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The Methanotrophic Fluidized Bed Bioreactor: From Laboratory to Field Demonstration at the Savannah River Site

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The methane provided is the only food source to the microorganisms, and it is poorly soluble in water. However, sufficient quantities of methane must be supplied, resulting in high flow rates through the reactor. To prevent the bacteria from being washed away, they are grown in a thin film on an inert substrate. In the fluidized bed reactor (FBR), this biofilm is grown on small (approximately 1 mm) inert particles which are heavier than water. Water flows upward through the reactor, causing the bed of particles to become fluidized.

The FBR design developed by GRI maximizes the surface area available for the growth of biofilms, and thus maximizes the density of active biomass in the reactor. Thus, for given kinetics, the reaction rate is maximized and the required reactor volume minimized. Plugging and channeling are unlikely because of the constant movement of the bed media. Methane and oxygen (feed gases) have to be supplied in dissolved form. Because of the large gas demand relative to the poor solubility of methane and oxygen, this mass transfer of gas can be a major design challenge. This problem can be circumvented by supplying the gases in the gas phase, as in a trickling filter; however, channeling of the packed bed, stripping of untreated VOCs, and lower biomass densities are drawbacks of this approach.

The growth characteristics of methanotrophic attached film in an FBR with and without exposure to TCE were defined with pelletized diatomaceous earth as the bed medium. Results of these studies showed that the bioreactor was highly stable while operating at single-pass hydraulic retention times as low as 15 seconds. The methanotrophs formed thin, dense films, exceeding 40 g of biofilm organics per liter of expanded bed reactor. Batch degradation rates followed the Michaelis-Menten enzyme kinetic model with a maximum rate (q_{max}) of 10.6 mg TCE/g volatile solids (VS)/day and a half velocity coefficient (K_s) of 2.8 mg/L. TCE degradation rates were up to 800 mg TCE/L-d⁵.

DESIGN OF THE METHANOTROPHIC FLUIDIZED BED DEMONSTRATION REACTOR

Ex Situ MTT Design Constraints

- Oxygen and methane are poorly soluble in water (ppm to tens of ppm levels), so a highly effective mass transfer process is necessary to dissolve them.
- Pure oxygen and methane can form explosive mixtures, so appropriate safety measures are essential.
- The hydraulic retention time must be sufficient for the desired degree of biological degradation to take place, and should be calculated from the kinetic parameters.
- Media size should be tailored to the expected upflow velocities. Velocities between 3 and 20 mms⁻¹ (5 and 30 gpm/sq.ft.) can be considered.
- For TCE reductions in excess of 90 to 95%, several biological stages in series are more economical than one.

Rationale for the MTT Demonstration

By early 1991, the MTT FBR proof-of-concept work was largely completed, and the results were promising⁵. The cost analysis indicated that the MTT FBR would be competitive with air stripping and LGAC. So, a field-scale demonstration was the next logical step.

At that time, Envirex Ltd and Michigan Biotechnology Institute (MBI) had recently developed a skid-mounted FBR for bioremediation of water contaminated with aromatic hydrocarbons (BTEX). The support medium was granular activated carbon (GAC), and the skid was equipped with a pressure-swing adsorption unit to generate technical oxygen. A downflow bubble contact aerator (DBCA) dissolved the oxygen into the water prior to its entry into the FBR. Full treatment was achieved in one pass with a capacity of 30 gpm.

This skid-mounted unit appeared to be an ideal starting point for a field-scale MTT FBR. The main modifications required would be the addition of a recirculation loop and a methane diffuser. Westinghouse Savannah River Company (WSRC) joined the GRI MTT development effort by offering a site at Savannah River and cofunding of the field demonstration.

Design and Construction of the MTT Demonstrator

Process modeling showed treatment cost reductions resulting from pressurization. This had to be balanced against the hazards of feeding methane and pure oxygen to a closed pressurized reactor. To safely achieve some pressurization, a vertical 8 m extension to the reactor was designed. This extension would be filled with stagnant water and provide about 0.75 atm overpressure, but would be open at the top, thus preventing the accumulation of explosive headspaces, while allowing access to the reactor for sampling. A detailed design was worked out with multiple control loops and safety interlocks. All electrical equipment was put on a separate skid to remain at least 15 ft away from the reactors and diffusers, for safety reasons. A reactor cover was designed with a lower extension to minimize the reactor headspace. All possible exit points for TCE were equipped with GAC canisters to allow a precise TCE balance to be made. A gantry was designed, to support the two reactors with their extensions and to provide access to both reactors over their full height (Figure 3). A biomass control impeller was included; excess biomass will exit with the effluent and be captured on basket strainers.

Demonstration Plan

Two complete demonstration units were built; GRI will make both available for the demonstration. One unit is assembled and ready to start at MBI, where it will be used for process shake-out. The other unit will be installed at the Savannah River Site (SRS) to treat groundwater containing approximately 1 mg TCE/L. Subsequently, the unit now at MBI will be transferred to SRS where it will become the second stage. Ultimately, the first stage will be converted to an anaerobic dechlorination unit.

PERFORMANCE OF THE METHANOTROPHIC FLUIDIZED BED REACTOR

MTT Development at MBI

A continuous flow bench scale granular activated carbon fluidized bed reactor (GAC-FBR) was constructed for TCE degradation studies at MBI⁶. An important advantage of GAC is that its adsorptive capacity makes it possible to temporarily store the target contaminant (i.e., TCE) on

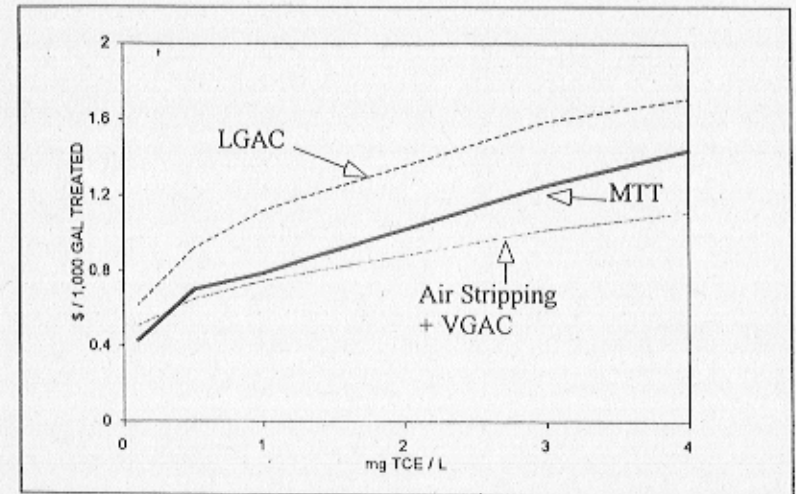


Figure 5. Cost of treatment versus TCE concentration, for three technologies.

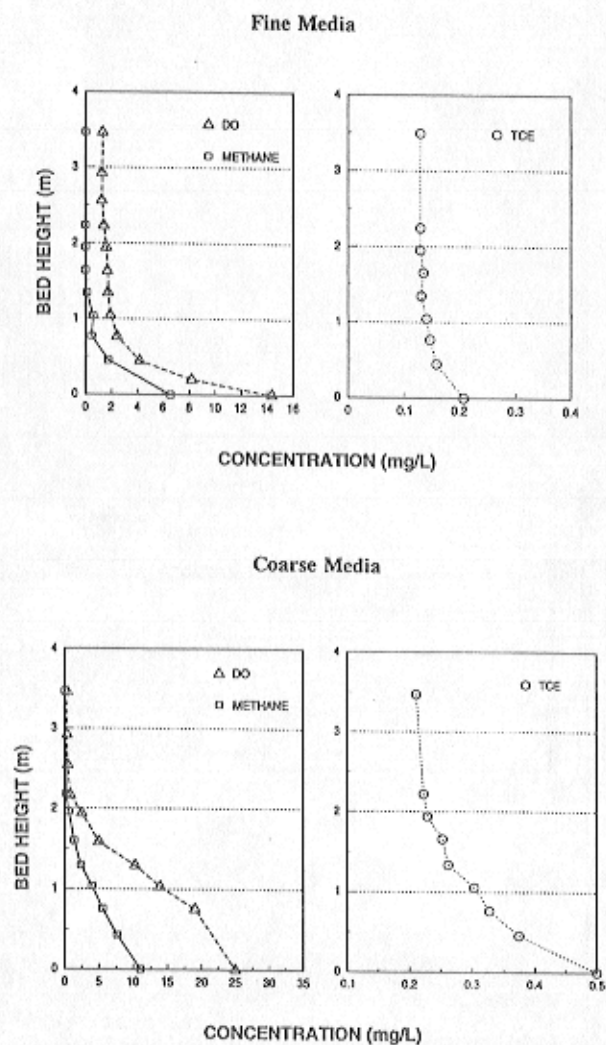


Figure 4. O_2 , CH_4 , and TCE concentration profiles versus depth in fluidized bed reactors.

the bed particles. This smooths reactor startup and equalizes fluctuations in contaminant concentration. The 12 L, 3.6 m deep glass reactors were constructed with evenly spaced sampling ports along the side of the reactor tube. Fluid samples can be withdrawn from these ports to determine dissolved methane, oxygen, and TCE concentrations. Methane-, oxygen-, and nitrogen-saturated water streams are prepared by circulating influent water through downflow bubble contact aerators. No effluent was recirculated. TCE feedwater was prepared by mixing neat TCE in a reservoir bottle to provide for complete dissolution. The feedwater was delivered into the reactor through a metering pump. The reactors were operated without recirculation (one pass mode) to allow the researchers to investigate reaction kinetics at high TCE concentrations. The drawback of one-pass mode is a low efficiency of conversion due to the extremely short retention time of a few minutes. Some representative results are summarized on Table 1.

Several runs were conducted using fine-grained GAC (12 x 40 mesh, 0.4 - 1.4 mm) and TCE concentrations varying between 250 and 3,300 μg TCE/L. The upflow velocity limited the flux of dissolved methane and oxygen supplied, so that only the lower 1/3 of the bed showed biological activity. After a change to coarser media (10 x 25 mesh, 0.7 - 1.7 mm) and higher flow rates, methane metabolism and TCE cometabolism were observed in the lower 2/3 of the bed (see Figure 4). The influent concentration of 430 μg TCE/L was reduced by 50% in an empty bed contact time of 3.3 minutes.

The main findings of the MBI experiments were:

- GAC was a better support medium for the biofilm than PDE;
- Increasing oxygen and methane concentrations from half saturation to saturation did not improve performance;
- Addition of formate or methanol had little effect on TCE removal;
- TCE epoxide toxicity may degrade performance in the long run.

The MTT FBR process was modeled and the model calibrated to the MBI results⁷. Data points with excessive dissolved oxygen (>25 ppm influent or >3 ppm effluent) were eliminated, as well as those possibly tainted by net adsorption of TCE on to the bed particles. Michaelis-Menten kinetics were determined via a best fit to a Lineweaver-Burke plot, resulting in the following parameters:

$$q_{\max} = 61 \text{ mg TCE/L expanded bed/day;}$$

$$K_s = 0.29 \text{ mg TCE/L.}$$

The half velocity constant (K_s) value of 0.29 mg TCE/L is remarkably low compared to literature values of 1.6 mg TCE/L for a suspended growth culture⁸, and 2.8 mg TCE/L for a biofilm on PDE⁵. This suggests that the use of GAC as a support medium results in a lower apparent K_s .

ANAEROBIC DECHLORINATION IN THE FLUIDIZED BED REACTOR

Anaerobic Dechlorination of Chlorinated Ethenes

The need to transfer large volumes of sparingly soluble oxygen and methane into the feedwater is a significant challenge for FBR technology. It can be obviated if chlorinated ethenes are instead reductively dechlorinated in an anaerobic environment and in the presence of an electron donor. Tetrachloroethylene (PCE) is rapidly dechlorinated to TCE under those conditions. The latter is further dechlorinated into dichloroethylene (DCE), then vinyl chloride (VC), and finally into ethene and ethane.

This approach eliminates mass transfer problems because an easily soluble electron donor such as sucrose or ethanol can be used and no oxygen needs to be dissolved. PCE's frequent presence along with TCE in groundwater is an additional incentive for investigating anaerobic biodegradation (PCE is refractory to aerobic degradation). Potential drawbacks include the persistence of an organic residual and possibly vinyl chloride (VC) in the effluent.

Rapid dechlorination of PCE is reported, but some authors report a virtual blockage of dechlorination at the level of VC⁹. This is a problem because VC is the most toxic chlorinated ethene and it doesn't adsorb well to activated carbon. However, de Bruin et al.¹⁰ dechlorinated 9 μ M PCE and documented complete disappearance of VC in 1.2 hrs @ 10 °C with 1 mM lactose as the electron donor.

Results Obtained and Demonstration Plans

One 3.6 m reactor at MBI was converted for anaerobic operation¹¹. TCE was fed at 1 mg/L, with molasses and methanol as electron donors and a hydraulic retention time of 0.84 hrs. No DCE or VC were detected in the effluent, 75% of the TCE was degraded, and ethene was detected in the headspace. Although these results are preliminary, they argue well for the future of anaerobic dechlorination in anaerobic GAC FBRs.

Retrofitting the existing demonstration unit for anaerobic operation is relatively simple. Oxygen and methane supplies will be disconnected, while a tank of electron donor solution with a metering pump will be added; the bed medium may be changed to a finer grade, for the lower upflow velocities expected.

POTENTIAL OF METHANOTROPHIC TREATMENT TECHNOLOGY

Schrab & Jackson¹² found that most of the sites with chlorinated hydrocarbon contamination are within reach of the national pipeline grid. This would insure that natural gas is available to apply MTT at these sites.

The cost of full scale MTT FBR operation was estimated⁷. Roughly one third is projected to be applied to debt service, and another third to final polishing with GAC. The methane consumed only represents 6% of the total cost.

The cost of MTT was compared to that of its most common competitors, air stripping with VGAC, and direct adsorption on LGAC (see Figure 5). Within the error margin of these

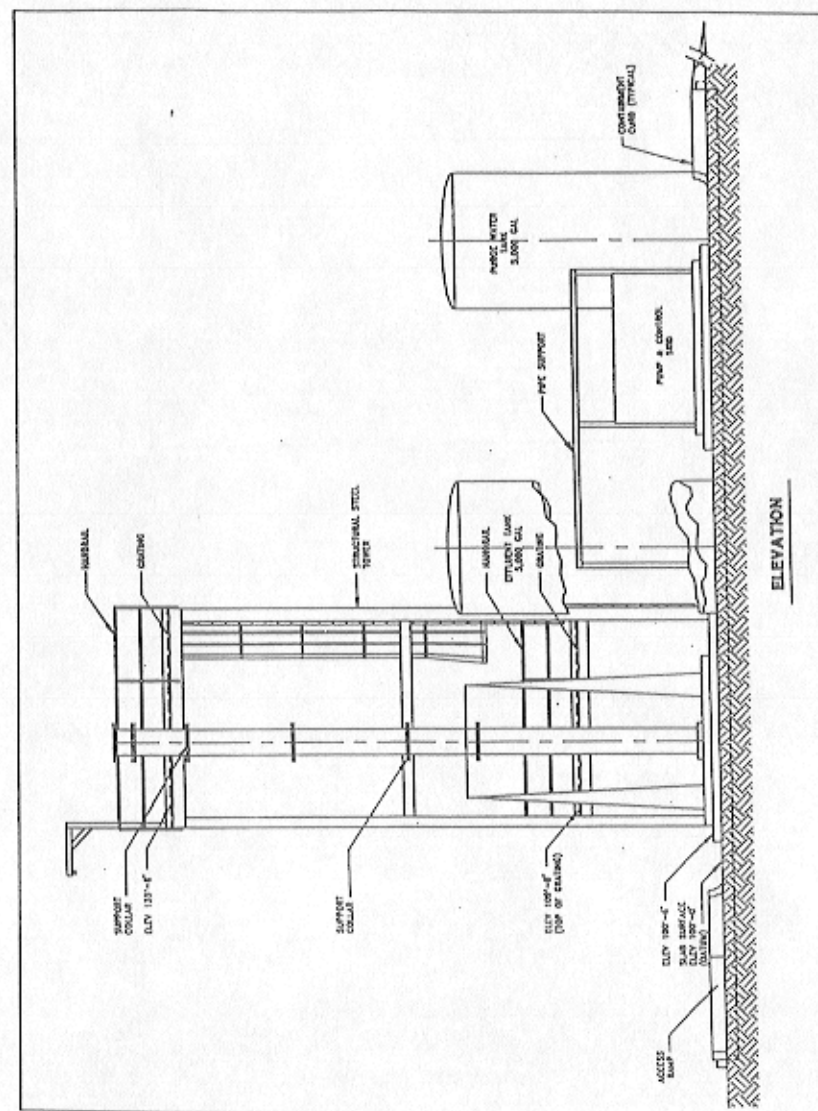


Figure 3. MTT demonstration unit: elevation.

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Table 1. Performance of methanotrophic bioreactors at MBI.

Selected Datapoints Obtained at MBI Using a 10 ft (3 m) GAC Fluidized Bed Reactor
(The Large Diameter Media Experiment is Shaded.)

Identifier (*)	R4Per2 Ph2	R1Per2 Ph2	R2Per2	R2Per3 Ph1	R2Per3 Ph2	R2Per4 Ph2	R2Per4 Ph3
Media Size (mm) (mesh)	0.7-1.7 10 x 25	0.4-1.4 12 x 40	0.4-1.4 12 x 40	0.4-1.4 12 x 40	0.4-1.4 12 x 40	0.4-1.4 12 x 40	6 0.4-1.4 12 x 40
Influent mg TCE/L	0-43	0.25	0.31	1.02	1.01	3.29	2.89
HRT (min (a))	3-3	5.6	5.4	5.8	5.3	5.1	5.2
DCH4 in (ppm)	9.6	12.3	7.1	8.1	5.8	6.4	5.4
DCH4 out (ppm)	0.0	1.7	0.0	0.0	0.1	0.0	1.2
DO in (ppm)	22.8	24.9	16.4	19.7	13.1	13.0	8.2
DO out (ppm)	1.4	0.3	2.4	2.3	0.9	0.8	0.2
% TCE removal	50	35	34	17	13	6	6
mg TCE/Leb/d	114	24	21	43	36	56	57
g CH4/g TCE	40	120	68	49	53	34	19

(a) HRT based on empty reactor; actual residence time shorter
(*) R = reactor, Per = period, Ph = phase

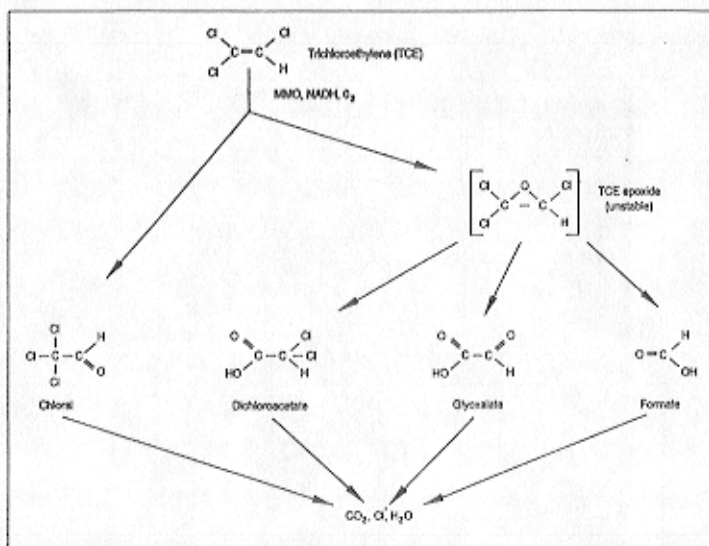


Figure 1. Cometabolic oxidation of trichloroethylene (TCE): pathways.

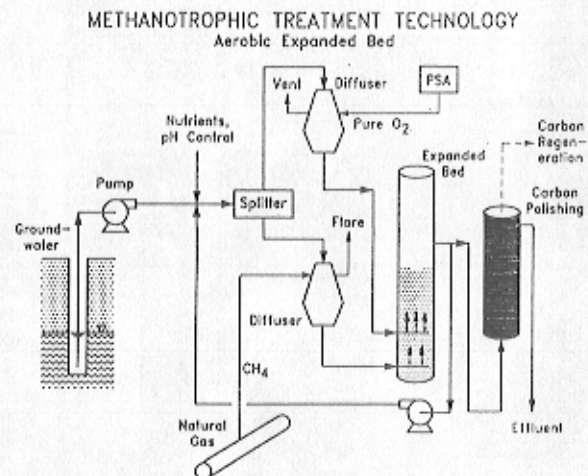


Figure 2. Fluidized bed reactor for methanotrophic treatment.

estimates, air stripping and MTT are virtually equal, while LGAC is clearly more expensive. The graph indicates that MTT is competitive with state-of-the-art physical technologies, especially if one considers that most groundwater TCE contamination is below 3 ppm. The results also indicate that economies of scale disappear rapidly above 500 gpm for all technologies.

CONCLUSIONS

- Methanotrophic Treatment Technology (MTT) is feasible and has proven effective at destroying TCE in groundwater, both in a reactor and in-situ. Degradation of TCE appears feasible down to $\mu\text{g/L}$ levels in-situ and tens of $\mu\text{g/L}$ in a bioreactor.
- MTT provides on-the-spot destruction of the contaminant and minimizes transfer to granular activated carbon (GAC) with all the related handling and waste management concerns.
- MTT is projected to have approximately the same cost as air stripping with VGAC and to be less expensive than LGAC. MTT may be less expensive than air stripping with VGAC if large diameter support media and high superficial velocities are used.
- The cost of methane represents only about 6% of total MTT costs.
- The bench-scale experiments at MBI indicate that very high concentrations of oxygen and/or methane are not helpful. Gas concentrations should probably be no more than half of the saturated value.
- The same studies show that the use of GAC as the support media for the growth of biofilm reduces the apparent Michaelis-Menten half velocity concentration (K_m) to 0.29 mg TCE/L, as opposed to 1.6 and 3 mg/L reported by others.

MTT effectively destroys chlorinated ethenes on site. It is cost-competitive with existing technologies and does not have the off-site liabilities. Anaerobic dechlorination promises to simplify the process, provided vinyl chloride production can be controlled.

ACKNOWLEDGEMENTS

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