Desulfurisation of biogas by biofiltration

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ABSTRACT

A biofiltration system to eliminate volatile fatty acids (VFAs) and hydrogen sulfide (H_2S), using a microbial consortia, was established. The characterization of lava rock, vermiculite and glass rings, as potential packing materials, was previously performed. Vermiculite showed higher VFAs degradation rates than the ones obtained using lava rock; however, some compaction was noticed when this material was used as support. In the lava rock biofilter (1.7 L packed volume) acetic (AA) and propionic (PA) acids were completely removed from the gas and liquid phase, reaching 100% of removal efficiency (RE). Maximum elimination capacities (EC_{max}) for AA and PA in gaseous phase were 15.2 and 24.5 $g/m^3_{bioifilter}h$, respectively; while in the liquid phase an EC_{max} of 76.3 and 122.5 $g/m^3_{bioifilter}h$ were attained. Empty bed resident times (EBRT) of 85 and 31 s were assessed for increasing H_2S inlet loads (36 - 396 g/m^3h) into the biofilter. At 85 s, an EC_{max} of 142 $g/m^3_{bioifilter}h$ was determined, with RE of around 99% for all the evaluated inlet loads. At 31 s, a maximum EC of 232 $g/m^3_{bioifilter}h$ and a RE of 95 % were found. Complete removal of VFA and H_2S from the biogas was obtained in the lava rock biofilter.

1 INTRODUCTION

Recent data showed that in 2005 around 12,500 ton/day of waste were produced in Mexico City (INEGI, 2005), the limited landfill capacity and the demand for sustainability technologies for the reduction and treatment of the solid waste are becoming increasingly necessary. Anaerobic digestion systems (ADS) are an effective technology for the reduction of the organic matter and the simultaneous production of energy when they are efficiently applied for treating municipal solid waste and sewage of water treatment plants. The process is environmentally friendly and cost effective because the heat required is generated by bacterial action, few additions of chemicals

are needed, and the final product can be readily applied. The main products of the process are carbon dioxide (CO_2) and methane (CH_4), but minor quantities of nitrogen, hydrogen, ammonia, VFAs and H_2S (1000- 3000 ppm) are also generated (Angelidaki *et al*., 2002). CH_4 can be utilized to generate different forms of energy (heat and electricity) or be processed for automotive fuel, but VFAs and H_2S are toxic and odorous. Many different types of control for these compounds have been successfully used, including chemical scrubbers, activated carbon, and biofilters. Some studies have demonstrated that biofilters can readily handle the odorous and toxic air coming from ADS in a cost-effective and low-maintenance manner (Pride, 2002). Biofiltration is one of the most promising clean technologies for reducing emissions of pollutants into the atmosphere (van Groenestijn and Hesselink, 1993). This technology based on microbial degradation of compounds from a gas stream is considered an attractive alternative when compared to chemical and physical treatments. It is economic and environmental friendly since generates less residues that others technologies, due to total biological oxidation of the pollutants. Many studies have been conducted to study the design and operational parameters, as well as the microbial process involved in biofiltration systems, showing that the system effectively controls and removes odors in diluted gas streams contaminated basically with sulphur compounds (Yang and Allen, 1994; Smer *et al*., 1998; Ergas *et al*., 1995; Morton and Caballero 1998).

In the biofiltration process the type of packing materials is essential for a proper performance. The support material acts not only as a surface for microbial growth, it also provides the water required to promote the metabolic activity and in some cases can also act as buffer in shielding microorganisms from inhibitory substances while adsorbing high initial concentration of substrate and progressively releasing it for microbial degradation of some sulphur compounds (Ng *et al.*, 2004). In some literature reports, various materials have been used as the support media for microbial growth and significant differences have been reported in the performance of biofilters for H_2S removal packed with different materials. Van Langenhove *et al.* (1986) used wark woods, Hirai *et al.* (1990) used peat, Yang and Allen (1994) used compost, Chung *et al.* (1996) used calcium alginate pellets, Morton and Caballero (1998) used lava rock and Wani *et al.* (1998) used various mixtures of compost-perlite hog fuel. Cedar Rapids reports and discusses the issues of the selection of the packing materials and provides insight on some potential beneficial properties of lava rock (Martin *et al.*, 2002).

H_2S elimination, as the main odor compound, has been extensively studied in biofiltration systems (Cho *et al.*, 2000; Oyarzún *et al.*, 2003; Ng *et al.*, 2004; Duan *et al.*, 2006). Less is known about the aerobic degradation of VFAs, the anaerobic elimination of VFAs from waste water has been proved in biofilters and biotrickling filters. Yun and Ohta (1997) reported the characteristics of the microorganisms capable of assimilating VFAs, as their sole source of carbon and energy, and more recently

describe the feasibility of the removal of VFAs by an immobilized strain of *Rhodococcus* sp (Yun and Ohta, 2005).

The main goal of this work was to couple a biofilter to an ADS while treating vegetable waste in order to eliminate the malodors pollution and the H_2S produced during the anaerobic process. Potential packing materials for the biofiltration systems were characterized and the biofilter performance to degrade VFAs as well as high concentrations of H_2S was determined. Different substrate loads and empty bed resident times were also evaluated to characterize the biofiltration system.

2 MATERIALS AND METHODS

2.1 Microbial culture and packing material

A microbial consortium was cultivated in 2 L Erlenmeyer flask with 1 L of mineral media and enriched with VFAs by injecting a gas stream saturated with these acids. The same consortia were adapted to sulfur compounds by adition of sodium thiosulphate ($Na_2S_2O_3$) in the mineral media. The mineral media contains (g/L): $(NH_4)_2SO_4$, 3; KH_2PO_4, 0.6; K_2HPO_4, 2.4; $MgSO_4 \cdot 7H_2O$, 1.5; $CaSO_4$, 0.15; $FeSO_4$, 0.03. The supports evaluated as potential packing materials for the biofiltration systems were: vermiculte, glass rings and lava rock. Characterization of these packing materials was performed by using standard methods. The three different support materials were packed in the biofilter. *In situ* immobilization was facilitated by recirculation of the microbial culture previously adapted to VFAs and $Na_2S_2O_3$ using a peristaltic pump, at a flux of 0.11 L/min.

2.2 Microcosm

4 g of the packed material with the immobilized biomass were introduced in serum bottles of 125 ml of total volume. Initial concentrations of 40 mg/L of acetic, propionic, butyric and valeric acids were injected separately to determine its consumption.

Headspace samples were periodically taken to evaluate the CO_2 production due to the VFAs assimilation.

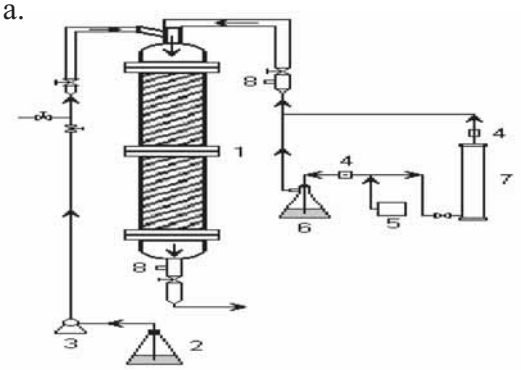
2.3 Experimental setup

2.3.1 VFA consumption

Lava rock biofiltration system (Figure 1a) consists in a glass column of 0.94 m length and 5.5 cm of internal diameter (1.7 L of packed volume). An empty bed residence time EBRT of 120 s was used for VFAs elimination tests. The gas stream was humidified and fed at the top the biofilter using a mass flow controller. Different loads of the VFAs were introduced into the biofilter to evaluate its performance (from

6.1 to 24.5 $g/m^3_{bioifilter}h$). Sample ports were located in the output and input of the gas stream. Gas samples were taken directly using gas tight syringes.

a.



b.

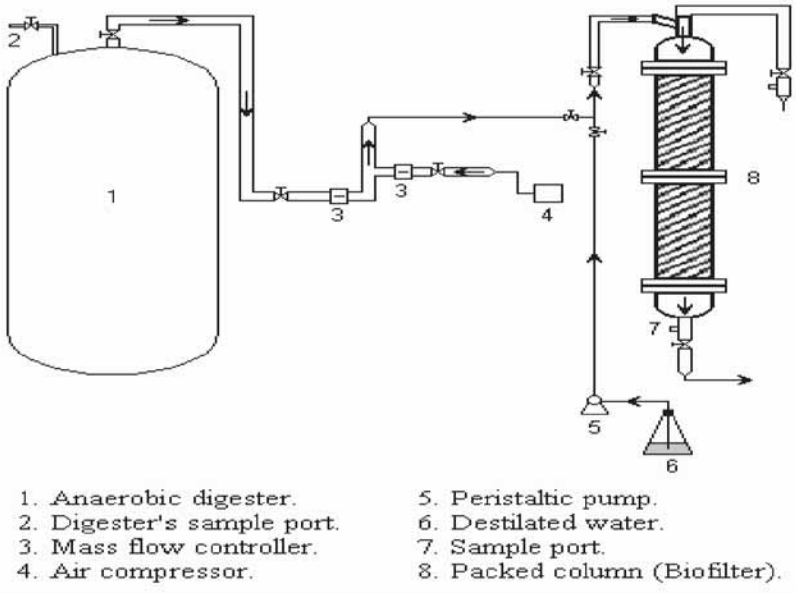


Figure 1. Experimental systems packed whit lava rock: a. Configuration used for VFAs elimination test, b. biofiltration system coupled to the ADS used to evaluate H_2S consumption.

2.3.2 H_2S consumption

H_2S removals were determined in the biofiltration system coupled to the ADS. The scheme is shown in Figure 1b. The biofilter (1.7 L volume) was packed whit lava rock. Different amounts of humidified air were mixed with the biogas stream and fed into the biofilter to obtain increasing H_2S inlet loads, from 36 to 144 gH_2S/m^3h for an EBRT of 85 s and from 99 to 396 gH_2S/m^3h when an EBRT of 31 s was established.

2.4 Analytical methods

CO_2 productions were measured by injecting headspace samples of the microcosms in a gas chromatograph (GowMac) equipped with a thermal conductivity detector. A CTR1 packed column was used for the analysis. Temperatures in the column, injector and detector were 30, 75 and 120ºC, respectively. Helium was used as the carrier gas at a flow of 65 mL/min. VFA in the biofilter samples were measured using a gas chromatograph (Buck Scientific) equipped with a flame ionization detector and a 4 - 6.9 feet packed column (Hayesep R 80/100 Mesh, Chromatography Research Supplies, Inc, Louisville, USA). The column temperature was 190ºC and the injector/detector temperature was 200ºC. Nitrogen was used as the carrier gas at a flow of 30 mL/min. Data integration was accomplished by Peak Sample software. Inlet and outlet H_2S concentrations were determined using a H_2S analyzer Jerome 631-X (Arizona Instruments LLC, USA).

3 RESULTS AND DISCUSSION

3.1 Packing material characterization

Density, water retention capacities (WRC), pH and particle size distribution of the different packing materials were determinated. Moisture is one of the most important parameters for the development of the biofilm and the microbial activity. The WRC of the packing materials were different, vermiculite exhibited the higher WRC (65%) compared with lava rock and glass rings.

Vermiculite has been reported as a good packing material; its water retention capacity was high compared to those obtained with the other materials, however, when mineral medium was circulated in the reactor to favor the biofilm establishment, some disintegration of the particles was noticed, reducing the original volume and provoking some compaction. The glass rings showed the lower value of water retention; however this material was evaluated because its good mechanic characteristics that could allow water addition by irrigation in order to maintain the moisture in the biofilter. Lava rock showed a WRC of 15%, which was lower to the one reported by Cho *et al.* (2000). These authors evaluated the physical characteristics of lava rock, used as support for malodorous gases (H_2S, methandiol, dimethyl sulfide and ammonia) removal, WRC between 25 and 47% were determined in this study.

Similar initial pH was obtained for vermiculite and for glass rings, 6.7 and 6.9, respectively, while a pH of 8.1 was measured for lava rock. The pH in the biofiltration systems is an important factor for its application, lower pH inhibits the activity of the deodorizing microorganisms, it was reported that the deodorization efficiency significantly decreases at lower pH values. The VFA and other intermediate products could provoke a drop of the pH in the biofilter. Thus, buffering capacity of a carrier, to resist pH change, is important to maintain biological activity for a long term biofilter operation (Cho *et al.*, 2000). Yun and Ohta (2005) reported the necessity of controlling de initial pH between 8 and 9 for the effective removal of VFA by *Rhodococcus* sp. B216. The results of the physic properties (WRC and initial pH) showed that vermiculite and lava rock were of potential interest to be used as packing materials for eliminating VFAs. However, for effective removal of the pollutant's odors within the biofiltration system is essential to evaluate the microorganisms adhesion and the microbial activity in these supports.

3.2 VFA CONSUMPTION EXPERIMENTS IN MICROCOSMS

Once the different packing materials were physically characterized, they were packed in the biofilter divided into two separate sections each one packed with one of the supports and divided by using a Teflon mesh. The biofilm in the packed material was obtained by a periodic circulation of mineral medium containing the microbial community, previously adapted with acetic acid for one month. Once a visible growing was evident, after approximately 2 weeks, initial VFAs concentrations of approximately 40 mg/L were injected, as only carbon and energy sources in closed systems.

The evolution of the CO_2 production was periodically determined, as a measure of the substrate assimilation. Data obtained with the microbial community developed in vermiculite are presented in Figure 2a, the degradation started after the first hours of culture, showing a short adaptation period. The substrates were oxidized in different extends as it is presented in Table 1, acetic, butyric and valeric acids were almost completely mineralized to CO_2, obtaining 84, 85 and 88 % of conversion, respectively, in approximately 40 hours of cultivation. Meanwhile, less extent of transformation was determined for propionic acid. Using the theoretical estoichiometric equation a degradation rate could be calculated, the degradation rates are summarized in Table 1. A higher degradation rate was attained with acetic acid compared to those rates obtained with the others VFAs evaluated. A similar analysis was performed using the microbial community attached to lava rock, the CO_2 productions are presented in Figure 3b, VFA degradation started during the 10 hours of cultivation, acetic, propionic and valeric acids were 79, 68 and 77% mineralized to CO_2 (Table 1), butyric acid was only partially degraded obtaining for it a 55% of mineralization.

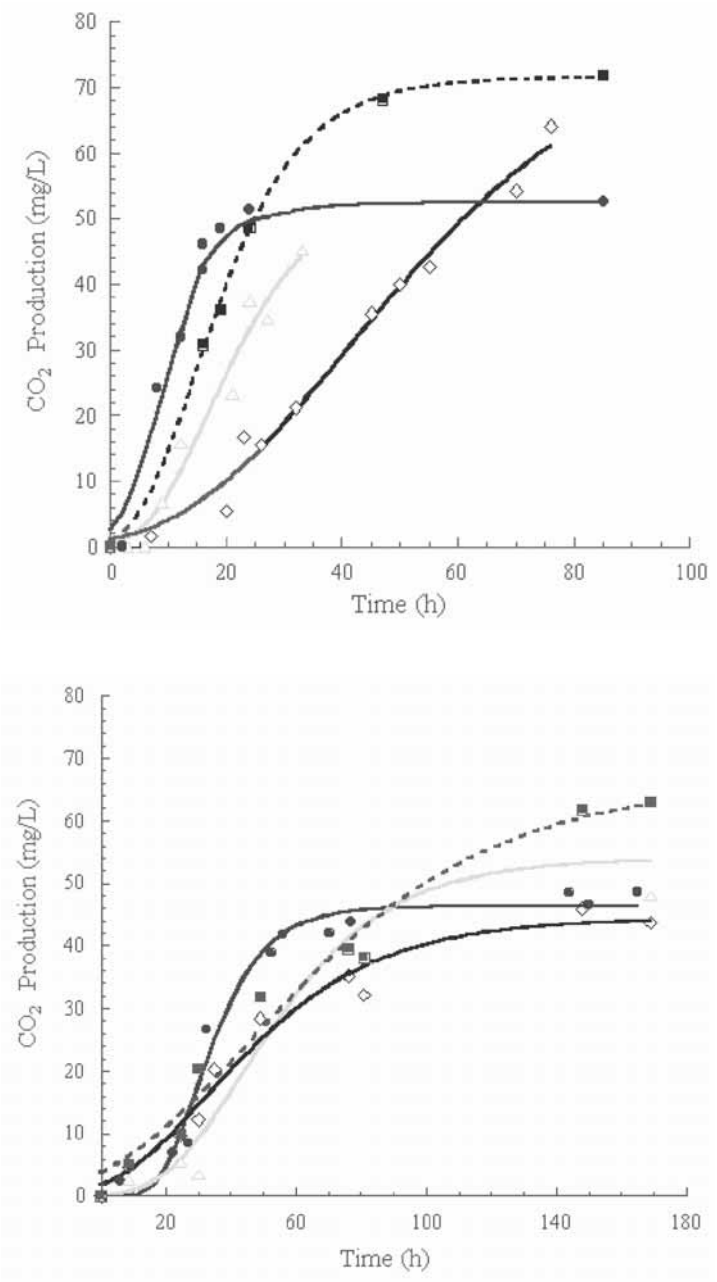


Figure 2. $C0_2$ produced by the assimilation of VFA; —●— acetic acid, —△— propionic acid, —◇— butyric acid, --■-- valeric acid, respectively in microcosm's.
Data obtained from the biofilm developed in vermiculite (a) and lava rock (b).

Higher amount of biomass was established in vermiculite (8.5 x 10^5 UFC/g) compared to the biomass determined for lava rock (6.5 x 10^4 UFC/g). This was a possible explanation for the better activity (higher VFAs elimination rates) determined in the vermiculite samples. This fact was also correlated with the WRC, vermiculite showed higher WRC (65%) compared to the one of lava rock WRC (15%), which allowed both, better growth and metabolic activity.

Table 1.
Removal efficiency and degradation rates obtained with the microbial consortium developed in three packing materials evaluated with four VFA.

Acid	Packing Material					
	Glass Rings		Vermiculite		Lava rock	
	Removal Efficiency (%)	Removal Rates (mg/Lh)	Removal Efficiency (%)	Removal Rates (mg/Lh)	Removal Efficiency (%)	Removal Rates (mg/Lh)
Acetic	-	-	84	1.46	79	0.41
Propionic	-	-	64	0.94	68	0.37
Butyric	-	-	85	0.42	55	0.16
Valeric	-	-	88	0.71	77	0.24

Less biofilm development was obtained using the glass rings, no biological activity with the VFA as substrate was detected. These results could be due to the low water retention capacity of this support, probably the lower water content inhibit the metabolic activity of the microbial community. Yun and Ohta (2005) reported the elimination of high concentrations of acetic, propionic, butyric and valeric acids from a waste-food solution by immobilized cells of Rhodococcus sp. B261, the consumption of the VFA was initiated after 48 hours, then acetic and propionic acids were removed in 64 hours. Butyric and valeryc acids were depleted in 72 hours. During the present study, acetic, propionic and valeric acids were degraded in low concentration by the microbial consortium fixed in vermiculite and lava rock, while the butyric acid was partially removed. Higher degradation rates were obtained with the microbial biofilm developed in vermiculite. However, under biofiltration conditions, in the section packed with vermiculite some compaction and fungal growth was noticed due to the drought of the support and the fast decrease of the moisture.

3.3 VFA CONSUMPTION UNDER BIOFILTRATION CONDITIONS

Based on the preliminary results, lava rock was used as packing material in the biofilter. Since the main goal of the present study was to eliminate the malodors

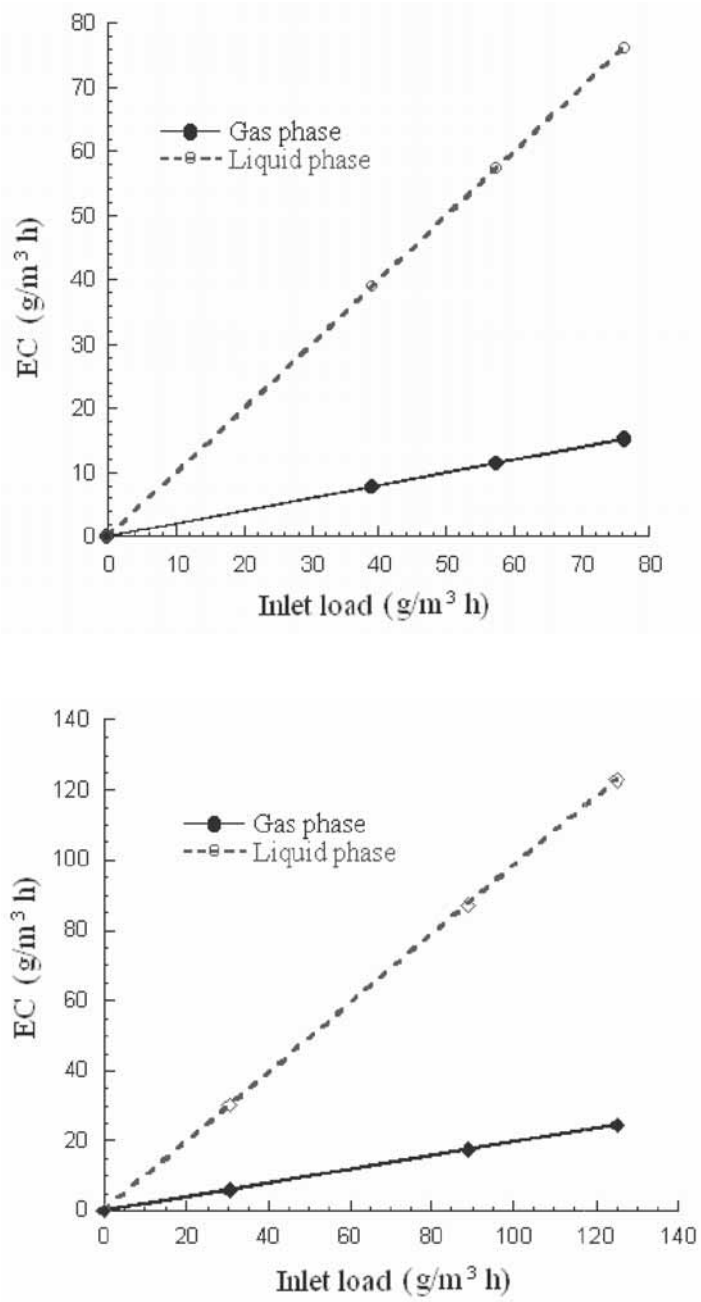


Figure 3. Relationship between inlet load and elimination capacity of lava rock biofilters to acetic acid (a) and propionic acid (b).

pollutants emitted in the ADS by using a biofiltration system, and considering that during the initial phase of the anaerobic digestion process high amounts of VFA (mainly acetic and propionic acids) was produced. Some experiments were performed to evaluate the VFA elimination under biofiltration conditions. Increasing inlet loads of acetic and propionic acid were fed into the biofilter. In Figure 3a and 3b the elimination capacities (ECs) vs the inlet loads obtained with acetic and propionic acid, respectively, are presented. All the inlet concentrations of the pollutant evaluated were 100% removed. Considering that VFA are highly soluble in the liquid phase, and the relation of water/gas in the biofilter was around 5 (288g of water, for an initial moisture of 55%, and 1.12L of air), an EC in the liquid phase could be calculated and it is shown in Figure 3.

The EC obtained for acetic and propionic acids are in the range of the EC reported for the elimination of other compounds in biofiltration systems. The system reached an EC of around 120 g/m^{3}h of the propionic acid with 100% of removal efficiency. Higher inlet loads were not evaluated to avoid saturation and accumulation of the VFA in the liquid phase. An important decrease in the pH, to values around 4.3, was determined in the biofiltration when the experiments were performed, enhanced acetic and propionic acids removals could be expected by controlling and adjusting the pH, which increases the immobilized cells number. Yun and Ohta (2005) demonstrated that higher valeric acid removal rate was obtained when the pH was between 8 and 9 and more cells were immobilized and developed in the ceramic support, attaining 1.4 x 10^{9}CFU/g-ceramic beads.

3.4 H_2S elimination in the biofiltration system

The evolution of the elimination capacity with different H_2S inlet loads is shown in Figure 4. At EBRT of 85 sec. (Figure 4a) increasing H_2S inlet loads of 50, 80, 120 and 150 g/m^{3}h were 99% removed by the biofiltration system, reaching a maximum EC of 148 g/m^{3}h. When the EBRT was reduced to 31 sec. (Figure 4b), H_2S inlet loads of 100 and 200 g/m^{3}h were complete degraded (100% removal efficiency), an increment in the inlet load to 300 g/m^{3}h reduced the removal efficiency in the system to 90%, inlet load of 400 g/m^{3}h inhibited the biological activity and the removal efficiency dropped to 50%, this load corresponds to a very high concentration of pollutant, as high as 1500 ppm of H_2S. A maximum EC of 232 g/m^{3}h was reached by the biofiltration system, which is three times higher that those reported by Cho *et al.* (1991) and Ootani *et al.* (1991), using a *Thiobacillus* sp. HA43 and an activated sludge, respectively. Similar to the ones obtained by Cho *et al.* (2000), these authors reported EC of around 342 and 428 g/m^{3}h (Table 2).

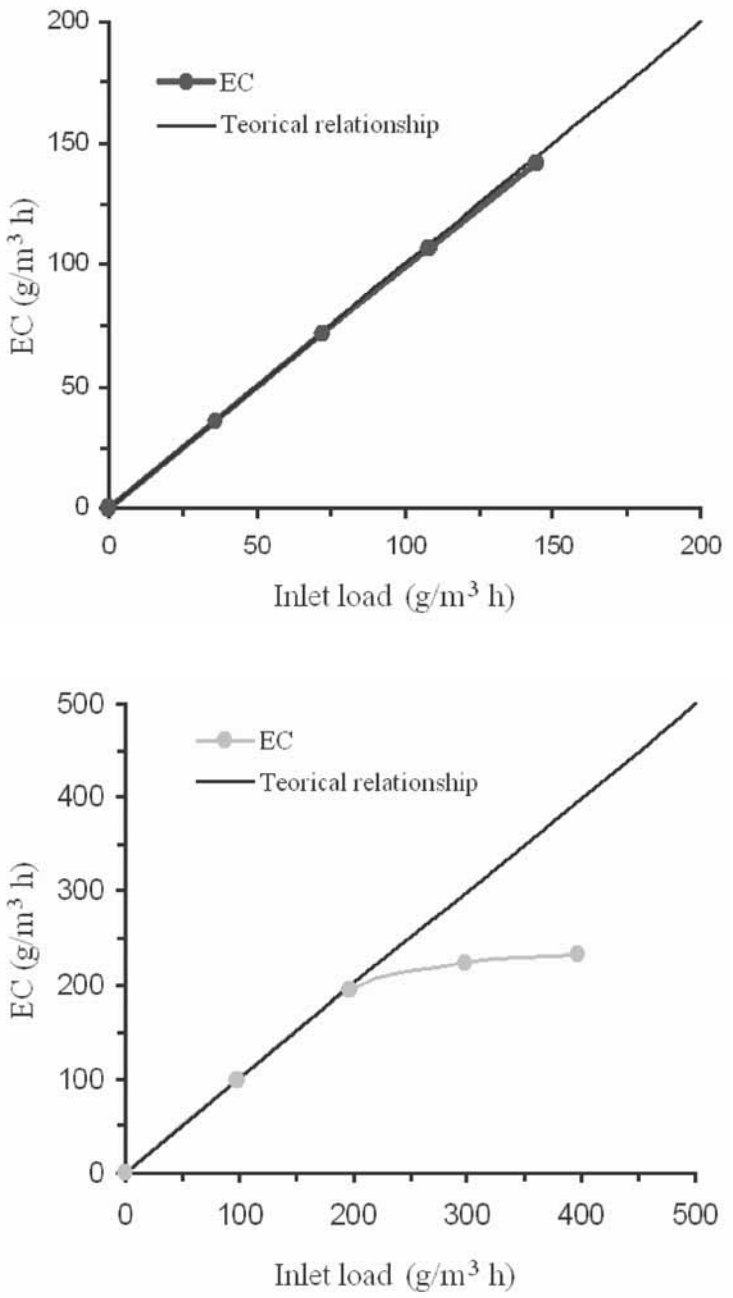


Figure 4. Relationship between inlet load and elimination capacity of lava rock biofilters to H_2S at an EBRT of 85 s (a) and 31 s (b).

Table 2.

Reference	EC_{MAX} (g/m^3h)
Wani *et al*., 1998	120
Cho *et al*., 2000	392
Park *et al.,* 2001	7
Oyarzún *et al.,* 2003	55
Ng *et al.,* 2004	52
Duan *et al.,* 2006	181
This work	**232**

4 CONCLUSIONS

The microbial consortium, previously adapted to VFA and $Na_2S_2O_3$, showed higher biological activity for the degradation of propionic, butyric and valeric acids when it was immobilized in vermiculite, compared to lava rock and glass rings. No biological activity was detected in glass rings due to its low water retention capacity. However, humidity losses which in turn allowed fungal growth in vermiculite provoked compaction of this support under biofiltration condition. Analyses conducted in the lava rock biofilter demonstrated that the acetic and propionic acids were completely removed from the gas and liquid phase at increasing concentration, reaching 100% of removal efficiency in all the evaluated concentrations. Tests with the ADS stream showed that all the components of the gas phase are almost completely removed in the biofilter. The results strongly suggest the feasibility of the biofiltration system to degrade and eliminate VFA and H_2S emitted from the ADS. This will allow both, to eliminate the odors problems and the removal of the H_2S in order to use the biogas as an alternative source of energy.

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