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Long term studies on the anaerobic biodegradability of MTBE and other gasoline ethers

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ABSTRACT

Anaerobic biodegradation of methyl *tert*-butyl ether (MTBE) using electron acceptors such as nitrate, Fe(III), sulfate and bicarbonate, may be more cost effective and feasible compared to aerobic treatment methods, for dealing with the MTBE problem. Currently, there are a few reports in the literature which have documented anaerobic biodegradation of MTBE in batch studies. However, some of the reports have been controversial, additionally many other studies have failed to document anaerobic biodegradation. Experiments were conducted over a long term period in both batch and continuous reactors to investigate the anaerobic biodegradability of MTBE and other gasoline ethers. Inoculums collected from various environments were used, along with different electron acceptors. Only one set of the batch experiments showed a 30–60% conversion of MTBE to *tert*-butyl alcohol under Fe(III)-reducing conditions, using complexed Fe(III). The use of complexed Fe(III) created an initial low pH of 1–2 in these batches due to its acidic nature, therefore, the removal may be due to acid hydrolysis rather than biological processes. Based on the findings obtained, caution should be applied in the interpretation of experimental data in which complexed Fe(III) is used for bioremediation of MTBE.

1. Introduction

Methyl *tert*-butyl ether (MTBE) was developed in the 1970s as an octane enhancer to replace toxic additives such as lead in gasoline [1]. Since the 1990s many brands of gasoline sold in Europe and the United States contained MTBE, used both for octane and oxygen enhancement. Its use as an oxygenate results in a cleaner burning fuel with reduced ozone forming smog, carbon monoxide, particulates, unburnt hydrocarbons as well as other toxic air pollutants. In Europe, the typical content in gasoline is 1–5% (v/v); however, it may be as high as 15% in some countries [2,3]. MTBE producers predict its use will remain stable [4].

Due to the widespread usage of MTBE, and its mobility and persistence, it has become an important contaminant in groundwater. The most severe forms of MTBE contamination of groundwater occur through leaking underground storage tanks and by accidental releases [5,6]. Its presence in drinking water causes tastes and odor problems, and it can be detected at concentrations as low as 2 μg/L [7]. In the state of California, USA, a drinking water guideline limit of 5 μg/L has been set [8]. In Denmark, the guideline limit has also been set at 5 μg/L, but preferable below 2 μg/L [9]. The application of biodegradation is considered an important option for removing this contaminant from groundwater.

Currently, there are numerous studies on the aerobic biodegradation of MTBE [10–13]. Comparatively, documentation of positive results on anaerobic biodegradation has been rather sketchy. Some of the results purporting anaerobic degradation have even been controversial [14]. Table 1 shows a summary of major reports so far on the removal of MTBE under anaerobic conditions in batch studies. The list illustrates that there have been reports of degradation under the most common terminal electron acceptors found in anaerobic groundwater. The removal rates are shown to be mostly $\ll$1 mg/(L d), these are very low compared to mineralization rates for aerobic degradation in reactors, which are in the range of 500–1500 mg/(L d) [10,15–17].

Anaerobic degradation of MTBE still remains an important challenge, which will require considerable research in order to be considered as a remediation option for contaminated groundwater. Its observation is rather a rarity than a norm; there are several studies that have documented no degradation under anaerobic conditions using different electron acceptors [18–21]. In many of the reports on anaerobic MTBE degradation the percentage removed was low.

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Table 1
Summary of the major reports of MTBE degradation under anaerobic conditions in batch reactors

Inoculum	Redox	Initial con. (mg/L)	Final con. (mg/L)	Rate (mg/(L d))	Lag time (days)	Ref.
Fuel impacted river sediment	HCO_3^-	48	22	0.51	152	[19]
Petroleum impacted aquifer	HCO_3^-	1	0.1	0.003	175	[26]
Surface water sediments (oasis)	SO_4^{2-}	1.5	1.38	0.00072		[27]
Petroleum impacted estuary	SO_4^{2-}	100	0	0.8	1160	[20]
Fe(III)-reducing reactor	Fe(III)	5	0	0.012	3	[28]
Surface water sediments (oasis)	Fe(III)	1.5	1.32	0.0011		[27]
Petroleum impacted aquifer	Fe(III)/HS[a]	50	5	1.13	275	[29]
Surface water sediments (oasis)	Mn(IV)	1.5	1.08	0.0025		[27]
Surface water sediments (oasis)	NO_3^-	1.5	0.525	0.006		[27]
Petroleum impacted stream	NO_3^-	1.76	1.32	0.006		[30]

[a] Humic substances.

The degradation was also mostly partial, with *tert*-butyl alcohol (TBA) being the dead end metabolite [22,23]. TBA is considered just as undesirable in groundwater as MTBE [14].

Anaerobic bioremediation of MTBE either under in situ conditions in the subsurface or in engineered reactors could be the most convenient method of removing it from groundwater. Gasoline impacted plumes are normally anaerobic, since aerobic degradation process in the aquifer quickly depletes the oxygen present [24]. Adding oxygen to groundwater can be expensive; in contrast, the electron acceptors used under anaerobic conditions are often already present. For example, ammonium and Fe(II) oxidized in aquifers, whether naturally or by engineered remediation activities, could become available for denitrification and Fe(III) reduction, with MTBE as the electron donor. Furthermore, electron acceptors such as nitrate and sulfate, which have very high solubilities, can be easily injected into aquifers to promote anaerobic MTBE removal. For these reasons, research into this topic is worthwhile conducting.

The ethers ethyl *tert*-butyl ether (ETBE), diisopropyl ether (DIPE) and *tert*-amyl methyl ether (TAME) can all be used as substitutes for MTBE [1]; they also have a similar fate and behavior in the environment. Kharoune et al. [25] and a preliminary undocumented study by us have shown that under aerobic conditions all ethers tested can be degraded. The degradation rates are in the following order: ETBE > MTBE, TAME > DIPE. Due to the similar chemical and physical properties of these ethers with MTBE they have also been included in the anaerobic degradation studies.

Both batch and continuous experiments were carried out to investigate the anaerobic biodegradability of the ethers MTBE, ETBE, DIPE and TAME. The experiments were conducted using inoculums from various sources with the likelihood of containing ether degraders, and by using different terminal electron acceptors.

2. Materials and methods

2.1. Analytical methods and chemicals

The analysis of sulfate and nitrate were conducted using Spectroquant® measuring kits (Merck, Germany) and a spectrophotometer (Spectroquant® NOVA 60). Methane was measured by gas chromatography (GC) with flame ionization detector (GC–FID) (Shimadzu GC-14A; Koyoto, Japan). The pH was measured using electrodes (WTW, Germany). MTBE, ETBE, DIPE, TAME and TBA were measured using the Purge and Trap method. A Tekmar LSC 2000 instrument coupled to a Shimadzu GC 14B instrument with flame ionization detector was used, according to US EPA method 5030C [31]. The GC was initially set to 40 °C, and ramped at 10 °C/min to 140 °C. The detector was set at 340 °C, and nitrogen was used as the carrier gas, set to 50 KPa. The GC was fitted with an Agilent Technologies HP-5 column of length 50 m, internal diameter 0.2 mm, and film thickness of 0.11 μm. Samples were normally stored at −18 °C, prior to analysis. Chemicals used were purchased from Merck (Darmstadt, Germany) or Sigma–Aldrich.

2.2. Batch reactors setup

Batch experiments were conducted using 200 mL serum vials capped with 1 cm thick butyl rubber septum and aluminum crimped caps. The liquid content of most of the batches were made with a nutrient media containing trace elements, vitamins, reductants and $NaHCO_3$ [32]. Only normal tap water (non-chlorinated) from Lyngby near Copenhagen, Denmark, was used in preparing two sets of the batches under Fe(III)-reducing conditions, which are discussed. Batches were inoculated with different types of inoculums (Table 2). Generally, the volume of the innoculum was one third to one half of the volume of the entire liquid. The vials were

Table 2
Inoculum source and type for batch experiments

Inoculum source	Inculum type	Comments
Petroleum refinery (Kalundborg, Denmark)	Primary sludge	Samples obtained from the primary pond at the wastewater treatment plant (WWTP). The pond had a depth of ca. 2 m, retention time of about 10 years and was anaerobic.
	Secondary sludge	Samples collected from an activated sludge unit down stream of the primary pond; the biomass retention time was about 9–10 months. This unit may have been anaerobic in some sections.
	Contaminated soil	Sampled at a depth of 10 cm from a field used to landfarm oily sludges which were removed from the primary pond at the WWTP.
Biogas plant	Digested manure	Samples obtained from a farm anaerobic digester in Jutland, Denmark.
Upflow anaerobic sludge bed reactor (UASB)	Granular sludge	Samples obtained from an industrial UASB reactor treating the effluent from a paper mill.
Forest	Manure	Samples obtained from a deer park in Lyngby, Denmark.
Membrane bioreactor	Biomass	Samples obtained from an MTBE degrading Fe(III)-reducing reactor [28]. The samples were a gift from Amy Pruden at the Colorado State University, Department of Civil Engineering, Colorado, USA.
Packed bed reactor	Biofilm	Samples obtained from a reactor fed with MTBE under aerobic conditions for over 3 years.