TOXICITY OF AIRCRAFT DEICING FLUID ADDITIVE IN ANAEROBIC ENVIRONMENTS

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ABSTRACT:

Aircraft deicing practices at commercial and military airports generate millions of gallons of contaminated runoff and concentrated wastes each year. In the United States, glycol based deicing fluids, containing high concentrations of other chemical additives (>2% v/v), are currently in use. Preliminary data suggest that aircraft deicing fluid (ADF) additives confer toxicity to biological treatment systems, fish, and zooplankton at low concentrations (Cornell et al., 1999; Pillard et al., 1995). Insufficient data are available regarding the environmental fate and treatability of the chemical additives found in ADF. Because of its extreme oxygen demand, ADF waste will induce anaerobic conditions in the environment; thus, the true environmental impact of ADF cannot be determined until the fate of these additives is resolved.

Unacclimated bench-scale reactors, designed to replicate full-scale mesophilic anaerobic digesters, operated at an SRT of 15 days, ceased gas production within 1 SRT of receiving 10 mg/L of MEBT. Approximately 10 - 30% of the MEBT introduced to the digesters sorbed to the biomass; this sorption could be modeled with a freundlich isotherm. Under these sustained (approx 9 months) reducing conditions, no breakdown of MEBT was detected. Classical anaerobic toxicity assays were used to determine the impact of MEBT on established anaerobic microbial communities. The toxicity threshold was determined using biogenic gas production. MEBT caused a statistically significant decrease in microbial activity in batch reactors at a threshold level that may be found in the subsurface near deicing operations or in wastewater treatment systems.

INTRODUCTION:

Propylene glycol-based deicing fluids are currently being applied with significant concentrations of chemical additives. These additives result in deicing formulations that are considerably more toxic than pure glycols (Strong-Gunderson et al., 1995; Pillard, 1995; McGahey and Bower, 1992; Cancilla et al., 1997). Methyl-benzotriazole (MEBT) is added to ADF for corrosion inhibition and reduction of flammability. Negative impacts imparted on wastewater treatment facilities by ADF wastes have caused utilities to begin enforcing strict discharge limits and assessing substantial fees for loadings from airports. As a result, airports and airbases are investigating alternative treatment methods for ADF wastes (Iachetta, 1996; Carter, 1997).

Anaerobic treatment of deicing wastes. In industrial treatment scenarios, anaerobic treatment is often preferred because it results in less sludge production, increased solids loading rates, no aeration requirements, and possible energy (methane) recovery (Speece, 1996). The primary constituent of ADF waste, propylene glycol (88% v/v), has been shown to be easily degraded under anaerobic conditions (Veltman, 1998).

Anaerobic toxicity. Wastewaters that show good potential for anaerobic degradation (e.g. ADF waste) may contain chemicals that are toxic to anaerobic bacteria. *Methanogens*, sensitive microorganisms in the consortium of anaerobes, are usually the phylum most adversely affected by a toxicant (McCarty, 1964). Inhibition of *methanogenic* bacteria results in acid accumulation (due to acetate build up) and inhibition of standard anaerobic digestion processes. Anaerobic systems can treat wastewaters that contain a toxicant if its concentration remains below the toxicity threshold. Efficient treatment can be achieved if the toxicant is sequestered or chelated (i.e., not bioavailable) under treatment conditions.

Anaerobic treatment with granular activated carbon. Activated carbon may be added to adsorb waste constituents and reduce their exposure to microbes during anaerobic treatment processes. Anaerobic fluidized-bed granular activated carbon (GAC) reactors have been used for over a decade to treat coal gasification waters containing N-aromatic compounds (Wang, 1984; Berchtold et al., 1995). In more recent work, highly inhibitory wastewaters containing chlorophenols and 2,4-dinitrotoluene have been treated effectively using anaerobic fluidized-bed reactors (Suidan, 1996; Berchtold et al., 1995).

At Albany County Airport (Albany, NY), a pilot test was performed using an Anaerobic Fluidized-Bed Reactor (AFBR) with activated carbon as the support medium for treatment of ADF waste. During this time, the operators saw 92-99% chemical oxygen demand (COD) removal with a loading rate up to 15 kg COD/m^3/day (Applied Science and Technology, 1998). Albany County Airport is currently operating a full-scale AFBR for ADF waste treatment.

Research objective. The purpose of this research was to assess the toxicity of MEBT to anaerobic treatment systems with and without GAC and to investigate the fate of MEBT under sustained reducing conditions.

MATERIALS AND METHODS:

Anaerobic digesters. The digester sludge used in this research was collected from the activated sludge facility in Boulder, Colorado. Two bench-scale anaerobic digesters were established in 4L Erlenmeyer flasks. Digesters were stirred intermittently with Teflon coated stir bars (1.5 cm dia. X 20 cm length) and shaken vigorously every 48 hours to ensure adequate mixing. The digesters were maintained at 37 ± 2°C. The pH was maintained at 7.0 ± 0.2 units. Sodium Bicarbonate (7.5g/L) was added as necessary for pH adjustment. Operational parameters of these bench-scale digesters are listed in Table 1.

Analytical Methods. Headspace biogas concentrations were quantified using an isothermal GC/TCD (Gowmac 350). MEBT analysis was measured by isocratic-elution HPLC. MEBT (Cobratec TT-100) was provided by Cincinnati Specialties, Inc. COD was measured using the USEPA approved reactor digestion method (HACH Method 8000) for High Range CODs (0-1500 mg COD/L). Dilutions were required for samples outside the method range. VFAs and pH analyses were performed in accordance with Standard Methods for the Analysis of Water and Wastewater, 18th Edition

Anaerobic toxicity assays. Toxicity assays were carried out in 125 mL serum vials (Wheaton No. 223748) with gray butyl rubber stoppers and 20 mm aluminum crimp seals. MEBT (0 to 1000 mg/L) was added to each vial of digester sludge. Samples were prepared in triplicate. A mixture of centrifuged primary sludge (3500 mg COD/L) and PG (13,000mg COD/L) were used as substrate. The headspace was flushed with 20% CO_2/H_2 prior to incubation. The reactors were allowed to equilibrate for 48 hours on a shaker table at 37°C.

Following equilibrium, the serum vials were fed again. Gas analysis was done periodically. CH_4 and CO_2 production were measured for each sample. Selected samples were analyzed for MEBT concentration to eliminate the possibility of degradation during the experiment. Assays were run for 5 days without re-feeding in order to observe the response to the different MEBT concentrations. COD, pH, and TS/VS analyses were performed at the beginnning and end of the incubation period. This experiment was repeated with the addition of GAC (biomass/GAC = 10% w/w) for 0, 500 and 1000 mg/L MEBT.

DISCUSSION:

Sorption Studies. A Freundlich isotherm equation best describes the sorptive behavior of MEBT on anaerobic digester sludge (Figure 1). The Freundlich constants are 1/n (slope) and K_f (adsorption coefficient). The affinity of MEBT for anaerobic digester sludge is low as indicated by the low absorbent capacity (K_f). In the presence of GAC (biomass/GAC=10%), no MEBT was found in solution.

Anaerobic Toxicity Assays. The toxicity threshold for MEBT in anaerobic digesters is 300 mg/L (one tailed t-test, $\alpha = 0.05$) (Figure 2). Addition of GAC to anaerobic digester systems (biomass/GAC = 10%) will significantly reduce toxic effects of MEBT (one tailed t-test, $\alpha = 0.01$) (Figure 3). MEBT is sequestered by the GAC.

The percent methanogenic activity (based on control of 0 mg/L MEBT) decreases with an increase in MEBT concentration (Figure 4). The effective yield decreases with an increase in MEBT concentration (Figure 5). This decrease is reduced with the addition of GAC.

CONCLUSIONS:

- MEBT persists in anaerobic environments and sorbs to biomass.
- MEBT will reduce the efficiency of anaerobic treatment systems at concentrations above the toxicity threshold.
- The addition of GAC to an ADF waste treatment system may diminish the toxic effects of MEBT.

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FIGURE 1: Sorption of MEBT to Digester Sludge
Freundlich Isotherm: Log X/V = 0.933 Log Ce + Log 0.31
error bars = 99% CI

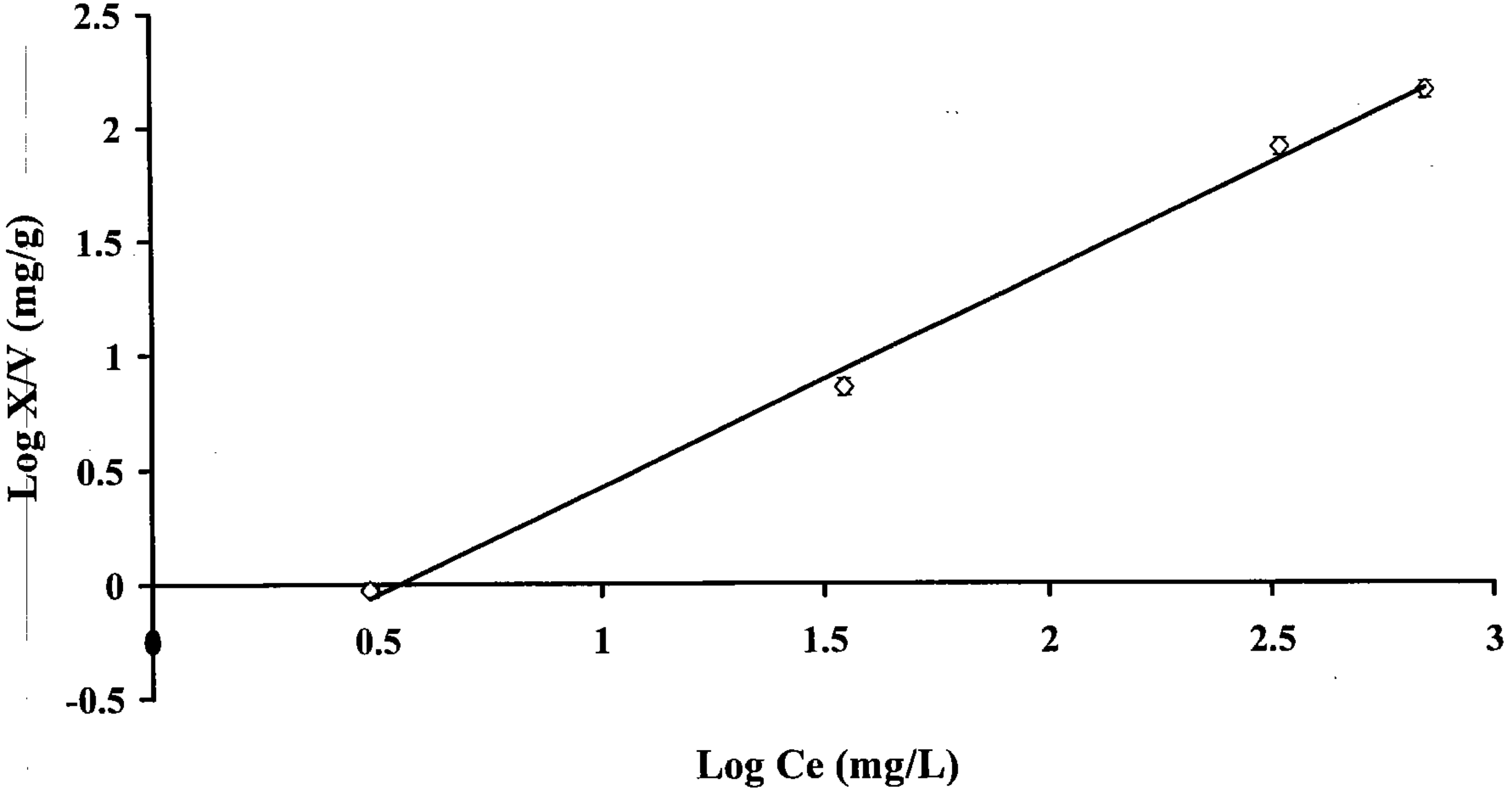

FIGURE 2: Toxicity of MEBT to Anaerobic Digesters

error bars = 1 std error

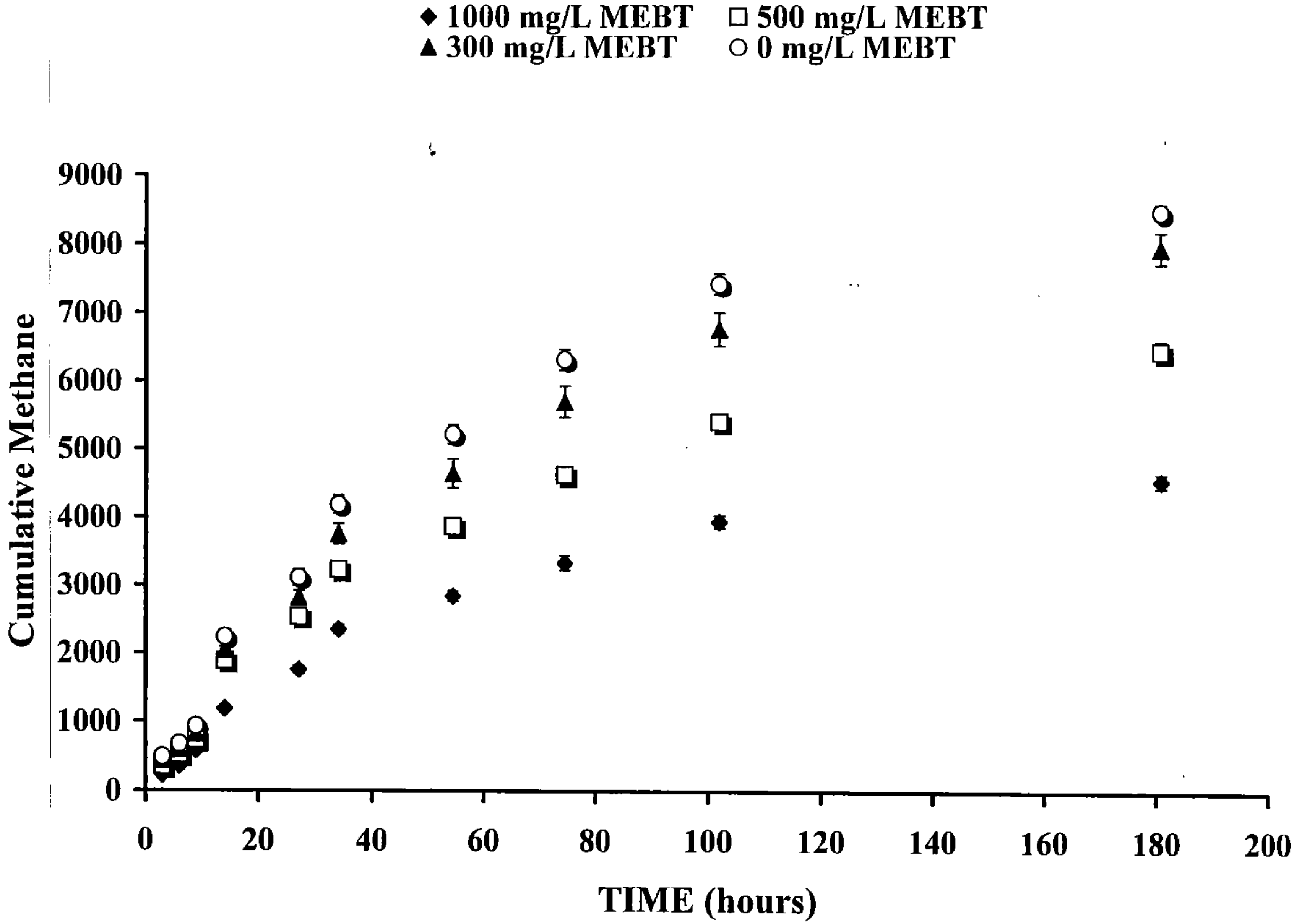

FIGURE 3: Toxicity of MEBT to Anaerobic Digesters with GAC (biomass/GAC = 10%) error bars = 1 std error

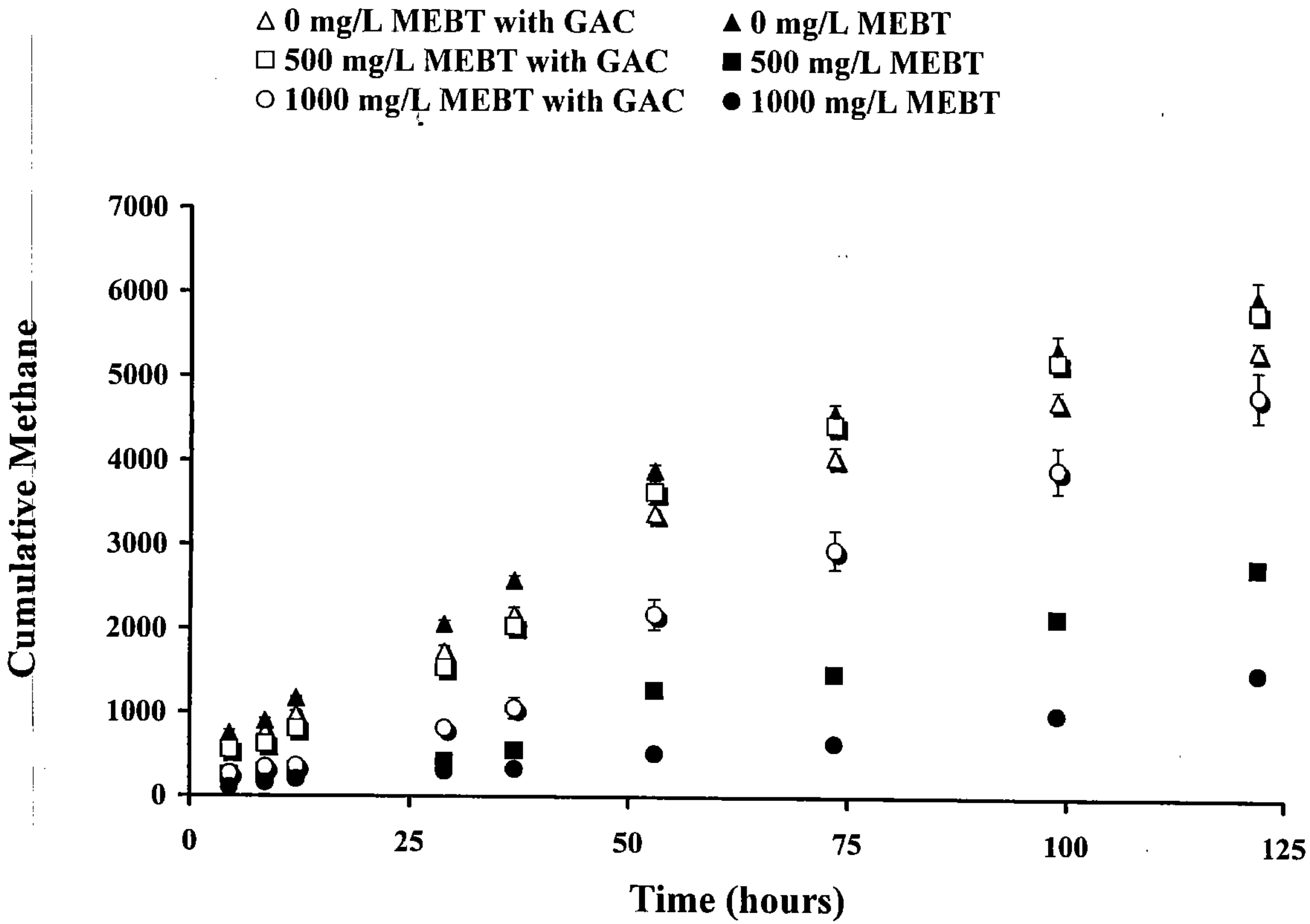

FIGURE 4: % Methanogenic Activity

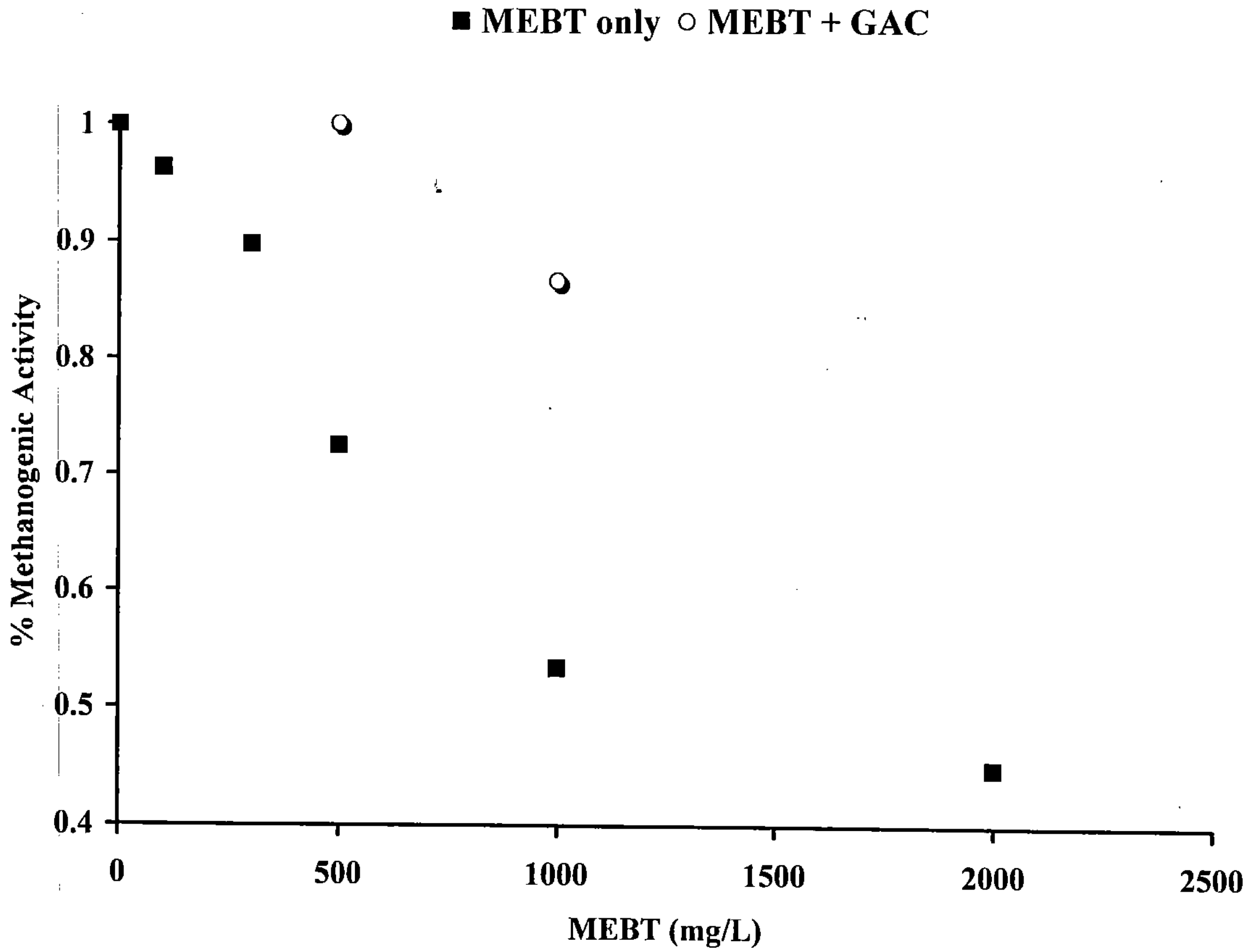

FIGURE 5: Effective Yield