites on the toluene removal performance.

Toluene and CO_2 concentrations in gas phase as well as NO_3^- and NO_2^- concentrations in the liquid phase were periodically monitored. On-line measurements of pH and temperature were acquired each 4 h with calibrated probes via a multiparameter analyzer C-3020 (Consort, Belgium) connected to a computer. The pressure drop (ΔP) across the packed column of the BTF was determined with a water U-tube manometer. A detailed diagram of the experimental set-up is shown in Fig. 1.

2.4. Biodegradation performance

Toluene biodegradation performance was evaluated in terms of elimination capacity (EC, g m^{-3} h^{-1}) and removal efficiency (RE, %) as defined by Muñoz et al. [14]. The carbon mineralization efficiency (CME, %) was defined as:

$$\mathrm{CME} = \frac{\mathrm{C-CO_2\ \ produced}}{\mathrm{C-Toluene\ \ degraded}} \times 100 \quad (1)$$

2.5. Molecular biology analysis

Biomass samples at day 0 (inoculum of the BTF) and day 60 (end of BTF operation) were collected and stored immediately at −20 °C to evaluate the richness and composition of the bacterial community. Genomic DNA was extracted according to Lebrero et al. [15]. The PCR mixture (50 μL) was composed of 25 μL of BIOMIX