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Methyl tert-butyl ether (MTBE) elimination by cometabolism: laboratory and biofilter pilot-scale results.

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ABSTRACT

At the present, Mexico produces and imports MTBE to achieve its demands (9% in gasoline). Compared to other volatile organic compounds, there are relatively few studies on MTBE biodegradation. In general, MTBE biodegradation has been observed as cometabolism, although there are some reports of its biodegradation as the only carbon source. This work presents results of MTBE degradation by cometabolism with gasoline vapors and pure substances from laboratory experiments and with gasoline vapors from a pilot-scale biofilter. At laboratory-scale, MTBE degradation rate was determined in microcosms using pure cultures and consortia. MTBE cometabolism in a pilot-scale biofilter was studied over a 260 day period. The pilot-scale biofilter was inoculated with a consortium previously adapted and fed with gasoline vapors for three months.

MTBE degradation rate by cometabolism with pentane determined in microcosms was 0.017mg/h·mg. Among the organic compounds tested, pentane was the best inductor for MTBE degradation. Cometabolism of MTBE with structurally simpler molecules such as pentane, diethyl ether and iso-butanol was observed but no degradation of tert-butyl alcohol, isoamyl alcohol and sec-butanol was observed with any of the inocula tested. Overall, higher cometabolic rates were observed using consortia as inocula versus pure cultures.

The pilot-scale biofilter system treating gasoline vapors presented higher MTBE elimination capacities and total hydrocarbon elimination capacities than those reported 3.8 g MTBE/m^3/h and 16 g/m^3h respectively. In addition, degradation of other compounds was determined. In general, linear alkanes and aromatics were rapidly degraded, while branched alkanes had lower removal

efficiencies. Pilot-scale biofilter elimination capacities for hexane, iso-octane and toluene were 3.24 g hexane/m^3/h; 3.13g iso-octane /m^3/h, and; 1.49 g toluene /m^3/h. Removal efficiencies for toluene were the highest and the most stable

INTRODUCTION

Methyl *tert-* Butyl Ether (MTBE), used extensively as an additive in gasoline, has been considered an important ground water pollutant because of its mobility, persistence, toxicity and its high water solubility (50 g/L at ambient temperatures) and its massive and extended use in gasoline[1].

Since 1993, all gasoline sold in Mexico contains around 9% (v/v) MTBE[2] (it substituted lead tetra-ethyl). At the present, MTBE is produced in different refineries of Mexico such as Tula, Salamanca, Cadereyta and Salina Cruz. In addition to its production, Mexico imports MTBE to satisfy its demand. Although all reports of MTBE potential toxicity[3] and the banning of its use in some states in the USA[4] there are no signs of restrictions of its use as gasoline additive in Mexico[5]. In fact, plans for construction of new MTBE production plants and/or converting one of the existing plants to MTBE production are still being considered.[6]

Few studies have been undertaken on the biodegradability on MTBE and other fuel oxygenates under both, aerobic and anaerobic conditions. Fortin and Deshusses[7] (1999) have demonstrated that an adapted consortium was capable of high MTBE degradation rates in a biotrickling filter. Results using the same consortium in microcosms and column scale are further reported by Morales[8] *et al.* (2000). Hanson[9] *et al.* (1999) demonstrated that a pure strain (PM1) was able to grow and rapidly mineralize MTBE. Few studies have addressed the cometabolic degradation of MTBE by pure cultures (Steffan[10] *et al.*, 1997). In Garnier[11] *et al.* (1999), it was established that a *Pseudomonas aeruginosa* strain, enriched from polluted soil, was able to degrade MTBE present in gasoline vapors. Dupasquier[12] *et al.* (1999) reported experimental data and a model for MTBE cometabolic degradation in presence of pentane.

Biodegradation of gasoline vapors in biofilters systems have also been reported by several authors.[13,14,15] In addition, reports on degradation of specific compounds present in gasoline such as BTEX have been published.[16,17,13,18] Overall, gasoline vapors elimination capacities have been reported around 10 g C/m^3/h. In contrast, there are only few studies of MTBE biodegradation in presence of gasoline vapors[13,14] and in presence of BTEX compounds.[19,20]

The present work presents results of MTBE degradation by cometabolism with gasoline vapors at laboratory and pilot scale. At laboratory-scale, MTBE cometabolic degradation rate with other compounds was also determined. For laboratory scale studies cometabolic rates were determined using three pure cultures and two consortia. MTBE cometabolism at pilot scale studies were performed in pilot scale biofilter which was inoculated with a consortium previously adapted and fed with gasoline vapors during 260 days.

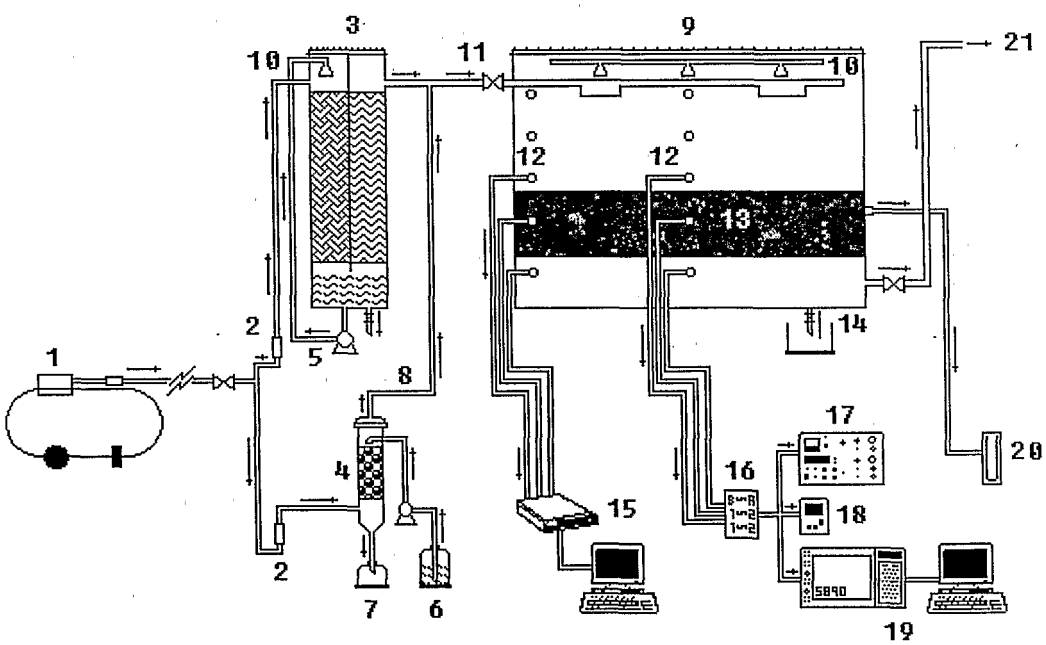
MATERIALS AND METHODS

Laboratory studies. MTBE cometabolic studies were carried out in microcosms following a the method described by Acuña[21] *et al* (1999). Modification of the method consisted of using 20 ml of mineral solution containing trace metals. The concentration of MTBE and the concentration of the different substrates studied were determined by using a Gas Chromatograph (GC) equipment (5890 series II Hewlett Packard), with a Flame Ionization Detector (FID) (methyl silicon column: 30 m x .32 mm x 0.25 mm, Quadrex Corporation). MTBE cometabolism with compounds present in gasoline was determined, four microbial consortia isolated from contaminated soils by enrichment in gasoline were used.[22]

MTBE cometabolism with compounds similar to the MTBE molecule, was determined using: a consortium called G and three pure cultures: G consortium resulted in a mixture of the four consortia previously mentioned; two pure cultures of *P. aeruginosa* (ATCC25619 and CDBB-B 1230) and *Pseudomonas sp.*

Pilot studies. The pilot scale biofilter used to determine MTBE and gasoline degradation has been described by Cárdenas[23] et al (2000). The system shown in Figure 1, consisted of a skid-mounted system built in stainless steel composed of a humidification module (32 L) and a biofilter unit (260 L).

Figure 1. Pilot scale biofilter.



1)Compressor, 2)Flowmeter, 3)Humidifier, 4)Evaporator, 5)Water pump, 6)Gasoline reservoir, 7)Recovered gasoline, 8)Gasoline vapor, 9)Biofilter, 10)Water nozzles, 11)Inlet of the pollutant, 12)Gas sampling ports, 13)Biofilter medium, 14)Leachate, 15)Temperature data system acquisition, 16)manifold 17)Total Hydrocarbon Gas analyzer, 18)CO_2 Infrared analyzer, 19)Gas chromatograph, 20)"U" tube manometer, 21)Exhaust air.

The system was packed up to a total volume of 73.6 L with a mixture of yard waste compost and pine bark (70:30 volume). Crushed oyster shells were used as a buffering agent. The biofilter medium was inoculated with an adapted consortium. The consortium was formed from different sources: leachate from a biofilter treating BTX; 4 strains of microorganisms that degrade toluene; an extract of gasoline contaminated soil and a dehydrated activated sludge. This mixture was maintained on a mineral solution and fed every four days with gasoline for three months prior its use.

The pilot scale biofilter was operated for 260 days. Gasoline vapors total elimination capacity – (TEC) as g $CH_4/m^3/h$ and CO_2 production measured as g $CH_4/m^3/h$, were determined over time with a Total Hydrocarbon Gas Analyzer (Model 23-500, GowMac, Bridgewater, NJ), equipped with a FID. An Infrared analyzer (3400 Gas Analyzers, California Analytical Instruments Inc., CA) with a 4 mm cell length installed to determine inlet and outlet CO_2 concentration.

Biodegradation of four representative compounds present in gasoline vapors (MTBE, hexane, iso-octane and toluene) was determined over time. To determine the inlet and outlet concentrations of this compounds FID- gas chromatography (5890 Hewlett Packard, Wilmington, DE, USA, equipped wit a HP-624 column), was used. To determine temperature at different points in the biofilter, type K thermocouples (Recisa, Mexico City) were used. The monitoring equipment was coupled to a computer system for on line data acquisition (Model Mac 14 Cole Palmer Chicago IL).

For carbon balance, CO_2 produced by endogenous respiration of the biofilter media was determined.

RESULTS

***Cometabolism studies*:** Cometabolic biodegradation of MTBE in gasoline was observed with the four consortia tested (see Table 1). Kinetic rate constants were determined using the Gompertz model as described by Acuña[21] et al (1999). MTBE cometabolism with gasoline and 6 different compounds was determined. No degradation of tert-butyl alcohol, isoamyl alcohol and sec-butanol was observed with any of the inocula tested. In contrast, cometabolism of MTBE with structurally simpler molecules such as pentane, diethyl ether and iso-butanol was observed. Cometabolic rates are shown in Table 2. The best inductor substrate for the cometabolic experiments was pentane by *P. aeruginosa* (CDBB-B 1230) with a cometabolic rate of 0.038 mg MTBE/mg protein h. Using data reported for MTBE cometabolism with pentane[11] and propane[10], degradation rate constants of 0.064 mg MTBE/mg protein h, and 0.21-0.49 mg MTBE/mg protein h respectively, were calculated. MTBE cometabolic rate constants with pentane and gasoline reported here were lower. This difference could be explained by the fact that biodegradation capabilities of consortia are generally better than those of pure cultures. This observation can also be made based on the results shown in Table 2. As it can be seen, pure cultures cometabolic rates are lower than those obtained with consortia.

Table 1 Kinetic data for Magna SIN gasoline degradation at 100 hours of culture.

Consortium	Gasoline mg/mg protein·h	MTBE mg/mg protein·h	% Gasoline degradation	% MTBE degradation	g MTBE/g gasoline
C1	0.105	0.078	94.54	99.81	0.743
C2	0.195	0.094	96.87	99.70	0.482
C3	0.081	0.051	90.97	99.14	0.630
C4	0.144	0.121	96.36	99.18	0.840

Table 2 MTBE cometabolic rate (mg MTBE/mg protein·h) in the presence of the indicated substrates and cometabolic coefficients.

	Rate (mg/mg protein·h)			Coefficients (mg MTBE/·mg substrate)		
Microorganism	Pentane	Diethyl Ether	Isobutanol	Pentane	Diethyl Ether	Isobutanol
CDBB-B-1230	0.038	NC	0.003	0.096	NC	0.005
CDBB-B-999	0.027	NC	0.011	0.091	NC	0.013
Pseudomonas sp.	0.017	NC	NC	0.106	NC	NC
Consortium G	0.017	0.019	NC	0.024	0.221	NC

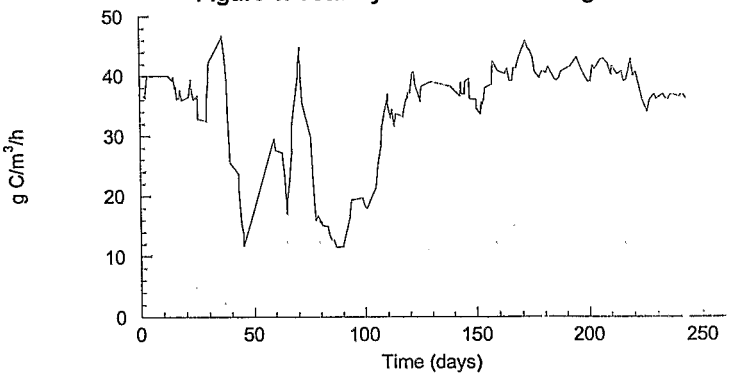
NC: Not Cometabolized

Pilot studies. The pilot scale biofilter has been in operation for 260 days. Empty bed residence times were in the range of 59 to 68 seconds. Total hydrocarbons and MTBE loading rates were in the range of 24 to 44 g CH4/m^3/h (Figure 1) and 5.3 a 9.3 g/m^3h MTBE, respectively. These broad load ranges were due to variations in the inlet flow during the first 150 days as well as variations in ambient temperatures over time.

Biofilter medium moisture content and pH was maintained at approximately 48±3% and 7.8±0.1 respectively. Water was added to reestablish biofilter medium moisture content by spraying fine drops of water over the surface at low rate.

During the 260 days of operation, the average MTBE removal efficiency was 30.6±15.8% (the maximum but not sustained was approximately 66%). Higher removal efficiencies were observed from day 210 to 260 (50±5%), probably due to the better moisture control and therefore better microbial colonization. Evolution of the microbial population was determined by plate counts of colony forming units for bacteria and fungi (results not shown).

Figure 1. Total hydrocarbons loading rate



Figures 2 and 3 display average total hydrocarbons and MTBE elimination capacity which were 10.5±4 g $C/m^3/h$, and 2.1±1.1 g $MTBE/m^3/h$, respectively. For the other compounds, maximum elimination capacities were: 3.24 $g/m^3/h$ for hexane, 3.13 $g/m^3/h$ and 1.49 $g/m^3/h$, for iso-octane and toluene respectively. Differences in removal efficiencies of the four different compounds monitored over time were observed. Among the four compounds analyzed, toluene presented the highest and more sustained removal efficiencies as shown in Figure 4. Overall, linear alkanes and aromatics were rapidly degraded, while branched alkanes had a lower removal efficiency. Higher elimination capacities for total and specific compounds were observed during the last 50 days of the study (day 210 to 260). During this last period, average total hydrocarbons and MTBE elimination capacity were 16±4 g $C/m^3/h$, and 3.8±1.1 g $MTBE/m^3/h$, respectively). These two values are higher than those reported in similar studies.[14, 13]

An analysis of the carbon balance showed that 91% of the carbon degraded was recovered as CO_2. This value was obtained of the elimination capacity (g $CH_4/m^3/h$) and production of CO_2 (g $CO_2/m^3/h$) data over time (results not shown).

Current microcosms studies are centered on the analysis of the cometabolic interactions between the different chemical species and its effect on MTBE degradation.

Figure 2. Total elimination capacity

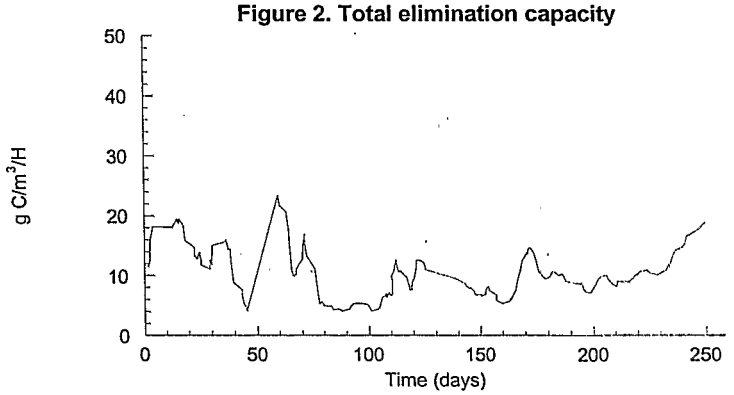


Figure 3. MTBE elimination capacity

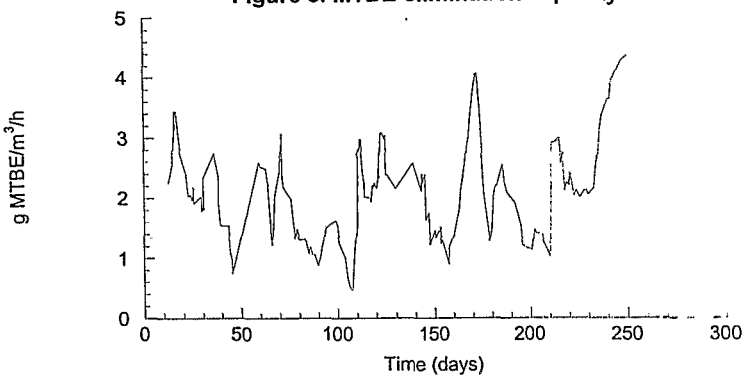
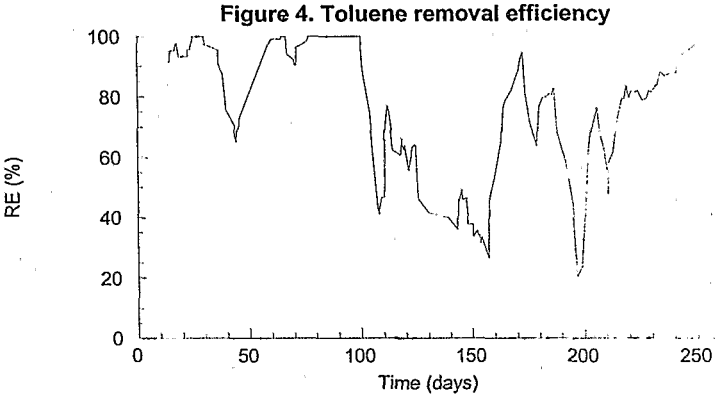


Figure 4. Toluene removal efficiency



Conclusions

With microcosms studies, three different strains and two consortia were able to degrade MTBE through cometabolism of gasoline in a mineral solution. Four different consortia were tested for their cometabolic capability to degrade other organic compounds. No degradation of tert-butyl alcohol, isoamyl alcohol and sec-butanol was observed with any of the inocula tested. In contrast, cometabolism of MTBE with pentane, diethyl ether and iso-butanol was observed. Cometabolic rate constants for pentane found in this work were in the same order of magnitude of other reports. Overall, there were no pure cultures or consortia able to degrade MTBE as their only carbon and energy source. MTBE degradation present in gasoline vapors was also observed with a pilot-scale biofilter which has been in operation for 260 days. Higher average elimination capacities for MTBE and total hydrocarbons than reported values were observed during the last 50 days of this study (3.8±1.1 g MTBE/m^3/h and 16±4 g C/m^3/h, respectively). Variations of total and specific compounds loading rates over the period of study were reflected on variations in elimination capacities. The gasoline evaporator set up used, is thought to be the main reason for the variation. Maximum elimination capacities for other compounds present in gasoline

vapors were determined as 3.24 g/m^3/h for hexane; 3.13 g/m^3/h for iso-octane; and 1.49 g/m^3/h for toluene. Current microcosms studies using pilot-scale biofilter medium will allow us to identify the interactions among certain chemical species and MTBE.

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Key Words

MTBE biodegradation, microcosms, pilot scale biofilters, VOCs, vapors gasoline