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Research article

Control of VOCs from printing press air emissions by anaerobic bioscrubber: Performance and microbial community of an on-site pilot unit

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ABSTRACT

A novel process consisted of an anaerobic bioscrubber was studied at the field scale for the removal of volatile organic compounds (VOCs) emitted from a printing press facility. The pilot unit worked under high fluctuating waste gas emissions containing ethanol, ethyl acetate, and 1-ethoxy-2-propanol as main pollutants, with airflows ranging between 184 and 1253 m^3 h^{-1} and an average concentration of 1126 ± 470 mg-C Nm^{-3}. Three scrubber configurations (cross-flow and vertical-flow packings and spray tower) were tested, and cross-flow packing was found to be the best one. For this packing, daily average values of VOC removal efficiency ranged between 83% and 93% for liquid to air volume ratios between $3.5 \cdot 10^{-3}$ and $9.1 \cdot 10^{-3}$. Biomass growth was prevented by periodical chemical cleaning; the average pressure drop was 165 Pa m^{-1}. Rapid initiation of anaerobic degradation was achieved by using granular sludge from a brewery wastewater treatment plant. Despite the intermittent and fluctuating organic load, the expanded granular sludge bed reactor showed an excellent level of performance, reaching removal efficiencies of 93 ± 5% at 25.1 ± 3.2 °C, with biogas methane content of 94 ± 3% in volume. Volatile fatty acid concentration was as low as 200 mg acetic acid L^{-1} by treating daily average organic loads up to 3.0 kg COD h^{-1}, equivalent to 24 kg COD m^{-3} bed d^{-1}. The denaturing gradient gel electrophoresis (DGGE) results revealed the initial shift of the domains Archaea and Bacteria associated with the limitation of the carbon source to a few organic solvents. The Archaea domain was more sensitive, resulting in a drop of the Shannon index from 1.07 to 0.41 in the first 123 days. Among Archaea, the predominance of *Methanosaeta* persisted throughout the experimental period. The increase in the proportion of *Methanospirillum* and *Methanobacterium* sp. was linked to the spontaneous variations of operating temperature and load, respectively. Among Bacteria, high levels of ethanol degraders (*Geobacter* and *Pelobacter* sp.) were observed during the trial.

1. Introduction

The flexographic sector represents 17% of the European printing sector, contributing around 1.7% of the total turnover in 2003 (Ernst and Young, 2007). The consumed solvents are mainly oxygenated compounds, such as ethanol, ethyl acetate, 1-propanol, 2-propanol, 1-methoxy-2-propanol, n-propyl acetate, 1-methoxy-2-propyl acetate, acetone, and 1-butanol (Granström et al., 2002). Flexographic air emissions are characterized by high flow rates and low volatile organic compound (VOC) concentrations (Sempere et al., 2012), with temperatures ranging from 40 to 70 °C and relative humidity varying from 5 to 15% (Rothenbuhler et al., 1995). According to the European Directive on Industrial Emissions (Council Directive 2010/75/EC), these air emissions must be controlled.

Biotreatments represent well-developed air pollution control techniques for removing VOCs in these conditions (Deshusses, 1997). Among biotreatments, bioscrubbers can handle higher gas loads than biotrickling filters and biofilters, and their capacity is up to 3000–4000 m^3 m^{-2} h^{-1} (Kennes et al., 2009). However, there are few available studies on aerobic bioscrubbers. Le Cloriec et al. (2001) reported removal efficiencies of 90.1–100% in a laboratory-scale bioscrubber, with liquid to air ratios ranging

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between $0.6 \cdot 10^{-3}$ and $2 \cdot 10^{-3}$, and with ethanol concentration in waste gas from 18.8 to 291.7 mg-C m^{-3}. Granström et al. (2002) investigated an onsite pilot-scale system for the treatment of waste gas from printing processes. In this study, the major VOC of the waste air was ethanol, with smaller amounts of ethyl acetate, 1-propanol, 2-propanol, 1 methoxy-2-propanol, and 3-ethoxy-1-propanol. The flow of the waste gases varied from 1.68 to 3.73 m^3 h^{-1}, with 99.6% VOC removal efficiency, excluding evaporation losses. Nevertheless, aerobic bioscrubbers are still not widespread within the biotreatment market due to the high energy consumption of aerobic bioreactors. In contrast, anaerobic bioscrubber could be an alternative for recycling waste gases into bioenergy, thereby resulting in a positive net energy balance.

To the best of our knowledge, no previous literature exists on the use of anaerobic bioscrubbers for the treatment of VOC waste gases, although the anaerobic degradation of solvents, such as alcohols (Eichler and Schink, 1985; Widdel, 1986; Zellner and Winter, 1987) or esters (Oktem et al., 2008; Yanti et al., 2014) is well documented. Recently, Lafita et al. (2015) demonstrated that anaerobic degradation of glycol ethers is feasible by reporting the treatment of synthetic packaging wastewater, which contains a mixture of ethanol and 1-methoxy-2-propanol in a mass ratio of 4:1. These authors achieved removal efficiencies of up to 94% at 18 °C and 97% at 25 °C in an expanded granular sludge bed (EGSB) reactor, with organic loading rates of methoxy-2-propanol of 6.4 and 9.3 kg COD m^{-3} d^{-1}, respectively.

The anaerobic degradation of organic solvents in granular sludge reactors relies on the microbial population developed in the anaerobic granules, which should in turn maintain its physical integrity. Leclerc et al. (2004) studied the microbial populations of 44 anaerobic digesters treating effluents from several sectors. These authors indicated that the occurrence and prevalence of the different species are influenced by the running and environmental conditions. Anaerobic granulated sludge coming from breweries is a common source of biomass for other industrial sectors. In this sense, the study of the evolution of the microbial population is an interesting tool to investigate the effect that a change in the substrate composition could have on the feasibility and robustness of the anaerobic degradation of solvents.

The characterization of microbial populations can be carried out using molecular biology tools, such as denaturing gradient gel electrophoresis (DGGE). This is based on the electrophoretic separation of polymerase chain reaction (PCR) products of the same length, but with different sequences, on a linear denaturing gradient polyacrylamide gel (Muyzer and Ramsing, 1995). DGGE has been applied to evaluate the microbial diversity of anaerobic reactors, such as an upflow anaerobic sludge blanket (UASB) reactor treating brewery wastewater; this study showed that the dominant archaeal bands were closely related to *Methanosaeta* and *Methanobacterium* (Chan et al., 2001). The DGGE technique has also shown that the microbial population of a UASB treating wastewater from an unbleached pulp plant persisted throughout the experimental period (Buzzini et al., 2006). DGGE studies can also demonstrate the importance of environmental conditions in the diversity of microbial populations; for example, LaPara et al. (2000) indicated that a thermophilic reactor showed less biodiversity than a mesophilic one by treating wastewater from a pharmaceutical facility.

The present study provides the first successful example of an on-site pilot plant of anaerobic bioscrubbers controlling VOC emissions from a flexographic printing facility (Waalkens et al., 2015). The purposes of our work were as follows: (1) to evaluate the best scrubber configuration to achieve high VOC removal efficiencies, and at same time, control pressure drop; (2) to determine the maximum organic load that the EGSB can handle under intermittent and variable waste gas emissions; and (3) to study the dynamics of the microbial community of the EGSB reactor inoculated with granular sludge from a brewery anaerobic reactor using the DGGE technique.

2. Material and methods

2.1. Anaerobic bioscrubber setup

The pilot plant was provided by Pure Air Solutions (Heerenveen, The Netherlands) and was operated on-site in Altacel Transparant Verpakkingsind (Weesp, The Netherlands) by treating a fraction of its air emissions. The flexographic site operates on a two-shift (16 h) basis from Monday to Friday and on a one-shift (8 h) basis on Saturday. The pilot plant comprises a variable-speed fan with a maximum flow of 1500 m^3 h^{-1}, as well as several centrifugal pumps. The two main units were the scrubber and the anaerobic reactor (see Graphical Abstract). The scrubber unit had a total height of 3.06 m and a diameter of 0.5 m. The available height for the packing material was 2.0 m. The scrubber unit was assembled onto a bottom tank of 2 m^3 in volume. The anaerobic reactor had a total height of 5.08 m and diameter of 1.59 m, with an effective water volume of 8.7 m^3. Two intermediate tanks completed the setup; resulting in 16 m^3 of total effective water volume.

The scrubber was operated in the countercurrent mode during the working hours of the facility; VOC-polluted air coming from the factory was introduced to the bottom by the blower, and the water was sprayed from the top and collected in the bottom tank. From there, it flowed to an intermediate tank for supplementation with macronutrients (N, P, S, K) and sodium carbonate for pH control prior to pumping it to the anaerobic reactor for solvent degradation. Ca, Mg, trace metals (B, Co, Cu, Fe, Mn, Mo, Ni, Se, Zn), and yeast extract were discontinuously supplemented. The anaerobic reactor consisted of an EGSB operated at 3 h of hydraulic residence time. The EGSB was filled with granular sludge from an internal circulation (IC) reactor treating brewery wastewater (Heineken, The Netherlands) without further acclimation to simulate operational protocols at the industrial scale. The expansion of the granular bed to 3 m^3 was achieved by mixing the influent water with 50% of the effluent of the reactor; the upflow velocity was kept constant at 3 m h^{-1}. The pilot unit worked in water-closed recirculation, with <10% daily water renewal. The daily purge was done overnight when no biogas production occurred. The plant setup was equipped with a programmable logic controller (PLC) with Twinsoft software (Servelec Technologies, United Kingdom) to monitor and control the parameters, such as the air and liquid flowrates, water and air temperatures, pH, conductivity, and water level in the tanks.

A flame ionization detector (FID) analyzer (model RS 53-T, Ratfisch Analysensysteme, Germany) continuously monitored the VOC concentration in the inlet and outlet of the gas phase. The composition of the inlet and outlet gases was measured by carbon sorbent tubes and post Gas Chromatography analysis. Biogas production was continuously measured by a gas meter (Bellows-BG 4 Gasmeters, Ritter, Germany), and its composition was determined by a dual-wavelength optical infrared analyzer (Combimass GA-m, Binder, Germany). The main parameters of the liquid phase were monitored twice a week with photometric commercial kits as follows: chemical oxygen demand (COD); volatile fatty acids (VFAs); nutrients ($N-NH_4^+$ and $P-PO_4^{3-}$) with LCK 014, LCK 365, LCK 303, and LCK 348 kits from HACH Lange GmbH (Germany); and alkalinity with a titrimetric kit (MColortest™, Merck Millipore, Germany).

The pilot unit was operated for 484 days. The experimentation was divided into five stages characterized by a change in the