# Control of dissolved CH<sub>4</sub> in a UASB reactor effluent from municipal wastewater treatment

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#### Abstract

The direct anaerobic treatment of municipal wastewater represents a technology that is adaptable to the conditions of developing countries. The recovery of dissolved methane in anaerobic effluents should be considered for this technology to be more widely applied because methane is a potent greenhouse gas. In this study, a pilot-scale system was operated for 106 days to recover dissolved methane in the effluents of an upflow anaerobic sludge blanket reactor (UASB), in which a biofilter packed with compost was used to oxidize methane. The system operated at two conditions of anaerobic effluent flow (0.9 and 1.88 m<sup>3</sup>/h) and an air-to-water ratio of 1:1 or 1:2. In both conditions (CH<sub>4</sub> volume of 2.7 and 4.3%, respectively), the desorption column recovered 99% of the dissolved CH<sub>4</sub>, in addition to approximately 30% of H<sub>2</sub>S, whose desorption was limited due to the high pH (> 8) of the effluent. The biofilter removed 70% of the average CH<sub>4</sub> load (60 gCH<sub>4</sub>/m<sup>3</sup>h) and 100% of the H<sub>2</sub>S load considering an empty bed retention time of 23 min. The average temperature inside the biofilter was  $42 \pm 9$  °C because the oxidation of CH<sub>4</sub> is exothermic. Due to high temperatures, the moisture level in the filter medium must be efficiently controlled.

#### Keywords

Anaerobic sewage treatment, dissolved methane, methane emissions, biofilter, methane oxidation, hydrogen sulfide oxidation.

#### Introduction

The anaerobic treatment of municipal wastewater in Mexico and the majority of Latin American countries represents a viable technology for the operating agency of municipal water systems due to its low operation costs. This technology shows great potential for application in the developing countries of intertropical regions, although several factors have limited its application, including the generation of odors, the accumulation of floating material inside gas separators and the presence of dissolved methane, a potent greenhouse gas, in effluents, whereby methane is subsequently released to the environment (Noyola et al., 2006; Chernicharo et al., 2015). Overall, the quantity of  $CH_4$  generated by municipal wastewater systems is low due to the low concentration of organic matter. In this sense, the production of energy from the anaerobic treatment of this type of effluent is not feasible unless wastewater flow surpasses 500 L/s (Noyola et al., 2012).

In Mexico and elsewhere in Latin America, the majority of small anaerobic wastewater treatment plants (flow < 25 L/s) that treat municipal wastewater do not adequately manage the biogas that is produced, which is often released into the atmosphere instead of being recovered or burned (Noyola et al., 2012). Notably, during the anaerobic treatment of municipal wastewater, between 30 and 60% of the total CH<sub>4</sub> generated is dissolved in the effluent (Noyola et al., 1988; Souza et al., 2011; Heffernan et al., 2012). Once outside the reactor, the CH<sub>4</sub> dissolved in effluents is desorbed due to the turbulence or agitation to which outflows are subjected. This process contributes to the emission of CH<sub>4</sub> into the atmosphere, where CH<sub>4</sub> has a global warming potential up to 34 times greater than that of CO<sub>2</sub> (Myhere et al., 2013) and represents approximately 23% of total greenhouse gas emissions worldwide. The concentration of CH<sub>4</sub> in the atmosphere has reportedly increased at two times the rate of CO<sub>2</sub> (USEPA 2006). Thus, the recovery of methane produced by wastewater treatment systems is one important strategy for limiting global warming (Nikiema et al., 2005; Noyola et al., 2006). The objective of this study was to evaluate a pilot scale system for recovering  $CH_4$  emissions dissolved in wastewater effluent. The system contained a methane desorption column, in which methane was subjected to biological oxidation with the use of a biofilter. This system may be applied in small anaerobic treatment plants.

# Methods

The experimental portion of the study was carried out at the wastewater treatment plant of the Acatlan campus, National Autonomous University of Mexico (UNAM), State of Mexico. The installations contained an upflow anaerobic sludge blanket reactor (UASB) with a capacity of 5 L/s, followed by the disinfection of the activated sludge effluent via sand and anthracite filtration. The experimental device formed a combined pilot system to desorb and biologically eliminate the dissolved  $CH_4$  in the effluent of the UASB reactor. The system consisted of a desorption column and a biofilter (Figure 1a). A schematic diagram is presented in Figure 1b.



Figure 1a. Pilot system for the biological removal of CH<sub>4</sub> in the effluent of a UASB reactor.



Figure 1b. Schematic diagram of the pilot set-up composed of a desorption column and a compost biofilter.

Desorption column. For the design of the desorption column, simulations were performed in the

software Berkeley Madonna (University of California, USA), and the Onda model was used (Onda et al., 1968) to determine the mass transfer coefficients. The column was constructed with PVC material and had a diameter of 0.15 m and a packed height of 1 m. The packing consisted of Pall plastic rings (diameter and height of 2.5 cm, specific area of 280  $\text{m}^2/\text{m}^3$  and void fraction of 90%). The column was operated under counter-flow conditions. The wastewater (effluent of the UASB reactor) was fed through a centrifugal pump to the upper end of the system and the air, originating from the post-treatment aeration system to the lower portion. A differential manometer was installed at the column entrance to identify drops in pressure. The column operated under two wastewater flow conditions (air-to-water ratios of 1:1 and 1:2), in which a constant air flow of 0.9 m<sup>3</sup>/h (15 L/min) was maintained. In Table 1, the two operating conditions of the desorption column are described.

Table 1. Operating conditions of the description condition									
_	Desorption column								
	Flow of wastewater	Flow of air feed	Air-to-water	Temperature <sup>‡</sup>					
	feed $(m^3/h)$	$(m^{3}/h)$	ratio						
Condition I	0.9	0.9	1:1	$17.6 \pm 1^{\circ}C$					
Condition II	1.88	0.9	1:2	$20.5 \pm 1.5^{\circ}C$					

Tabla 1	Operating	conditions	of the	desor	ntion	column
Table 1.	Operating	conditions	or the	uesor	puon	COIUIIIII

<sup>+</sup> Temperature of wastewater entering the desorption column

*Biofilter*. For the biofiltration system, a polyethylene recipient 1 m in height with a diameter of 0.85 m was used; the filtration material was a mix of 338 kg of fresh compost and 127 kg of acclimatized compost from another biofilter used to treat unpleasant odors in a wastewater treatment plant in University City, National Autonomous University of Mexico (Ciudad Universitaria, UNAM), Mexico City. The filtering material had a volume of 0.340 m<sup>3</sup>, resulting in a packed height of 0.60 m. The biofilter had four sampling ports, spaced 15 cm apart along the length of the filter medium. A differential manometer was installed at the entrance of the biofilter to detect any drops in pressure, and a temperature sensor 60 cm in length was placed inside the second sampling port to continually monitor the inside temperature. The air flow across the biofilter was set at 15 L/min, corresponding to an empty bed retention time (EBRT) of 23 min. Under condition I, the concentration of CH<sub>4</sub> as a percentage of volume was 2.7%. Under condition II, it was 4.3%. The feeding loads were 35 and 56 gCH<sub>4</sub>/m<sup>3</sup>h, respectively. The average ambient temperature at the site was 25 °C (max: 31 °C; min: 2 °C). In Table 2, the operating conditions of the biofilter are detailed.

*Monitoring*. The experiment had a duration of 106 days (29 d under the condition I and 77 days under condition II). The concentrations of different gasses (CH<sub>4</sub>, H<sub>2</sub>S, CO<sub>2</sub>, O<sub>2</sub>) in the influent (exiting the desorption column) and the effluent of the biofilter were measured with a portable device (BIOGAS 5000, Geotech, USA). The flow of the air supply to the column was measured with a calibrated rotameter (Cole-Parmer), and the flow of the wastewater was determined based on the volumetric capacity. The concentration of dissolved CH<sub>4</sub> in the influent and the liquid effluent of the desorption column were determined by pH, according to the method proposed by Souza et al. (2011) and Martí et al. (2012). A pH meter (Orion 4 Start 9157BNMD, Thermo Scientific, USA) was used to measure the pH of the influent and effluent of the desorption column and in the biofilter (filtering medium). The moisture content of the biofilter was determined by gravimetry.

## **Results and discussion**

Desorption of dissolved  $CH_4$ . Figure 2 shows the behavior of the  $CH_4$  concentration at the input and output of the column for the duration of the experiment. The percentage of  $CH_4$  in the desorbed gas was related to its concentration in the liquid effluent. Under condition I during the first 29 days of

operation, the average concentration of dissolved CH<sub>4</sub> was 12.5 mg/L; however, in output water measured at 20°C and at a gas stream of 80%, corresponding to the typical atmospheric pressure of Mexico City, a saturation concentration of 11 mg/L was obtained, indicating a low level of CH<sub>4</sub> removal. The concentration of CH<sub>4</sub> in the desorbed gas was 2.7%. Under condition II and an effluent:air ratio of 2:1, the CH<sub>4</sub> percentage in the desorbed flow increased to approximately 4.3%, resulting from an increasing flow of effluent to the column while maintaining the flow of air constant. Under the second set of operating conditions of the desorption column, 99% of the dissolved CH<sub>4</sub> in the effluent of the UASB reactor was recovered.



Figure 2. Concentration of CH<sub>4</sub> in the input (dissolved, mg/L) and output (gas, %) of the desorption column.

*Desorption of*  $H_2S$ . The concentrations of  $S^{2-}$  in the column input and of  $H_2S$  in the desorbed gas were 15 mg/L and 419 ppmv, respectively, corresponding to the first set of operating conditions and representing an average desorption efficiency of 28%. For the second set of conditions, 15 mg/L and 422 ppmv were obtained for an average efficiency of 32%. The desorbed  $H_2S$  did not follow the same tendency as  $CH_4$  given the dissolved level of  $S^{2-}$  in the effluent input to the column. In contrast to  $CH_4$ , the desorption of  $H_2S$  was directly related to the pH of the liquid effluent due to the dissolved gas on the pH of the effluent input to the desorption in the desorbed gas on the pH of the effluent input to the desorption column may be observed.



Figure 3. Concentration of  $H_2S$  in the desorbed gas on the pH of the anaerobic effluent at the entrance of the desorption column.

An inverse relationship existed between the pH of the wastewater input and the concentration of  $H_2S$  in the desorbed gas. As pH decreased, the concentration of  $H_2S$  in the gas increased, and vice versa. This was consistent with the equilibrium reaction for the dissociation of this compound in liquids. At pH = 7 in water,  $H_2S$  and its ionized form HS<sup>-</sup> are equally distributed (pKa = 7.0); when pH = 9, the  $H_2S$  form disappears, and the ionized form HS<sup>-</sup> becomes prevalent. This compound is further dissociated to S<sup>2-</sup> at pH > 11. The pH of the anaerobic effluent between days 35 and 59 was higher than 8.2, except three days; therefore, the recovery of gaseous  $H_2S$  was negatively impacted. Overall, the average pH of the input to the desorption column was 8, resulting in the low desorption efficiency of  $H_2S$ .

*Removal of CH*<sup>4</sup> *by the biofilter*. The change in the CH<sub>4</sub> load and the capacity for its removal are presented in Figure 4. During the first phase of biofilter use (day 1 to day 23), the CH<sub>4</sub> removal capacity increased until reaching an efficiency of 75%. An additional period (day 23 to 45) was observed during which the biofilter operated under inadequate conditions due to the flooding of the lower portion of the biofilter with wastewater proceeding from the desorption column, which caused a decrease in efficiency. Upon identifying this problem, the filtering material was removed, and the excess water was eliminated. The filtering material was then homogenized and returned to the biofilter (day 45). After three days of operation, the biofilter achieved stable values of CH<sub>4</sub> removal, returning to a recovery efficiency of 70–75%.



Figure 4. Input load and elimination capacity of CH<sub>4</sub> of the biofilter.

The average removal capacity of the biofilter was 42 gCH<sub>4</sub>/m<sup>3</sup>h, considering an average load of 60 gCH<sub>4</sub>/m<sup>3</sup>h, for an efficiency of 70%. The obtained results may be compared with the report of Turgeon et al. (2011), in which a biofilter was operated with a packed volume of 350 L of peat and wood. In this study, an average elimination capacity of 60 gCH<sub>4</sub>/m<sup>3</sup>h was obtained for an inlet load of 95 gCH<sub>4</sub>/m<sup>3</sup>h, showing an efficiency of 85%.

*Removal of*  $H_2S$  *by the biofilter.* The H<sub>2</sub>S was completely removed by the biofilter, which had a stable efficiency level of nearly 100%. The average inlet load (1.17 g/m<sup>3</sup>h) in this study was lower than that of Morgan and Noyola (2006), who used a compost biofilter to remove varying levels of H<sub>2</sub>S (4, 7 and 15 g/m<sup>3</sup>h). In addition, the EBRT (23 minutes) in our study was two orders of magnitude greater than other retention times reported in the literature (37 seconds, Allen and Yang, 1991; 48.6 seconds, Morgan and Noyola, 2006). However, this residence time was set based on the oxidation of CH<sub>4</sub> and not H<sub>2</sub>S, which has more rapid oxidation kinetics. The specific rates of consumption by the distinct methanotrophic microorganisms vary between  $7x10^{-3}$  and  $1.4x10^{-2}$  gCH<sub>4</sub>/g<sub>biomass</sub> h (Rocha et al., 2009), while for sulfur-oxidizing microorganisms, this rate is 0.53 g HS<sup>-</sup>/g<sub>protein</sub> h (Alcantara et al., 2002). The oxidation of CH<sub>4</sub> requires a longer retention time because its oxidation is limited by mass transfer processes and high hydrophobicity (Estrada et al., 2014). Taking into account these considerations, the retention time for the oxidation of CH<sub>4</sub> in compost biofilters has been between 4.5 minutes and 400 minutes; these times are associated with distinct CH<sub>4</sub> removal capacities (Nikiema et al., 2005, Plessis et al., 2003, Streese and Stegmann, 2003).

*Biofilter temperature and moisture content.* The temperature of the biofilter was monitored following day 46 of operation; an average value of  $42 \pm 9$  °C was measured, which was higher than the ambient temperature. This phenomenon was previously reported by Turgeon et al. (2011) yet has been scarcely mentioned in the literature on the biofiltration of CH<sub>4</sub>. This rise in temperature was due to the heat generated by the oxidation of CH<sub>4</sub>; this reaction is exothermic and has a  $\Delta H^{\circ} = -780$  kJ/mol of CH<sub>4</sub>. In Figure 5, the behavior of the temperature in the biofilter as a function of CH<sub>4</sub> recovery may be observed. Except the first 10 days, as temperature increased, the removal capacity also tended to increase, and the inverse occurred when temperature declined.



Figure 5. The temperature of the biofilter as a function of CH<sub>4</sub> removal capacity.

Initially, water was supplied daily and manually to the biofilter at a rate of 2 ml per  $m^3$  of treated gas, following the specifications of Moreno-Gutiérrez (2008). However, it was evident that a greater quantity was required, and water was increased to approximately 40 ml per  $m^3$  to a moisture content of 40% in the upper portion of the biofilter. This necessity was due to the high temperature registered inside the biofilter.

*Pressure drop in the biofilter*. The drop in pressure of the biofilter was  $3727 \pm 147.1$  Pa/m. Allen and Yang (1991) reported a drop in pressure of 1000 Pa/m for a biofilter destined for H<sub>2</sub>S removal with a diameter of 0.15 m and a packed height of 1 m. Morgan et al. (2003) found a drop in pressure of 1079 Pa/m for a biofilter 0.1 m in diameter and with a packed height of 1 m. The drop in pressure observed in the current study was greater than those reported in the literature, although the volume of the biofilter in the present study was also 20 times greater than those of the two above studies.

### Conclusions

The concentration of  $CH_4$  in the gas outlet of the desorption column was directly proportional to the concentration of gas dissolved in the liquid effluent. The desorption of  $H_2S$  occurred as a function of the pH of the liquid effluent.

Under the applied operating conditions and considering an average  $CH_4$  volume of 3.9% and 421 ppmv  $H_2S$  in the desorbed gas stream, the biofilter removed 75 and 100% of these gases, respectively. The  $CH_4$  removal capacity of the biofilter depended directly on the inlet load.

The average temperature inside the biofilter was  $42 \pm 9$  °C due to the heat generated by the exothermic reaction of the oxidation of CH<sub>4</sub>. Due to this characteristic of CH<sub>4</sub> biofiltration, the control of the moisture content of the filter medium is particularly important.

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## REFERENCES

- Alcantara, S., Velasco, A., Muñoz, A., Cid, J., Revah, S., Flores, E., 2004. Hydrogen Sulfide Oxidation by a Microbial Consortium in a Recirculation Reactor System: Sulfur Formation under Oxygen Limitation and Removal of Phenols. *Environ. Sci. Technol.* 38, 918-923.
  Allen E.R. and Yang Y., 1991. Biofiltration control of hydrogen sulfide emissions; Proceedings of Air and Waste Management Association 84th Annual meeting, Vancouver, Canada, June 16-21
  Allen E.R and Yang Y., 1994. Biofiltration Control of Hydrogen Sulfide 1. Design and Operational Parameters, *Air & Waste*, 44:7, 863-868,
  Chernicharo C.A.L, Van Lier J., Noyola A., Ribeiro T. 2015. Anaerobic sewage treatment: state of the art, constraints and challenges, Reviews in *Environmental Science and Bio/Technology* 14(4), 649-679.

- the art, constraints and chanenges, Reviews in Environmental Science and Dio Technology 14(4), 649–679.
  Estrada, J. M., Lebrero, R., Quijano, G., Perez, R., Figueroa I., Garcia, P., Muñoz, R., 2014. Methane abatement in a gas recycling biotrickling filter: evaluating innovative operational strategies to overcome mass transfer limitations. *Chemical Engineering*. 253, 385 393.
  Heffernan, B., Blanc, J., Spanjers, H., 2012. Evaluation of greenhouse gas emissions from municipal UASB sewage treatment plants, Journal of Integrative Environmental Sciences, 9, 127–127
- 127-137

- 127-137.
  Kevbrina, M., Okhakina, A., Akhlynin, D., Kravchenko, K., Nozhevnikova A., Gal, V., (2001). Growth of Mesophilic Methanotrophs at Low Temperatures. *Microbiologic*. 70, 444 451.
  Martí, N., Giménez, J.B., Ferrer, J., Seco, A., 2012. Methane recovery efficiency in a submerged anaerobic membrane bioreactor (SAnMBR) treating sulphate rich urban wastewater: Evaluation of methane losses with the effluent. *Bioresource Technology*. 118, 67 72.
  Morgan Sagastume, J.M., Noyola, A., 2006. Hydrogen sulfide removal by compost biofiltration: effect of mixing the filter media on operational factor. *Bioresour. Technol*. 97, 1546-53.
  Morgan Sagastume, J. M., Revah, S., Noyola, A., 2003. Pressure drop and gas distribution in compost-based biofilters: Medium mixing and composition effects, *Environmental Technology*, 24:7, 797-807.
  Moreno Gutiérrez, A., 2008. Efecto de la carga másica y altura del medio filtrante sobre la remoción de H2S mediante biofiltración. Tesis (Maestría en ingeniería ambiental). Ciudad de
- 24:7, 797-807.
  Moreno Gutiérrez, A., 2008. Efecto de la carga másica y altura del medio filtrante sobre la remoción de H2S mediante biofiltración. Tesis (Maestría en ingeniería ambiental). Ciudad de México, México, Universidad Nacional Autónoma de México, Instituto de ingeniería.
  Myhere, G., Shindell, D., Bréon, F., Collins, W., Fuglestvedt, j., Huang, J., Koch, D., Lamarque, J., Lee, D., Mendoza, B., Nakajima, T., Robock, A., Stephens, G., Takemura, T., Zhan, H., 2003. Antropogenic and Natural Radiactive Forcing. Clim. Chang. Phys.Sci. Basic. Contrib. Work. Gr. I to Fifth Assess. Rep. Intergov. Panel Clim. Chang. 659 740.
  Nikiema, J., Bibeau, L., Lavoie, J., Brzezinski, R., Vigneux, J., Heitz, M., 2005. Biofiltration of methane: An experimental study. *Chem. Eng. J.* 113, 111–117.
  Noyola, A., Capdeville, B., Roques, H., 1988. Anaerobic treatment of domestic sewage with a rotating-stationary fixed-film reactor. *Water Res.* 22, 1585–1592.
  Noyola A., Morgan Sagastume J.M. and López Hernández J.E., 2006. Treatment of biogas produced in anaerobic reactors for domestic wastewater: odor control and energy/resource

- produced in anaerobic reactors for domestic wastewater: odor control and energy/resource
- produced in anaerobic reactors for domestic wastewater: odor control and energy/resource recovery, Reviews in *Environmental Science and Bio/Technology*, 5, 93 114.
  Noyola, A., Padilla, Rivera, A., Morgan-Sagastume, J.M., Güereca, L.P., Hernández-Padilla, F., 2012. Typology of Municipal Wastewater Treatment Technologies in Latin America. *Clean Soil, Air and Water*. 40, 926–932.
  Onda, K., Sada, E., Takeuchi H., 1968. Mass Transfer Coefficients between Gas and Liquid Phases in packed columns. *Journal of Chemical Engineering*. 1, 56 62.
  Plessis, C., Strauss, J., Sebapalo, E., Riedel, K., 2003. Empirical model for methane oxidation using a composted pine bark biofilter. *Fuel* 82, 1359–1365.
  Rand, M. B., Cooper, D. E., Woo, C.P., Fletcher, G. C., Rolfe, F. K., 1981. Compost filters for H2S removal from anaerobic digestion and rendering exhausts. J. WPCF 53, 185–189.
  Rocha, R., J., Bordel, S., Hernández, S., Revah, S., 2009. Methane degradation in two-phase partition bioreactors. *Chem. Eng. J.* 152, 289–292.
  Souza, C.L., Chernicharo, C. L., Aquino, S.F., 2011. Quantification of dissolved methane in UASB reactors treating domestic wastewater under different operating conditions. *Water Sci. Technol.*

- Souza, C.L., Chemienaro, C. L., Aquino, S.F., 2011. Quantification of dissorved filediate in 07455 reactors treating domestic wastewater under different operating conditions. *Water Sci. Technol.* 64, 2259–64.
   Souza, C.L., Chernicharo, C. L., Melo, C.B., 2012. Methane and hydrogen sulfide emissions in UASB reactors treating domestic wastewater. *Water Sci. Technol.* 65, 1229–37.
   Straces L. and Stagman R. 2003. Miarchiel evidetion of methane from old landfills in hiofiltare.

- Streese J. and Stegman R., 2003. Microbial oxidation of methane from old landfills in biofilters. Waste Management, 23, 573–580
  Turgeon, N., Bihan, Y., Buelna, G., Bourgault, C., Verreault, S., Lessard, P., Nikiema, J., Heitz, M., 2011. Application of methanotrophic biofilters to reduce GHG generated by landfill in Quebec City (Canada). WIT Transactions on Ecology and the Environment, 147, 387 397.
- U.S. Environmental Protection Agency (USEPA), Global mitigation of non-CO<sub>2</sub> greenhouse gases, 2006, http://www.epa.gov/climatechange/economics/downloads/GlobalMitigationFullReport.pdf.