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One-stage biotrickling filter for the removal of a mixture of volatile pollutants from air: Performance and microbial community analysis

M. Estefanía López [a], Eldon R. Rene [a], Luc Malhautier [b], Janick Rocher [b], Sandrine Bayle [b], María C. Veiga [a], Christian Kennes [a,*]

[a] Department of Chemical Engineering, University of La Coruña, Campus da Zapateira, Rua da Fraga, 10, E-15008 La Coruña, Spain
[b] Ecole des Mines d'Alès, Laboratoire du Génie de l'Environnement Industriel, 6, Avenue de Clavières, F-30319 Alès Cedex, France

HIGHLIGHTS

- A single-stage BTF was examined for the removal of a mixture of VOCs and VICs.
- Inoculum: autotrophic bacteria, *Candida* sp., *Rhodococcus* sp., and *Ophiostoma* sp.
- EC_{max} were 302, 175, and 191 g m^{-3} h^{-1} for methanol, α-pinene and H_2S, respectively.
- Presence of methanol showed an antagonistic type removal pattern for α-pinene.
- PCR, DGGE and numerical analysis were done on biomass collected from the BTF.

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ABSTRACT

The biodegradation of gas-phase mixtures of methanol, α-pinene and H_2S was examined in a biotrickling filter (BTF), inoculated with a microbial consortium composed of an autotrophic H_2S-degrading culture, and pure strains of *Candida boidinii*, *Rhodococcus erythropolis*, and *Ophiostoma stenoceras*. The inlet concentrations of methanol, α-pinene and H_2S varied from 0.05 to 3.3 g m^{-3}, 0.05 to 2.7 g m^{-3}, and 0.01 to 1.4 g m^{-3}, respectively, at empty bed residence times (EBRT) of either 38 or 26 s. The maximum elimination capacities (EC_{max}) of the BTF were 302, 175, and 191 g m^{-3} h^{-1}, with 100%, 67%, and >99% removal of methanol, α-pinene and H_2S, respectively. The presence of methanol showed an antagonistic removal pattern for α-pinene, but the opposite did not occur. For α-pinene, inlet loading rates (ILRs) >150 $g_{\alpha\text{-pinene}}$ m^{-3} h^{-1} affected its own removal in the BTF. The presence of H_2S did not show any declining effect on the removal of both methanol and α-pinene.

1. Introduction

Wood industries have been constantly striving to reduce their emissions of odorous compounds from various plant operations that usually contain a mixture of volatile organic compounds (VOCs) and volatile inorganic compounds (VICs). Among those, methanol, α-pinene, and hydrogen sulfide (H_2S), are representative hydrophilic, hydrophobic, and inorganic pollutants present in emissions from some pulp and paper- and wood-related industries (Rene et al., 2010a). The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) and ACGIH threshold limit value (TLV) for industrial workers are set at 200 ppm (260 mg m^{-3}) for methanol, 100 ppm (560 mg m^{-3}) for α-pinene, and 10 ppm (15 mg m^{-3}) for H_2S, respectively, for a 8-h time weighted average concentration and a 40-h work per week (ACGIH, 1998).

Biodegradation is a well established method for the complete mineralization of volatile organic and inorganic compounds, present in both liquid and gaseous state (Kennes et al., 2009; Rene et al., 2010b). It exploits the advantage of the ability of microorganisms to transform hazardous and odorous pollutants into innocuous and inodorous end-products. Among the different bioreactor configurations used to carry out this biodegradation process, biofiltration appears to be a safe, reliable, eco-friendly and economic technique (Kennes and Veiga, 2001, 2013; van Groenestijn and Kraakman, 2005). Biotrickling filters (BTF) exploit the advantages of the conventional biofilter, and use a trickling nutritive medium that contains nutrients for sustaining microbial activity in the biofilm (Aroca et al., 2007; Hassan and Sorial, 2010). The packing in a BTF is generally made of chemically inert materials such as plastic supports, polyurethane foam, lava rock, pall rings, among others, that can be arranged either in a random or

* Corresponding author. Tel.: +34 981 167000×2036; fax: +34 981 167065.
E-mail address: Kennes@udc.es (C. Kennes).

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a structured manner (Aroca et al., 2007; Kennes and Veiga, 2002, 2013; Kim and Deshusses, 2008). Nevertheless, BTFs facilitate more consistent operation than traditional biofilters (BFs) due to better control of overall pressure drop, nutrient concentration, and pH, and enable higher pollutant elimination rates to be obtained for a broader range of pollutants (Kennes and Veiga, 2001). Hence, BTF are suitable bioreactors for the treatment of complex mixtures of various organic and inorganic pollutants such as mixtures of methanol, α-pinene, and hydrogen sulfide (H_2S).

There are a few publications that investigated the removal of H_2S and VOCs solely. The pH drop due to the accumulation of sulfuric acid from the conversion of H_2S can hinder the activity of microbial populations involved in the biodegradation of VOCs. To avoid bioreactor disfunction, a two-stage bioreactor configuration was recently tested in our laboratory for the combined removal of VOC and VIC. For the purification of waste-gases containing H_2S and VOCs (methanol and α-pinene), H_2S and methanol were degraded in the first-stage reactor by autotrophic bacteria and an acid-tolerant yeast, followed by the effective removal of α-pinene in the second stage by a fungus (Rene et al., 2010a). In order to improve the biological treatment of such a mixture and the bioreactor design, the development of one-stage bioreactors is suggested here. Previously, studies had been undertaken with a one-stage bioreactor for the removal of gas-phase methanol, α-pinene or H_2S as stand-alone pollutants (Jin et al., 2005, 2006). When considering VICs and VOCs mixtures, VOCs degrading microorganisms in one-stage BTFs have sometimes shown to tolerate the prevailing acidic conditions over a long period of time, with variable degradation rates, depending on the nature of the pollutants. In a pilot-scale BTF packed with lava rock, the efficient co-treatment of H_2S and VOCs at acidic pH was highlighted, revealing the activity of both chemoautotrophs (H_2S oxidizing bacteria) and heterotrophs (VOC oxidizing bacteria) within the BTF (Chitwood and Devinny, 2001). Cox and Deshusses (2002) reported that the pH (4.5 or 7) of operation did not affect long-term performance of a BTF used for the co-treatment of H_2S and toluene, but the start-up time was longer at the lowest pH of 4.5.

The aim of this work was then to develop a highly efficient one-stage BTF, by utilizing different microorganisms that had proven to be effective for the removal of the mixture of methanol, α-pinene and H_2S. In this context, our objectives were: (i) to evaluate the performance of a one-stage BTF, inoculated with different microbial species, for the removal of methanol, α-pinene and H_2S, (ii) to study the effect of the empty bed residence time (EBRT of either 38 or 26 s) on BTF performance, (iii) to understand the dynamics of pollutant removal in different sections of the BTF (substrate stratification), (iv) to identify the different types of interaction effects, i.e., antagonistic or synergistic, between pollutants and their removal pattern in the BTF, and (v) to perform microbial community analysis in different sections of the BTF after long-term operation using molecular biology tools.

2. Methods

2.1. Nutrient medium composition

The composition of the mineral medium used in the BTF, was (in g L^{-1} of de-ionized water); K_2HPO_4: 0.5, $MgSO_4{\cdot}7H_2O$: 0.1, KH_2PO_4: 4.5, NH_4Cl: 2, and 2 mL trace elements and vitamin solutions (Rene et al., 2010a).

2.2. Microbial consortium

The BTF was inoculated with a mixture of (i) an autotrophic H_2S-degrading culture (100 mL leachate from a previously operated BTF), (ii) *Candida boidinii*, a methanol degrading acid-tolerant yeast isolated in our laboratory (~3 g L^{-1}), (iii) a co-culture of *Rhodococcus erythropolis* (~3 g L^{-1}) and (iv) the fungus *Ophiostoma stenoceras* (~3 g L^{-1}) isolated in our research group (Jin et al., 2006, 2007a). The latter bacterium and fungus are capable of utilizing α-pinene as their sole carbon and energy source. The different microbial cultures were grown on agar plates (15 g L^{-1}), maintained in a closed jar at ambient temperature, and supplied with vapor phase methanol or α-pinene at low concentrations. The BTF was also inoculated with biomass obtained from the leachate (100 mL) of a previously operated two-stage bioreactor, i.e., a biotrickling filter + a biofilter (BTF + BF), as described elsewhere, where methanol, α-pinene and H_2S were collectively treated in gas-phase (Rene et al., 2010a).

2.3. Experimental setup

The schematic of the one-stage BTF is shown in Fig. 1. The BTF was constructed of glass (70 cm high × 9.4 cm inner diameter), and packed with polypropylene pall rings yielding a total working bed volume of 4.55 L. The pall ring bed had an initial porosity of 91% and a specific surface area of 350 $m^2\ m^{-3}$. The BTF was provided with gas sampling ports located along the height of the reactor, at 20 and at 60 cm (outlet port) from the inlet. The BTF was also provided with filter material sampling ports, to collect biomass samples, uniformly distributed along the column (10 and 50 cm from the inlet). Fittings, connections and tubings were made of either glass or Teflon.

2.4. Inoculation of the BTF

The microbial consortium described above was mixed with 2 L nutrient medium to obtain a uniform suspension of the initial inoculum. This culture was aseptically added to the BTF from the top; the leachate was collected in a collection tank and then continuously re-circulated at 2.77 L h^{-1} for the next 4 d, until visible biomass remained attached to the pall rings.

2.5. BTF operation

During BTF operation, the target concentrations of the individual pollutants; methanol (0.05–3.3 g m^{-3}), α-pinene (0.05–2.7 g m^{-3}) and H_2S (0.01–1.4 g m^{-3}) were generated at a sea level atmospheric pressure of 101.3 kPa, and at a laboratory temperature of 22 ± 2 °C, as described hereafter. A main stream of compressed air was split into two minor and one major flow. The two minor air streams were then bubbled through either liquid methanol or α-pinene, introduced separately in flasks. H_2S was generated by passing the major portion of the air stream over a H_2SO_4 solution into which a solution of Na_2S was dripped. Different gas phase H_2S concentrations were obtained by changing the Na_2S concentration and/or dripping rate (Jin et al., 2007a). The three streams were combined in a mixing chamber, and fed to the bottom of the BTF column in a counter-current flow mode. The aqueous mineral medium described above was continuously re-circulated over the packed bed using a peristaltic pump (323E/D, Watson-Marlow Limited, Falmouth Cornwall, England) at a constant flow rate of 2.8 L h^{-1}. The pH of the re-circulated nutrient medium was maintained constant, at 6.0 ± 0.4, by means of a pH electrode (EASYFERM 120, Hamilton) attached to the nutrient collection tank and a controller coupled to an electro-valve (DO 9765T, Dual 3½ Digit pH redox indicator and regulator, Italy), by dosing a 2 N NaOH solution to neutralize the acidic metabolites formed during the biodegradation process. Fresh nutrient medium was added once a week to the nutrient tank in order to compensate the loss of medium that occurred due to abiotic phenomena as well