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REMOVAL OF METHYL TERTIARY BUTYL ETHER (MTBE) VAPOUR FROM CONTAMINATED AIR STREAMS USING DIFFERENT BACTERIAL CULTURES IN BIOTRICKLING FILTERS

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ABSTRACT

The treatment of methyl tertiary butyl ether (MTBE) vapors in biotrickling filters for air pollution control was investigated using different bacterial cultures. In the first phase, reactor was inoculated by the indigenous organisms and in the next phase, an aerobic microbial consortium able to biodegrade MTBE was used for reactor bed inoculation. Result was obtained only by specific organism: reactor was able to remove MTBE, after a short adaptation phase. Laboratory scale biotrickling filters were able to degrade up to 25 g/m.h with removal efficiency of 90%. They also showed a low rate of biomass accumulation.

Key words: Methyl Tertiary Butyl Ether (MTBE), biotrickling filters, microbial consortium, air pollution

INTRODUCTION

Methyl tertiary butyl ether (MTBE) was firstly introduced in the Islamic Republic of Iran in the end of 2001 as gasoline octane enhancer. Ordinary, reformulated gasoline contains 11-15% (v/v) of MTBE. Because of its low production cost and excellent blending characteristics, its production has been grown exponentially in the world, reaching a value of over 33 million tons per year (Fortin and Deshusses, *et al.,* 1999). With respect to the widespread use of MTBE, (daily use of 75 thousand tons gasoline in Iran), it an extensive MTBE emission is expected as a result of the stacks and leakage from underground and aboveground fuel tanks. Relative recalcitrance of MTBE to natural attenuation combined with its physico-chemical characteristics is a threat to groundwater supplies and drinking water wells. Consequently, MTBE has been, the second most frequently detected contaminant in drinking water supplies (Fortin and Deshusses, *et al*., 1999). While MTBE is thought to be less harmful than other gasoline constituents, there is still relatively incomplete knowledge on its health effects (USEPA, 1997); so in 1997, USEPA issued a drinking-water advisory for MTBE, which is in the range of 20-40 µg/L. Unfortunately, MTBE has quite different physico-chemical properties, making it more expensive to treat MTBE wastes with conventional techniques (Fortin and Deshusses, *et al*., 1999).

In many remediation techniques, such as air sparring, soil vapor extraction, air stripping and wastewater treatment operations, large air streams contaminated with MTBE are generated that besides, a very large emission from stacks, require treatment. Therefore, biological treatment may prove to be more feasible as a remedial technology in comparison to conventional methods (Fiorenza *et al*., 2003). The most promising bioreactors for air pollution control are biofilters and biotrickling filters. Biofilters are kind of bioreactors where a humid stream of contaminated air is passed through a damp packing material, usually compost mixed with wood chips or any other bulking agent

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on which pollutant degrading bacteria are naturally immobilized. Biotrickling filters work in a similar manner, except that an aqueous phase is trickled over the packed bed, and usually the bed is made of some synthetic or inert materials like plastic rings, open pore foam, lava rock, etc. The trickling solution contains essential inorganic nutrients and is usually recycled. Biotrickling filters are more complex than biofilters but are usually more effective, especially for the treatment of recalcitrant compounds, such as MTBE. So far, laboratory experiments were successful in this field. A biofilter which did not show any activity for a year suddenly became very active (Eweis, *et al*., 1997). The performance was in the range of 6-8 g/m.h with 95-100% removal. Fortin (1999) used a laboratory-scale biotrickling filter for removal of MTBE vapor from air streams, which inoculated with groundwater samples and aquifer materials from two long-term MTBE contaminated sites. After an acclimatizing period of about 6 months, in presence of Peat Humic Substances (PH_S), consortium on the filter was able to degrade 42–50 g/m^3.h. Hence, the objective of this study was to apply the extracted indigenous organism which was previously isolated from the gasoline polluted origin and MTBE degrading consortium (Nikpey *et al*., 2005) to remove MTBE vapors in a laboratory scale biotrickling filter. This study was conducted in two phases. In the first phase which lasted 13 months, the reactor was inoculated with indigenous organism and in the second phase (4 months), the startup phase of MTBE degrading reaction was investigated using a MTBE biodegradation consortium, which was obtained during the previous study (Nikpey, *et al*., 2005).

MATERIALS AND METHODS

Setup the biotrickling filter and operating conditions

A laboratory scale biotrickling filter was manufactured using transparent plexy glass (Fig. 1). Reactor was consisted of a packed bed, height of 50 cm (overall reactor height: 100cm, internal diameter: 14.2 cm; bed volume: 7.8 L) and was filled with 4.22 kg of wet lava rock (0.5-2 cm diameter, initial bed porosity of 66%). An inexpensive method was also developed to

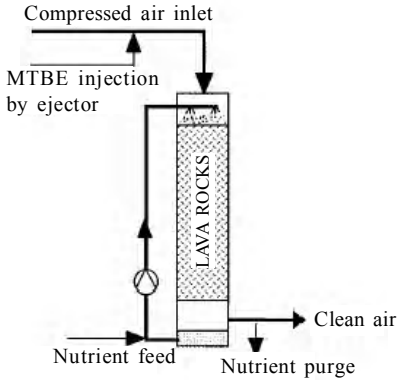

Fig. 1: Schematic drawing of the biotrickling filter

regulate the gas flow rate and injection of MTBE to the mainstream by using needle valves and ejector (Nikpey, *et al*., 2004). Hence, the synthetic gas waste, after mixing in the throat of ejector was introduced at the top of the reactor (co-current flow). The reactor temperature was adjusted at 22- 25 ºC. Trickling of recycle liquid at approximate rate of 2 L/h was established using two centrifugal aquarium pumps(RESUN, model-2500, China) at a volumetric flow rate of 0.15 m^3/h, with independent performance and equipped with a timer-controlled system (Theben timer 26- 230v/ 50Hz/0, 8w, Germany), to supply nutrient. Fresh mineral solution was prepared with the following composition: $MgSO_4.7H_2O$ (0.25); KNO_3 (0.5); $CaCl_2.2H_2O$ (0.009); KH_2PO_4 (0.5); K_2HPO_4 (0.5); NaCl (1.0) (in g/L) with addition of 1.0 mL/L of the solution of trace elements. The trace elements solution was consisted of: $FeCl_2{\cdot}4H_2O$ (1.5); $CuCl_2{\cdot}2H_2O$ (0.015); $NiCl_2{\cdot}6H_2O$ (0.025); $MnCl_2{\cdot}4H_2O$ (0.1); $COCl_2{\cdot}6H_2O$ (0.12); $ZnCl_2$ (0.07); $NaMoO_4{\cdot}2H_2O$ (0.025); H_3BO_3 (0.06); $EDTA{\cdot}4H_2O$ (5.2) (in g/L), with a final pH of 4.2 (Pfennig *et al*., 1989; Nikpey *et al*., 2005). Mineral medium was intermittently fed by a peristaltic pump (Watson-Marlow, Falmouth, Cornwall TR11; England) at an average flow rate of 1 L/d. All used chemicals were analytical grade. Humic and fulvic acids, which were extracted from a well humified organic soil, were added to the medium at a concentration of 0.25 mg/L at specific time intervals (Carter, 1993). A constant liquid volume of 3 L was kept at the bottom of the reactor by anoverflow outlet. The dynamic holdup in eachbiotrickling filter was kept constant at approximately 0.8 L.

Definitions and performance reporting

Operation and performance of biological reactors for air pollution control is generally reported in terms of removal efficiency, or pollutant elimination capacity as a function of the pollutant loading, or the gas empty bed retention time (EBRT). These terms can be defined as the following equations.

$$\text{Removal Efficiency} = \text{RE} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

$$\text{Elimination Capacity } (g/m^3h) = \text{EC} = \frac{C_{in} - C_{out}}{V} \times Q$$

$$\text{Empty Bed Residence Time } (S \text{ or } min) = \text{EBRT} = \frac{V}{Q}$$

$$\text{Polutant Loading } (g/m^3h) = L = \frac{C_{in} - Q}{V}$$

Where, C_{in} and C_{out} are the inlet and outlet concentrations of pollutant (usually in g/m^3); V, is the volume of the packed bed (m^3), and Q is the air flow rate (m^3/h).

Measuring techniques

Grab samples from either inlet or outlet streams were collected in one liter Tedlar bag and immediately analyzed by direct injection of 100 µL portions into the gas chromatograph, without further treatment. MTBE concentrations were determined using a PHILIPS PU-4410 gas chromatograph equipped with a flame ionization detector (FID). The compounds were separated on a %10 SE30 packed column (1.5 meter length, 0.4 mm ID). Column temperature was adjusted isothermally at 50°C, injector at 180°C and detector at 200°C. Nitrogen gas (20 mL/min) was used as the carrier gas. According to the analytical results from headspace and liquid samples of batch experiments, TBA and other byproducts were not found; therefore reactor evaluation was conducted by measuring MTBE in the gas phase.

Inoculum origins and culture conditions

Selected samples were soils and aquifer materials from many locations (such as Baft-cheme petrochemicals, Mahshahr port, discharge stream from above ground fuel tanks in Shar-e-Ray gas stations, etc.) with long-term exposure to gasoline. These samples were mixed and introduced in biotrickling filters for enrichment using MTBE at specific pressure. In the second stage of the study reactor was inoculated with 2 mg of wet MTBE biodegradable consortium (Nikpey *et al*., 2005).

RESULTS

To start the experiment, reactor was inoculated with indigenous organism. Results obtained are shown in Fig. 2. After 13 months of continued working of the reactor, no MTBE elimination was seen. MTBE was initially existed in the gas phase at a concentration of 0.2 – 0.5 g/m^3.

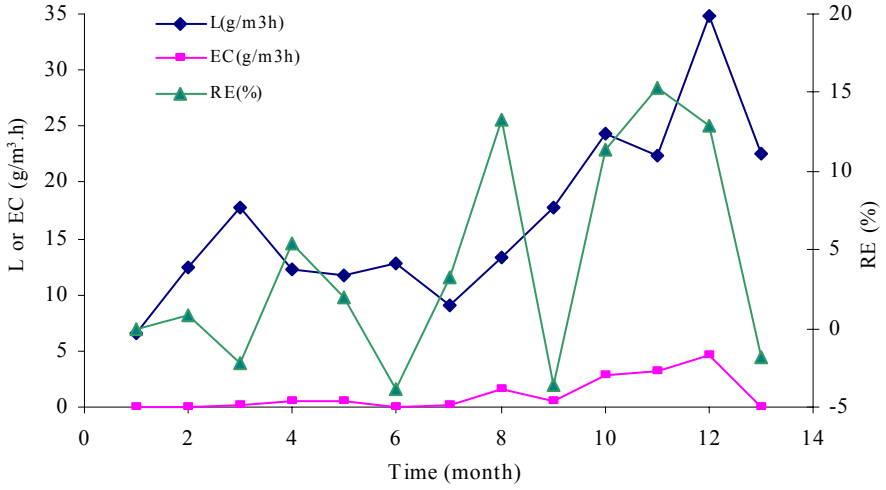

Fig. 2: MTBE loading, elimination capacity and percentage removal vs. time (incubated with indigenous consortium)

Several attempts (e.g. addition of yeast extract, B-complex vitamin, amino acid and 0.25-0.5 mg/L peat humic substance to promote biomass growth) were made to start the reactor up, but all of them were unsuccessful. At the end of the first phase, the elimination capacity of 5 g/m^{3}h was achieved in a MTBE loading of 27 g/m^{3}h with a maximum removal efficiency of 20%. While, MTBE removal was less than of 5% of the incoming feed, biodegradation was confirmed by draining the scrubbing solution out of the reactor.

At the startup stage, ammonium chloride was used as a nitrogen source, but caused a nitrification reaction and dropped the pH to around pH= 4; so, a nitrate salt was replaced to fix the pH. At the second stage of the study reactor package was replaced and inoculated with 2 g of wet biomass. MTBE was then fed to the reactor at a concentration of 0.6- 0.9 g/m^3 (Fig. 3).

A rapid startup at about 80 days was observed for MTBE removal in neutral pH of a biotrickling filter. After 4 months in an EBRT of 70 s, degradation rate was reached to an average elimination capacity of 25 g/m^{3}h with removal efficiency of 90% at MTBE loading of 0.6-0.7 g/m. Results of MTBE removal and elimination capacity are presented in Fig. 4. Fig .5 shows the loading and elimination capacities.

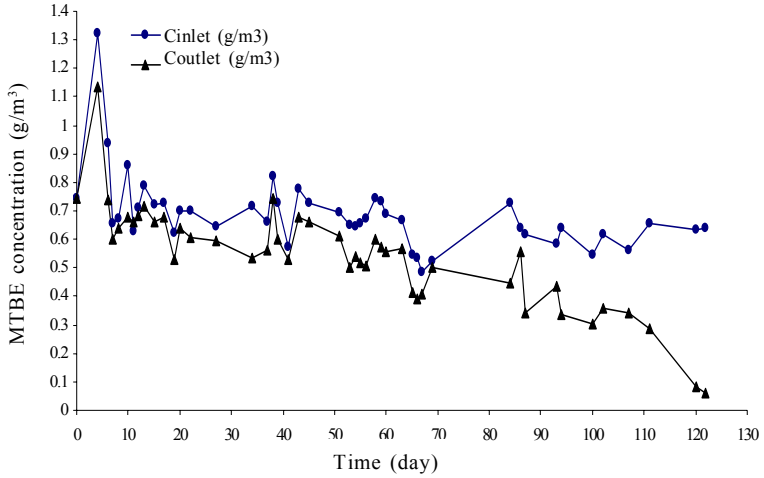

Fig. 3: Inlet and outlet gas phase MTBE concentrations in reactor incubated with MTBE microbial consortium vs. time

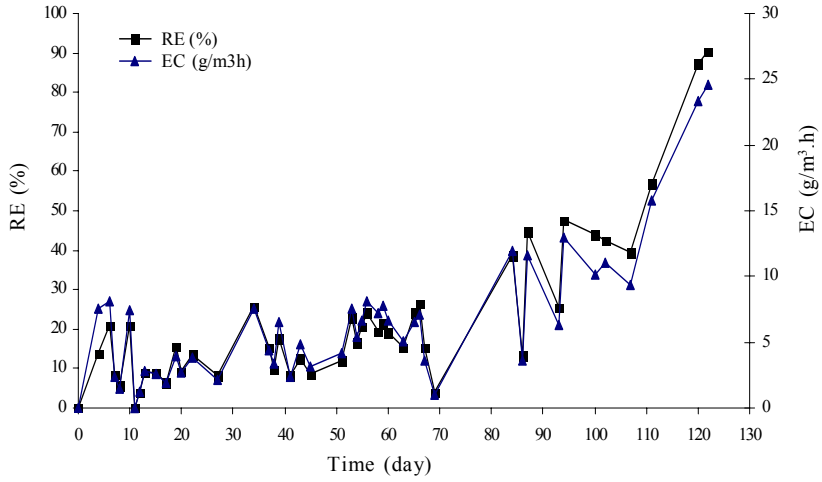

Fig. 4: MTBE elimination capacity and percentage removal vs. time (incubated with MTBE biodegradable consortium)

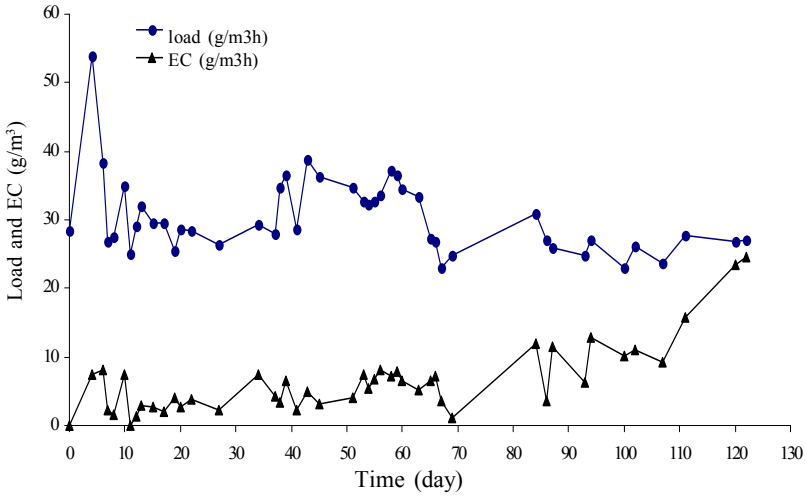

Fig. 5: MTBE loading, and elimination capacity vs. time (incubated with MTBE biodegradable consortium)

DISCUSSION

Bioremediation of recalcitrant compounds requires the suitable microbial culture. Inoculating the engineered controlling system with mixed or pure species with demonstrated MTBE degradation capability, shortened reactor startup could be expected. Even under optimal conditions, MTBE degradation requires a very long start-up for growth of an active population and full development of MTBE degradation ecosystem in biotrickling filter. This was probably affected by the slow growth and a poor biomass yield of MTBE degraders. Hence, there may be the possibility to increase the biomass yield and to shorten the startup by artificially increasing the MTBE inlet concentration. Average elimination capacity of 25 $g/m^3.h$, which was achieved during the experiments, is much higher than what is reported by (Eweis *et al*., 1997) in a biofilter, which reached a capacity of 8 $g/m^3.h$ for an EBRT of 1 min and comparable to maximum elimination reported by Devinny *et al*., (42-50 g/m^3h) after six months of continuous work reaching to a mature system in the presence of Peat Humic Substances as bio stimulator. It should be noted that the process culture in reactor was not fully developed yet and should be emphasized that the good performance could only be obtained after a proper density of a competent process culture was established. Therefore with respect to the used material, which was a very little inoculums source, the obtained results are promising. The use of easy carbon sources and the addition of peat humic substance (PH_S), yeast extract as an extra source of minerals, vitamins and amino acids could not stimulate the microbial growths and further studies are needed. Nitrate was an appropriate nitrogen source for MTBE degraders, at least for this consortium. Using nitrate instead of ammonia could prevent nitrification with the possible decline of the pH and accumulation of possible inhibitory levels of nitrite. According to the previous experiments performed in shake flasks, the specific growth rate of the bacterial consortium was 0.0312-0.0375 / day, or a doubling time 25-30 days (Nikpey *et al*., 2005), which has a good agreement with the 0.023 - 0.026 day^{-1} (Fortin *et al*., 1999), and 0.05 /day reported for MTBE degrading mixed culture by (Salanitro *et al*., 1994). Experimental work with reactor consistent with the slow growth rate of the MTBE degraders did not show any increase in pressure loss, with time for experiments performed in the shake flasks (Nikpey *et al*., 2005) and in the biotrickling filter confirmed that PH_S did not stimulate the growth of the consortium, however it should be emphasized that results presented here is valid for this consortium. With respect to the minor contradictions with other studies (Fortin *et al*., 1999) further investigations are needed.

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