

Biofiltration of Volatile Organic Compounds of Brazilian Gasoline

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ABSTRACT

Gasoline vapors pollute the atmosphere and can be harmful to human and animal health. Tons of particles of this pollutant are expelled to the atmosphere, generating great economic losses to the industries and serious damage to the environment. Biofiltration is an option of simple technology with low costs that can be used for the gasoline vapor treatment. The present study was carried out in two biofilter systems of laboratorial scale. The biofilter system 1 was operated with a total volume of 2.72 L (four columns) and the biofilter 2 with 2.04 L (three columns) of total volume. Both of them were operated in sequence, with airflow of 450 mL entering each one. Results obtained were as follows for the removal efficiency (RE) of different gasoline vapor concentrations in the air: 1.3 g.m⁻³ during 35 days, RE of 100%; 3 g.m⁻³ during 52 days, RE of 90%; 4.5 g.m⁻³ during 48 days, RE of 70-80% and 8g.m⁻³ during 28 days, RE of 70%.

Key words: biofiltration, volatile organic compounds, gasoline, atmospheric pollution

INTRODUCTION

Many petrochemical industries and refineries are getting more concerned toward the losses involved in the emissions of volatile organic compounds (VOC) to the atmosphere. These losses bring consequences as damages to the health of the workers, to the environment and also huge financial losses, because tons of products are thrown in the atmosphere. Atmospheric contamination by gasoline's vapors can be associated to the storage, distribution, supply of vehicles as long as the remediation of impacted areas due to accidental spilling of fuel and refined products. Impacted areas usually are submitted to a remediation process for vapor extraction from the ground (SVE-soil vapor extraction), or

ventilation (air sparging). The contaminated air from the generated from the fuel and from the soil remediation need an appropriated vapor treatment before releasing to the atmosphere. The recovery of gasoline's volatiles helps to reduce the risks to the environment and the health of workers, customers and the neighborhood of the plants that produce, store, or commercialize it (Soares 2006). Biofiltration is the biological removal of pollutants by immobilized aerobic microorganisms on a porous and solid matrix. Inside each biofilters, the air passes through a biologically active filling material where the organic or inorganic pollutants are degraded by the microorganisms and used as the only source of carbon and energy (Converti and Zilli 1999). Pollutants are degraded to carbon dioxide and water, or incorporated into biomass

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(Hodge and Deviny 1994). The pollutant is removed from the air by dissolution, sorption and bio-oxidation; in other words, it is dissolved into the active biofilm and adsorbed by the support, being available for biological oxidation, a process that remains dynamically (Soares 2006). Biofiltration processes can be economic and efficient due to their low operational and capital costs, together with the effective removal of the pollutant, low pressure drop and their ability to treat acid-producing contaminants (Gerrard et al. 2010).

In the USA, the maximum of ethanol allowed concentration is 10%, while in Europe it is only 5%. For economic and environmental reasons, "C gasoline" is commercialized in Brazil. "C gasoline" is a mixture of gasoline with 20-25% (V/V) of ethanol (Rizzolo et al. 2012). In Brazil, flex fuel cars, i.e. vehicles that can run both with gasoline and ethanol, were firstly commercialized in 2003. Since then, production increased continuously, reaching 87% of national car production in 2010 (ANFAVEA 2009).

The objective of the present study was to evaluate the performance of two biofiltration systems at laboratory-scale exposed to increasing Brazilian gasoline ("C gasoline", with 20-25% of ethanol) concentrations, related to the total petrol hydrocarbon (TPH) degradation.

MATERIAL AND METHODS

System of biofiltration

Two lab-scale biofiltration systems were used under identical conditions, operating in parallel. The biofiltration system 1 (BS1) was fitted with four columns placed in sequence and the

biofiltration system 2 (BS2) with three columns, also placed in sequence. The columns were made of glass with 6.6 cm of internal diameter and 20 cm of bed height and 680 mL of working volume each. The BS1 had a total volume of 2.72 L (four columns) and the BS2 2.04 L (three columns). To maintain the temperature of the columns, they were immersed into a warm bath maintained at 30°C, supported by the collector bottles fixed to the bottom tank by claws. Periodically, the columns were humidified with Bushnell Hass mineral medium, sprinkled at the top of each one to avoid bed drying. The liquid that passed through the column was recovered at these collector bottles placed at the bottom of the columns. The gasoline used in this work contained 20-25% of ethanol (C gasoline).

Support

The medium support was constituted by organic compound product obtained from the composting process and from tire scraps in the ratio of 2:1 (in volume). The organic compound used was mainly organic matter obtained through the biological decomposition of vegetable scraps and animal waste by microbial action during the composting process. The company that provided the organic compost applied a technology for rapid composting of organic waste, such as sludge from the sewage treatment plants, organic fraction of urban waste and tree pruning. The materials were sifted out to select the particles between 2.8 – 4.2 mm. Tire scraps were prepared by cutting the old tires into small pieces. The biofiltration process was carried through during 190 days in the mounted biofilters as shown in Figure 1, with ascending air flow at the columns.

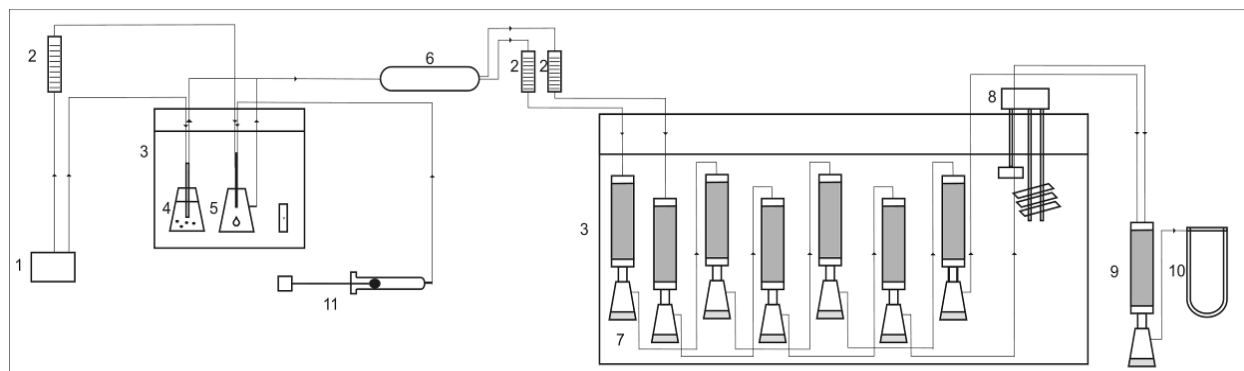


Figure 1 - Biofiltration setup: (1) Compressor; (2) Flowmeters; (3) Bath 30°; (4) Humidifier; (5) Fuel reservoir; (6) Mixer; (7) Columns; (8) Thermostat; (9) Charcoal column; (10) Pressure control system; (11) Syringe pump to feed the air contamination.

The air-flow was generated by a compressor at a rate of 900 mL.min⁻¹ (450 mL.min⁻¹ for each biofilter), resulting in six min of total retention time of the contaminant in BS1 and 4.5 min in BS2. The retention time was a relative measure of the contaminant residence time in the empty bed. Air enters into the system through two parallel lines: one for humidification and other to promote the volatilization of gasoline.

System to feed the contaminant

C gasoline was fed at the systems through a syringe pump (11), controlled by a plate for electronic assembly StepLab with microcontroller codified to pump a desired amount of fuel into the fuel reservoir (5) (beginner's all-purpose symbolic instruction code step). The gasoline was dripped into the fuel reservoir (5) kept at 30°C that also received air from the compressor at a flow of 100 mL.min⁻¹, enough to evaporate and carry the C gasoline contaminant to the mixer reservoir (6). The bottle of humidification (4) received the remaining air outflow of 800 mL.min⁻¹; the gasoline vapor and humid air flows were directed to a mixer (6). Then, the homogenized gas was divided in two flows to feed the two system filters (Fig 1).

The columns were humidified weekly with the mineral medium for nitrogen supplementation, minerals supply and to buffer and humidify the bed. Also, weekly the liquid that drained from the columns recovered at the flask placed at the bottom of each one was recirculated to the top of the columns. During the experiment to evaluate the systems performance the following gasoline vapor concentrations at the inlet air were tested: 1.3 g.m⁻³; 3 g.m⁻³; 4.5 g.m⁻³ and 8 g.m⁻³. The following operational parameters were evaluated:

Control of the flow

It was carried out by measuring the flow-meters (2).

Loss of load

It was determined by the measurement in distinguishing manometers of pipe in U filled with water; the result was expressed in mmH₂O.

Empty bed retention time (EBRT - empty bed residence time in minutes)

$$EBRT = \frac{V}{Q} \quad (\text{min})$$

Where EBRT (min), V: biofilter volume (m³) and Q: gas flow (m³.min⁻¹).

Elimination capacity (EC)

$$EC = \frac{Q(C_{in\ gas} - C_{out\ gas})}{V} \quad (\text{g.m}^{-3}.\text{h}^{-1})$$

Where EC (g.m⁻³.h⁻¹), Q: gas flow (m³.h⁻¹), C_{in}gas and C_{out}gas: TPH concentrations at the inlet and outlet of the biofilter, respectively, (g.m⁻³) and V: biofilter volume (m³).

Organic load (OL)

$$OL = \frac{C_{in\ gas}Q}{V} \quad (\text{g.m}^{-3}.\text{h}^{-1})$$

Where OL (g.m⁻³.h⁻¹), C_{in}gas: TPH concentration at the biofilter input (g.m⁻³), Q: gas flow (m³.h⁻¹), V: biofilter volume (m³).

Removal efficiency (RE)

$$RE = \frac{(C_{in} - C_{out})}{C_{in}} 100 \quad (\%)$$

Wherein ER (%), C_{in}gas and C_{out}gas: TPH concentrations at the inlet and outlet air of the biofilter, respectively, (g.m⁻³).

Chromatographic analysis

The analysis of the TPH was done using a gas chromatograph (CG) Schimadzu, model CG 17A, with detector of ionization of flame (FID - flame ionization detector). The chromatographic column used was a Hewlett-Packard, capillary column model HP-5 (Crosslinked 5% ME Siloxane), of 30 m length, 0.32 mm of internal diameter and film with 0.25 μm of thickness (Soares 2006). The temperature of the injector and detector were 300 and 225°C, respectively. The oven was programmed with a following temperature ramp initiating with 30°C, held for 5 min; elevation 2°C.min⁻¹ until reaching 40°C; elevation 25°C.min⁻¹ until 225°C maintained for 2 min; elevation 25°C.min⁻¹ up to 250°C and maintained for 2 minutes. In these conditions, the analysis time was 22.4 min. Each 15 days, the pH of the filters was evaluated through analytical ribbons, measured in the liquid that drained from the column during the humidification of the biofilters with mineral solution.

RESULTS AND DISCUSSION

The pH remained constant during the experiment around 7.0, considered excellent value for the microbial growth. The pressure drop of load was measured during the whole experiment time. At the end of the experiment, for BS1 the pressure drop was of 23 mm of H₂O and for BS2, it was of 30 mm H₂O. The pressure drop could be caused by several reasons, such as the compactation of the support and the microbial growth occupying the empty spaces. Considering the fact that the pressure drop was higher at BS2 with one column less, this condition led to a bigger organic load applied to the BS2, favoring the microbial growth, causing further pressure drop compared to the

BS1. This would also explain why the removal efficiency of both biofilter systems were similar even with BS2 having one column less. Soares (2006), working with the same apparatus of the present study, obtained for compost support, pressure drop of 11 and 13 mmH₂O for one column and for two columns in series, respectively. Using tire scraps as support, the system showed 9 and 12 mmH₂O for one and two columns in series, respectively after 210 days of biofiltration. Figures 2 and 3 present the removal efficiency of BS1 and BS2 along the experiment days for each gasoline concentration along with the concentration of inlets and outlets during the operating time.

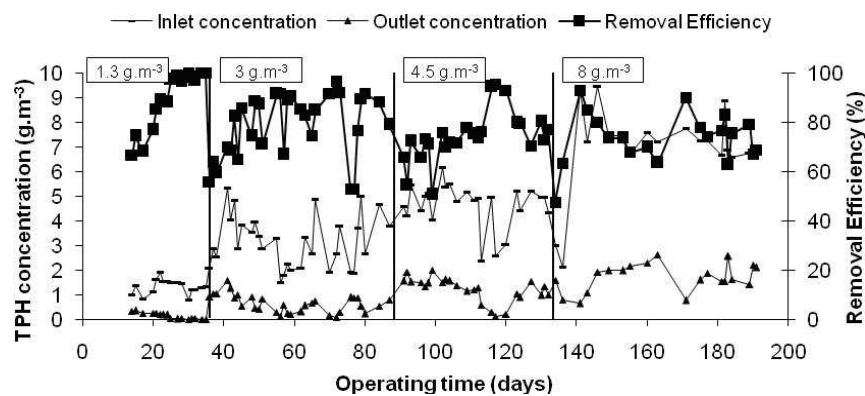


Figure 2 - Biofiltration system 1 performance, measured in the exit of the fourth column.

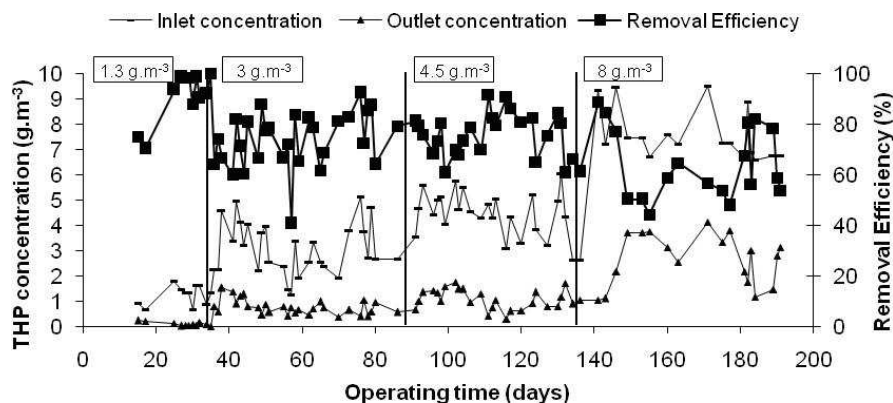


Figure 3 - Biofiltration system 2 performance, measured in the exit of the third column.

Even having a syringe pump to feed the contaminant to the biofilter systems, the gasoline vapor concentration of each organic load studied varied hardly, due to operational difficulties

concerning to the homogenization of mixture of gases, which affected the biofilters performance. There was a close correlation between the inlet and the outlet concentration of the pollutant and a

relatively constant performance of the systems at each period. Figures 2 and 3 showed that after increase in pollutant concentration increase at each point, the systems presented a corresponding increase at the TPH concentration at the exit of the system and a fall at the removal efficiency of the biofilters systems that tended to recover the efficiency after some time. This was due to the gradual adaptation of the microorganisms to the new imposed conditions.

The biofilters were operated with gasoline concentration at the inlet air of 1.3 g.m^{-3} during 35 days; 3 g.m^{-3} during 52 days; 4.5 g.m^{-3} during 48 days and 8 g.m^{-3} during 55 days. At the three first periods, no significant loss of efficiency removal was detected. After a short period of adaptation, both the systems recovered the activity. With the gasoline concentration at the inlet air of 8 g.m^{-3} , the removal efficiency of the systems fell considerably. However, after some days, it improved. Probably this concentration was excessively high for the microorganisms, demanding a longer time of acclimatization.

Although the two biofiltration systems presented similar efficiencies, but BS1 resulted in better efficiencies than BS 2, probably due to the presence of one biofiltration column. For BS 2, where the total residence time was smaller than at BS1, the RE oscillated a lot mainly with gasoline concentration at the inlet air of 8 g.m^{-3} , showing an instability degree and the importance of the total residence time. The total retention time at BS1 was of 6 min, considering that it had four columns, each one with the time of 1.5 min. For BS2, the total retention time was of 4.5 min for the three columns. As evident, around 20 days were enough to start-up the biofiltration process and to reach efficiency of removal of 100% for 1.3 g.m^{-3} . For higher gasoline concentrations at the inlet air, a longer period of time was required until the biofilter systems achieved a good microbial acclimatization and an improvement in the removal efficiency.

Misiaczek et al. (2007), studying the degradation of toluene in a trickle bed reactor with a constant inlet concentration of 100 mg.m^{-3} , achieved stable removal efficiency above 95% after a week of operation showing that lower pollutants concentration could be degraded much easier and much faster than higher concentration, even if they needed a time of acclimatization. Soares (2006) reported efficiencies of 90 to 100% for 2 g.m^{-3}

using one biofilter of compost and one of tire to treat A gasoline. Mathur et al. (2007), studying the biofiltration of BTEX reported efficiency of 100% for 0.681 g.m^{-3} . However, for 1.6 g.m^{-3} , the efficiency was of 60%. Namkoong et al. (2004) found that longer times of residence were required for complex mixtures as gasoline and they had used retention times of 4 and 10 min for gasoline vapors, getting better results with the longest time. Soares (2006), using retention time of 3.4 and 6.8 min for the biofiltration of gasoline vapors on different supports and varying pollutant concentrations, achieved the removal efficiencies higher than 94%, indicating that the removal efficiency was connected to the residence time. Smaller RE was obtained for a smaller retention time and longer residence times were more efficient for the biofiltration pollutant processes (Namkoong et al. 2004). Namkoong et al. (2003) reported ER around 80% of TPH during the study with compost media, with concentrations varying from 50 to 7800 mg.m^{-3} . Lu et al. (2006) studied the degradation of up to 2 g.m^{-3} of gasoline with three microbes together, achieving the RE of 82%. Table 1 shows the RE (%) of the BS1 and BS2 of the various inlet air concentration studied showing that mixing populations were efficient for the degradation of the components of the gasoline. The lower performance of the BS2 was due to the lower number of columns in the biofiltration system.

Table 1 - Average removal efficiency of the Biofiltration Systems 1 and 2.

Inlet air concentration of TPH (g.m^{-3})	Removal Efficiency (%)	
	BS1	BS2
1.3	100	100
3	90	80-90
4.5	80	80
8	70-80	70

Table 2 shows the organic load applied to the biofilters systems 1 and 2. The organic load (OL) was calculated for each average pollutant concentration at the inlet air of the biofilters systems (Table 2). BS2 received more contaminant per total bed volume (39.7 , 59.6 and $105.9 \text{ g.m}^{-3} \cdot \text{h}^{-1}$) than the BS1 (29.8 , 44.7 , $79.4 \text{ g.m}^{-3} \cdot \text{h}^{-1}$), from the concentration of 3 g.m^{-3} , 4.5 and $8 \text{ g.m}^{-3} \cdot \text{h}^{-1}$, because the BS2 had one column less than the BS1. However, only for the concentration of 1.3 g.m^{-3} , both systems were operated with four columns each.

Table 3 shows the elimination capacity (EC) of the biofilters systems 1 and 2. The elimination capacity was higher for BS2 because this system was mounted with only three columns, except for the organic load of 1.3 g of TPH.m⁻³, when both the systems were mounted with four columns each. But even operating with three columns for the other organic load tested, both the systems presented very similar removal efficiency. This meant that with less active volume, BS2 obtained practically the same gasoline removal and higher elimination capacity.

Table 2 - Organic Load of the Biofiltration System 1 and 2.

Inlet air concentration of TPH (g.m ⁻³)	Organic Load (g.m ⁻³ .h ⁻¹)	
	BS1	BS2
1.3	12.9	12.9
3	29.8	39.7
4.5	44.7	59.6
8	79.4	105.9

Table 3 - Elimination capacity of biofiltration system 1 and 2 (EC).

Inlet air concentration of TPH (g.m ⁻³)	Elimination Capacity (g.m ⁻³ .h ⁻¹)	
	BS1	BS2
1.3	12.9	12.9
3	28.2	37.5
4.5	35.7	47.6
8	55.6	63.5

Torkian et al. (2003) studied the biodegradation of toluene and xylene in a biofilter with compost support; the organic loads were 80 and 78 g.m⁻³.h⁻¹, respectively. The elimination capacity was of 73 g.m⁻³.h⁻¹ for both the contaminants. The results were lower than the present study. The authors studied just two types of contaminant while in this study, gasoline was used that contained high number of compounds and still the biofiltration was efficient. Álvarez-Hornos et al. (2008), studying the biofiltration of ethyl benzene vapors with turf support, reported a capacity of maximum elimination of 45 g.m⁻³.h⁻¹ for an organic load of 55 g.m⁻³.h⁻¹. Soares (2006) achieved 26.5 and 30.8 g.m⁻³.h⁻¹ of EC; 31g.m⁻³.h⁻¹ of OL for C gasoline, similar values to the values found in the present study.

CONCLUSIONS

The biofiltration of C gasoline vapors using the

compost support with tire scraps (2:1) revealed to be an adequate alternative and an efficient way for reducing these pollutants vapors concentrations from the air. The process was simple and cheap, presenting the advantage of using a waste (tire) and a treated residual organic material (compost) as support material for the biofilter bed. The biofilters presented constant pH around 7.0, indicating that there was no oxygen limitation, even for high organic load. The lack of oxygen would have created anaerobic condition with the production of acids and consequent reduction of the pH, a fact that did not occur. Therefore, according to the pH results, during the whole biofiltration process, there were an availability of final electron acceptors for the aerobic respiration and the aeration of 450 mL.min⁻¹ and the residence time of 6 min (BS1) and of 4.5 min (BS2) were appropriate for this. The removal efficiency obtained was excellent. The biofiltration was more efficient for the lowest gasoline vapor concentration. For 1.3 g.m⁻³, the RE was 100%; for 3 g.m⁻³ it was 90%; for 4.5 g.m⁻³ the RE was 70-80%, and for 8 g.m⁻³ it was 70%, but it was still a good result. This study showed that it was possible to test still higher concentrations to find a threshold of biodegradation of gasoline vapors in the studied conditions.

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