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Degradation of High Concentrations of Glycols, Antifreeze, and Deicing Fluids

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ABSTRACT

A microbial consortium (EG-c) capable of degrading high concentrations of glycol-based waste was isolated from soil enrichments. The isolate primarily responsible for glycol degradation was a gram-negative rod (EG-y) that produced a water-soluble pigment. Initial laboratory experiments measured the degradation of ethylene glycol (EG) and propylene glycol (PG) at 25°C. Cell biomass optical densities increased (660nm) from 0.01 to 0.5 within 48 h and reached a maximum of 0.73 at 72 h. Respirometry experiments showed oxygen consumption rates of ca. 1,000 mg/L/day with glycol degraded at a rate of ca. 2,000 mg/L/day, (confirmed with gas chromatography). Laboratory tests were expanded to evaluate the degradation of a commercial antifreeze (primarily EG based) and two deicing fluids (one PG and one EG based) at both 25 and 4°C (a more realistic winter temperature).

INTRODUCTION

Glycol-based products are used in numerous industries. Ethylene glycol (EG) is a primary component of equipment coolants and aircraft and runway deicing fluids, and is used in the pharmaceutical manufacturing industry. Approximately 4.93 billion pounds were produced in 1991, making it the 30th most produced chemical in the United States (American Chemical Society 1992). Propylene glycol (PG) is an antifreeze additive, as well as a preservative and emulsifier in food and bath products. More than 745 million pounds were produced in 1991 (American Chemical Society 1992).

One significant source of glycol waste is generated from spent deicing fluids. Millions of gallons of deicing fluids (EG/PG mixtures) are used each year at northern aircraft facilities, with estimates greater than 25,000 gal/y for one small military air base and 1.5 million gal for one commercial airline (1992-1993) (Airline representative, Minnesota, personal communication). Use of these deicing compounds results in large amounts of spent fluid discharged into sewer systems or collected for treatment at off-site facilities (Anon, 1989).

On-site degradation of high concentrations of deicing fluids and antifreezes may prove to be a cost effective-method for glycol disposal. Gycol waste is currently diluted to less than 10% before municipal facilities will accept it for treatment (Airline representative, Minnesota,personal communication). Wastewater treatment facilities usually specify 1 to 5% glycol as the maximum concentration for efficient microbial degradation and acceptable oxygen demands. Thus, the

degradation of glycol to concentrations < 5% can significantly reduce the volume of material discarded to municipal facilities.

This work focused on the isolation of bacteria capable of degrading a >10% concentration of glycol to <5% glycol. Preliminary resuls also showed contaminant degradation rates at 4°C that was only slightly slower than at 25°C.

EXPERIMENTAL PROCEDURES AND MATERIALS

Soil Enrichment

Soil samples were received from a site with a long history of glycol contamination. Soils (5 g) were established in 100 mL minimal salt medium (Little et al. 1988) in 250 mL milk bottles with varying carbon contamination. Propylene and ethylene glycol were analytical grade (J.T. Baker, Inc., Phillipsburg, New Jersey), the commercial antifreeze was ethylene glycol based, and the deicing fluids were concentrated unused ethylene glycol-based product (NDEG) and a dilute spent propylene glycol-based product (PPG).

All solutions were filter sterilized (0.2 µm filter) and kept at 4°C prior to use. Ethylene and propylene glycol, the commercial antifreeze, and concentrated deicing fluid (ethylene glycol-NDEG) were handled as pure solutions (100%). Propylene glycol-based deicing fluid was a spent solution with a concentration of ca. 7% propylene glycol (PPG) in rain water. Enrichments were established in duplicate at 1, 5, and 10 % solutions with the exception of the spent deicing fluid (1, 5, and 7%). Fresh transfers were made weekly (100 µL supernatant:100 mL minimal salts medium). Bottles were incubated at room temperature on an orbital shaker.

Culture Identification

Supernatant samples (100 µL) were plated onto nonspecific nutrient agar (Difco) plates and noble agar plates containing 1% ethylene glycol or 1% propylene glycol. Plates were incubated at room temperature for 3 to 7 days. Pure cultures were isolated and gram stains performed.

Analytical Assay

Quantitative degradation was verified using gas chromatography. Supernatant samples were filtered using a 0.8/0.2 µm stacked Acrodisc filter. Liquid injections of 1 µL were analyzed using a Perkin-Elmer Sigma 2000 gas chromatograph equipped with a flame ionization detector using a 30 m J & W Scientific DBWAX column (0.53 megabore, 1 micron film). Method conditions were oven temperature 160°C, injector temperature 250°C, and detector 230°C, with a nitrogen gas carrier flow of 5 mL/min.

RESULTS AND DISCUSSION

The microbial consortium (EG-c) isolated from soil enrichments initially consisted of 5 to 10 phenotypically different organisms and was able to degrade a variety of glycol-based products at high concentrations. The consortium was reduced to 3 isolates by maintaining colonies on plates containing only ethylene glycol or propylene glycol as the sole carbon source. The dominant isolate (EG-y) produced a water-soluble yellow pigment, however, biochemical tests and lipid analyses have not provided a conclusive identification for any of the gram negative isolates.

Microbial growth and respiration indicated different patterns of glycol metabolism. The greatest increase in optical density occured in cultures grown on PG, followed by cultures grown on PPG, EG, antifreeze and NDEG (Figure 1). However, respirometry results (Figure 2) showed

that growth on the spent deicing fluid (PPG), resulted in the greatest amount of oxygen consumed followed by the ethylene glycol deicing fluid (NDEG), pure EG and the commercial antifreeze and last, pure PG. Quantification for all test compounds was confirmed using gas chromatography (e.g. Figure 3). Ethylene glycol was reduced from 10% to <6% within 7 days, the commercial antifreeze (ethylene glycol based) was reduced from 5% to <2% with propylene glycol being the most recalcitrant. Typically, 10 to 40% of the initial concentration was degraded over a 7-day period, which corresponded to an average glycol metabolism of 1,000-4,000 mg/L/7-day period. Overall, the degradation of 1 to 5% glycol was not as significant as the 10% solutions.

The on-site biodegradation of glycol wastes may be a cost-effective disposal method for a variety of industries. Yet to have cost-effective degradation, other operating conditions must be evaluated and optimized. For example, we have begun to measure the degradation of deicing fluids at reduced ambient temperatures (≥4°C). This is important for the potential to bioremediate spent deicing fluids at Northern glycol-generating waste facilities during winter months.

Degradation of antifreeze and deicing fluids has the potential to significantly reduce the glycol concentration released to treatment plants, where it is the single most common compound during the winter months at numerous northern wastewater treatment facilities. Municipal airports could significantly reduce their waste disposal costs by reducing the concentration of glycol fed to a treatment facility. Information from this work will be applied to a field-scale demonstration addressing on-site degradation of spent deicing fluids.

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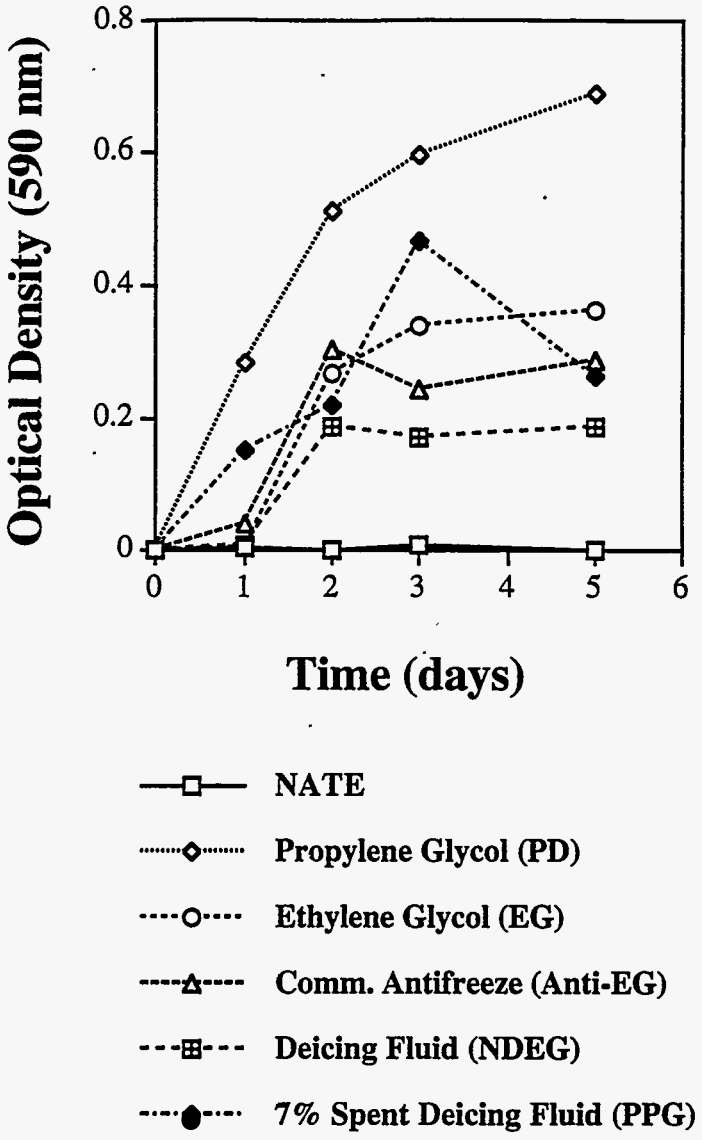

Figure 1. Qualitative measure of glycol degradation by increased optical densities. All carbon compounds were at 5% glycol in NATE (minimal salts media).