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Evaluation of Municipal Wastewater Treatment Plant Activated Sludge for Biodegradation of Propylene Glycol as an Aircraft Deicer

Justin D. Delorit

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EVALUATION OF MUNICIPAL WASTEWATER TREATMENT PLANT ACTIVATED SLUDGE FOR BIODEGRADATION OF PROPYLENE GLYCOL AS AN AIRCRAFT DEICING FLUID

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AFIT/GEM/ENV/12-M03

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AFIT/GEM/ENV/12-M03

EVALUATION OF MUNICIPAL WASTEWATER TREATMENT PLANT ACTIVATED SLUDGE FOR BIODEGRADATION OF PROPYLENE GLYCOL AS AN AIRCRAFT DEICING FLUID

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Presented to the Faculty

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In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Engineering Management

Justin D. Delorit, B.S.

Captain, USAF

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AFIT/GEM/ENV/12-M03

Abstract

Aircraft deicing fluid used at airport facilities is often collected for treatment or disposal in order to prevent serious ecological threats to nearby surface waters. This study investigated lab scale degradation of propylene glycol (PG), the active ingredient in a common aircraft deicing fluid, by way of a laboratory-scale sequencing batch reactor containing municipal waste water treatment facility activated sludge (AS) performing simultaneous organic carbon oxidation and nitrification. The ability of AS to remove PG was evaluated by studying the biodegradation and sorption characteristics of PG in an AS medium. The results indicate sorption may play a role in the fate of PG in AS, and the heterotrophic bacteria readily degrade this compound. Therefore, a field deployable SBR may be appropriate for use in flight line applications.

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For my girls

Acknowledgments

This work would not have been possible without the direct and indirect contributions of many people. In the interest of brevity, I have chosen to highlight those who have contributed the most. First and foremost, I would like to thank Major LeeAnn Racz for her clam, steadfast direction. I hold the deepest respect for your academic knowledge and hope that I can reflect your character. Thank you for giving me perspective. To my wife, you have made all of this possible. Your constant encouragement and unconditional support have provided me motivation and strength through this process, and challenged me to be a better husband and father. I love you. Captain Steven Schuldt, I will never forget your friendship. I am blessed to have worked with you during this process and look forward to sharing another assignment with you. I would like to recognize the musical genius of Donald Fagan and Walter Becker; your masterpieces accompanied me through many trying hours of lab work and technical writing. None of the aforementioned interactions or perceived successes would have been possible without the power and grace of God. All glory, laud, and honor to thee, redeemer, king.

Justin D. Delorit

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EVALUATION OF MUNICIPAL WASTEWATER TREATMENT PLANT ACTIVATED SLUDGE FOR BIODEGRADATION OF PROPYLENE GLYCOL AS AN AIRCRAFT DEICING FLUID

I. Introduction

Background

The use of chemical aircraft deicers (ADF) by airport facilities worldwide, as a preventive tool in the management of snow, ice, and frost accumulations on aircraft and airfield surfaces, has greatly improved flight safety (Halterman-O'Malley, 1997). Experimentation using differing chemical additives has resulted in the establishment of two industry standard active ingredients, Ethylene Glycol (EG) and Propylene Glycol (PG). The military has distinguished between PG and EG deicers as type I and II, respectively, based on their use (Johnson L. M., 1997). Type I ADF, which is PG based, is used primarily for deicing aircraft surfaces, while type II aircraft deicer and anti-icier (ADAF), which is three parts EG to one part PG, and provides continued anti-icing as well as deicing. Specified guidelines for application, viscosity, and corrosion inhibition are given by military specification MIL-A-8243, which specifies both type I and II deicer/anti-icier (Johnson, Varney, & Switzenbaum, 2001).

Problem Statement

Of substantial concern with respect to environmental impacts of deicing operations, is biological oxygen demand (BOD) of ADF materials contained in runoff as they enter natural waters (United States EPA, 2000). The organic carbon content in ADF is high enough in airfield runoffs to create considerable depletion of dissolved oxygen (DO) in receiving waters. DO is required at specific levels, and is a vital resource in the sustainment of aerobic, aquatic life. Aquatic life is considered stressed when dissolved oxygen levels drop below 5.0 mg L^{-1}. DO levels falling below 2 mg L^{-1}, for even short periods of time, can result in fish kills.

Recently, the Environmental Protection Agency (EPA) has begun to scrutinize ADF discharge at airfields, commercial and private. Airfield managers are now responsible for collecting and disposing of all used ADF in an approved manner. Available options include recycling, disposal under a waste contract, or onsite pretreatment (United States EPA, 2000).

When considering disposal courses of action, airfield managers must determine which options are available, as well as assess economic and environmental consquences. Recycling used ADF is typically the least costly method of disposal. Recyclers will take used ADF at no or limited cost to the user. Subsequently, the user is no longer considered responsible for its disposal. However, recyclers adhere to strict used ADF concentration minimums, generally 20% glycol, in order to turn profits (Technologies, 2007). This minimum concentration can be difficult to achieve based on variations in precipitation volume collected along with used ADF. For producers of used ADF, like the United States Air Force (USAF), consistency in disposal options is more important than overall cost savings. Therefore, recycling is typically not considered an acceptable option by the USAF.

Used by Wright-Patterson Air Force Base (WPAFB), Hazardous Waste contract disposal of used ADF, is another option available to airfield managers. Regardless of final concentration or content, a contractor is hired to perform proper disposal of used ADF. Of benefit to the USAF is the relative ease of disposal. Other than collection of used ADF, the USAF is responsible only for procuring a contractor and in no way is involved in treatment. Generally, the constituents of used ADF are not considered hazardous and thus do not require disposal under the same regulations as true hazardous waste. Additionally, volumes in excess of 5,000 gal are produced and collected annually by WPAFB, which is large with respect to hazardous waste contracts. A premium, is paid for hazardous waste analysis and disposal, and use of that service for used ADF can be considered captial misspent (Personal Communications, Zachary Olds, AFMC/CEANQ). Most hazardous wastes, disposed of under contract, are produced in quantities much smaller than used ADF. Prices for ADF disposal vary based on amount produced and contract used.

Neither recycling nor hazardous waste disposal methods are considered to be optimal under USAF deicing operational requirements. Therefore, this thesis focused on determining the feasibility of using onsite pretreatment of used ADF prior to release to a municipal waste water treatment facility, with specific attention to PG as the main ADF constituent.

Current on-site pretreatment models call for unsightly and odiferous treatment lagoons, which require large physical footprints and attract wildlife that pose flight safety risks (Caithness, Williams, & Bull, 1968). Batch tank reactors may be a treatment option better suited for airfield applications, as they serve as remedies for stated lagoon drawbacks (Tham P., 2004; Zitomer D. H., 2010; Sabeh & Narasiah, 1992).

Evaluating the suitability of using AS for on-site pretreatment in a sequential batch reactor (SBR) requires consideration of the AS bacterial consortium and the wastewater treatment process from which it is obtained.

Wastewater treatment is the process of physical, chemical, and biological contaminant removal from municipal waste (Metcalf & Eddy, 2002). See Figure 1.

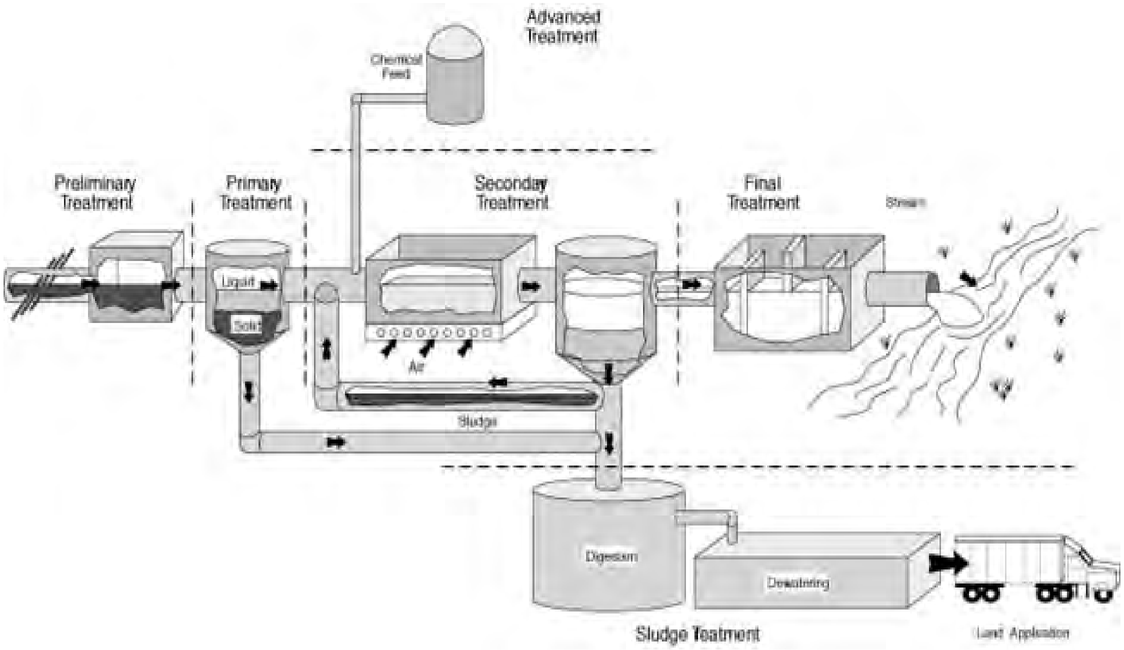

Figure 1. Wastewater Treatment Process (Mancl, 2012)

Wastewater treatment plants (WWTP) are designed to produce an environmentally safe stream of effluent to be injected into a receiving surface water body. The WWTP is based heavily on hydraulic retention times, where controlling water flow is paramount to removal of specific contaminants. Typically, a WWTP will have a pre-treatment phase in which large particles, considered non-biodegradable, including grit and foreign items like rags are removed via settling chambers, screens, and bars. Wastewater will then flow to process primary treatment where greases and oils will rise to the surface of large clarification basins, where they will be skimmed. Next, the wastewater will enter a secondary treatment process, which is where the majority of harmful biological content will be removed. Many options exist where by removal can be achieved, and a WWTP's type will be derived from this process. A secondary treatment process commonly used is removal by activated sludge (AS). While operational parameters and methods vary, the basic process involves the use of dissolved oxygen to encourage growth of a biological consortium capable of removing harmful contaminants.

The AS consortium contains many kinds of heterotrophic bacteria which are responsible for the consumption of organic carbon. Also, AS may contain autotrophic, nitrifying bacteria that can degrade organic carbon via cometabolism. It is important to understand the contributions of each type of bacteria because nitrifying bacteria are sensitive to many parameters including availability of NH_3 and O_2, changes in temperature, light transmittance (Datta et al., 2010). Also, the role of nitrifying bacteria in the degradation of PG will determine the suitability of AS in a full-scale application since a nitrifying culture may be more susceptible to system upsets under full-scale conditions. This study used an AS consortium as opposed to other consortium based on several factors. Mainly, the ease and cost of procurement and the many kinds of robust bacteria contained in the consortium allow for widespread use, in the event a field unit is designed.

This work evaluated the role of sorption in the fate of PG in AS. Sorption refers to the action of both adsorption and absorption. Adsorption occurs where the molecules of an adsorbate compound, through the consequence of surface energy, bond to the surface another compound, known as the adsorbent. (Alley, 1994) Absorption is described as the uptake of the absorbate compound into the volume of the absorbent. Chemical analytical methods exist to quantify both adsorption and absorption separately; however, this research is concerned only with the cumulative effect, known as sorption. The importance of sorption, in the context of this research is, if after degradation occurs, some amount of PG remains sorbed to AS, it may need to regarded as hazardous waste and disposed of as such.

Research Questions

The purpose of this study was to evaluate the ability of AS to remove PG, the main chemical component of Type I ADF. Specifically, this study determined to what effectiveness PG can be treated, and which bacteria type within the AS population account for PG removal. The study included determining sorption and kinetic rates in order to identify the effectiveness of biodegradation in laboratory-scale sequencing batch reactor.

The specific goals of this study included:

1. Determining the degradation of PG by municipal wastewater treatment plant AS in order to evaluate:
    - The effectiveness of AS to degrade actual PG concentrations in used ADAF, and
    - Degradation kinetics of PG in AS.
2. Determining the role of PG sorption in AS.
    - Sorbed PG that remains undegraded may require waste AS to be treated as hazardous waste.

Scope and Approach

This research effort was focused on lab scale evaluation of AS as a vehicle for the degradation of PG as an ADF. In order to achieve accurate, quantitative evidence, several laboratory analytical methods were used (Castro, Davis, & Erickson, 2004).

In determining sorption kinetic rates, batch samples testing were used, where a known volume and concentration of heat inactivated AS was combined with a known volume and concentration of PG. Contact time was varied in individual vials from 0 to 60 minutes, with solid and liquid phase extraction measurements taken at appropriate intervals, in order to show time of sorption.

In conducting sorption equilibrium isotherm experiments, the time of sorption found in the sorption kinetic experiment was used as the contact time between AS and PG. In the isotherm experiment, the concentration of AS was varied at known intervals, while known PG concentrations was held constant. The goal of this experiment was to determine how much PG sorbs to varied concentrations of AS through analysis of solid and liquid phase extraction, in order to predict sorption during degradation.

Degradation experiments focused on time required to degrade PG. Acceptable, treated concentrations are determined by interpreting existing discharge permits or by consulting the receiving entity. Typically the limit is set at 100 gal d^{-1} of 50% PG solution. (Fermilab, 2006) In this experiment, flasks of known concentrations of both AS and PG were aerated to resemble batch reactors. Degradation was measured at hourly intervals by testing extractions of the solid and liquid phase, as well as COD, Ammonia, and Nitrate.

In order to determine which constituents in the AS consortium are responsible for PG degradation, it was necessary to conduct two degradation experiments. The first was conducted under normal operating conditions, as previously described. The second experiment was conducted with nitrifying bacteria inhibited, using allylthiourea. If nitrifying bacteria are essential to degradation, the second experiment should have resulted in minimal degradation. Conversely, if nitrifying bacteria are not essential to degradation, results from both experiments should have been nearly identical, with variations resulting from AS concentration fluctuation

Preview

This thesis was written using the scholarly article format. Chapter 2 contains the manuscript for submission to Water Science and Technology, a peer-reviewed scientific journal. The manuscript includes an abstract, introduction, materials and methods, results, discussion, and conclusions. Chapter 3 offers a final discussion of the conclusions along with pertinent findings and future research not discussed in Chapter 2.

II. Scholarly Article

Abstract

Aircraft deicing fluid used at airport facilities is often collected for treatment or disposal in order to prevent serious ecological threats to nearby surface waters. This study investigated lab scale degradation of propylene glycol (PG), the active ingredient in a common aircraft deicing fluid, by way of a laboratory-scale sequencing batch reactor containing municipal waste water treatment facility activated sludge (AS) performing simultaneous organic carbon oxidation and nitrification. The ability of AS to remove PG was evaluated by studying the biodegradation and sorption characteristics of PG in an AS medium. The results indicate sorption may play a role in the fate of PG in AS, and the heterotrophic bacteria readily degrade this compound. Therefore, a field deployable SBR may be appropriate for use in flight line applications.

Introduction

The use of chemical aircraft deicers (ADF) by airport facilities worldwide, as a preventive tool in the management of snow, ice, and frost accumulations on aircraft and airfield surfaces, has greatly improved flight safety (Halterman-O'Malley, 1997). Experimentation using differing chemical additives has resulted in the establishment of two industry standard active ingredients, Ethylene Glycol (EG) and Propylene Glycol (PG). The military has distinguished between PG and EG deicers as type I and II, respectively, based on their use (Johnson L. M., 1997). Type I ADF, which is PG based, is used primarily for deicing aircraft surfaces, while type II aircraft deicer and anti-icier (ADAF), which is three parts EG to one part PG, and provides continued anti-icing as well as deicing. Specified guidelines for application, viscosity, and corrosion inhibition are given by military specification MIL-A-8243, which specifies both type I and II deicer/anti-icier (Johnson, Varney, & Switzenbaum, 2001). Application of ADF to aircraft is typically achieved via use of truck mounted pressurized sprayer arm. Procedures result in substantial drippage and overspray, to 85% of initial volume, which results in runoff.

Of substantial concern with respect to environmental impacts of deicing operations, is biological oxygen demand (BOD) of ADF materials contained in runoff as they enter natural waters (United States EPA, 2000). The organic carbon content in ADF is high enough in airfield runoffs to create considerable depletion of dissolved oxygen (DO) in receiving waters. DO is required at specific levels, and is a vital resource in the sustainment of aerobic, aquatic life. Aquatic life is considered stressed when dissolved oxygen levels drop below 5.0 mg L^{-1}. Levels sagging below 2 mg/l, for even short periods of time, can result in fish kills.

Recently, the United States Environmental Protection Agency (EPA) has begun to scrutinize ADF discharge at airfields, commercial and private. Typically the limit is set at 100 gal d^{-1} of 50% PG solution. (Fermilab, 2006) Airfield managers are now responsible for collecting and disposing of all used ADF in an approved manner. Available options include recycling, disposal under a waste contract, or onsite pretreatment (EPA, 2000). Recycling, while generally free to the waste producer, requires minimum waste ADF concentrations, which can be difficult to routinely ensure. Disposal of used ADF as hazardous waste requires use of contracts for which they are not intended, as PG is not considered a hazardous waste. These contracts are used because there may not be an accepted method of adequate disposal (Personal Communications, Zachary Olds, AFMC/CEANQ).

This research is a preliminary investigation of on-site biological pretreatment of used propylene glycol (PG), the active ingredient in aircraft deicer fluid (ADF). This work used activated sludge (AS), an easily obtainable, robust consortium of many kinds of heterotrophic bacteria which readily consume organic compounds, in a sequencing batch reactor (SBR) to treat PG. AS may also contain autotrophic, nitrifying bacteria that can degrade organic carbon via cometabolism (Ren et al., 2007a; Shi et al., 2004; Vader et al., 2000). We determed the role of sorption in the fate of PG in AS as well as the relative roles of heterotrophic and nitrifying AS bacteria in the degradation of PG. It is important to understand the contributions of each type of bacteria because nitrifying bacteria are sensitive to many parameters including availability of NH_3 and O_2, changes in temperature, light transmittance (Datta et al., 2010). Evaluating the role of nitrifying bacteria in the degradation of PG will determine the suitability of AS in a full-scale application since a nitrifying culture may be more susceptible to system upsets under full-scale conditions. This work concludes that an AS consortium may be suitable to treat PG in used ADF prior to further treatment in a municipal wastewater treatment facility.

Materials and Methods

Sequencing Batch Reactor Operation

A 2.0 L sequencing batch reactor (SBR) was seeded with sludge from the Fairborn Water Reclamation Facility (FWRF), Fairborn, Ohio. The operational and feed methods were modeled after Racz et al. (2010) in order to support AS that performed simultaneous organic carbon oxidation and nitrification. The feed included a peptone/micronutrient, simulated wastewater mix (Feed 1) and a sodium bicarbonate solution (Feed 2), capable of supporting both autotrophic and heterotrophic bacteria within the AS consortium. Municipal wastewater contains a complex mixture of organic compounds, including volatile fatty acids. As such, sodium acetate was added to simulate the volatile fatty acids present in municipal wastewater (Kindachi et al., 2004), and peptone was added as a complex organic carbon source (Goel and Noguera, 2006). Feed A contained (per liter) 44.6 g NaHCO3 and the composition of feed B was (per liter) 6 g peptone (5.38 g glucose in the second SBR), 1.25 g sodium acetate, 2.26 g NH4Cl, 6.86 g MgCl2·6H2O, 1.72 g CaCl2·2H2O, 0.6675 g KH2PO4 and 20mL of a trace element solution. The trace element solution, adapted from (Hesselmann et al., 1999), consisted of the following per liter of deionized water: 5.46 g citric acid, 4.0 g hippuric acid, 0.72 g Na3NTA·2H2O, 0.3 g Na3EDTA·4H2O, 3.0 g FeCl3·6H2O, 0.5 g H3BO3, 0.3 g ZnSO4·7H2O, 0.24 g MnCl2·4H2O, 0.14 g CuSO4·5H2O, 0.06 g KI, 0.06 g Na2MoO4·2H2O, 0.06 g CoCl2·6H2O, 0.06 g NiCl2·6H2O, and 0.06 g Na2WO4·2H2O. Daily reactor operations were based on two 12 h cycles consisting of four stages per cycle. The first stage began with a five minute filling sequence where 624 mL of deionized water, 38 mL Feed 1, and 8 mL Feed 2 were injected via peristaltic pump bringing total reactor volume to 2.0 L. The next stage was an 11.5 h aerobic reaction phase, during which the mixture of AS, deionized water, and feeds were mixed and aerated to ensure adequate contact and maintain dissolved oxygen concentrations. The typical dissolved oxygen concentration during the aerobic reaction phase was 7 mg/L. The next phase included 20 min of non-aerated settling followed by a decant phase where 670 ml of supernatant effluent was decanted. The hydraulic retention time was 33 h, while the solids retention time was 20 d.

PG extraction from AS

PG was extracted from both the solid and liquid phases of AS biomass by passing a 10 mL sample through a Büchner funnel with a 1.2 μm Whatman GF/C glass fiber filter paper. The filtrate was collected with a syringe and diluted with DI water as necessary for analysis by gas chromatograph / mass spectrometer (GC/MS). The GF/C filter paper containing the biomass solids was then placed in a beaker. Four mL methyl ethyl ketone was added to the beaker, and the beaker was covered with parafilm. Next, the beaker was sonicated for 10 minutes. After sonication, the liquid in the beaker was collected with a syringe and analyzed by GC/MS.

PG Analytical Method

In order to quantify PG present in solid and liquid phases, an Agilent Technologies, 6980N GC, and a 5973 Inert Mass Selective Detector MS were used to measure concentrations of PG in the samples. The injection volume was 1µL with split ratios ranging from 10:1 to 50:1 in order to achieve concentrations within the calibration curves. The oven temperature started at 35° C and reached a maximum temperature of 200° C with a gradient of 11.1° C/min. The PG calibration curves ranged from 0.984 to 0.990. The method outlined by Matuszewski et al. (2003) was used to determine PG recoveries in sorption kinetic and equilibrium as well as degradation experiments. The PG recoveries ranged between 93.2% and 99.9%.

.

Sorption Kinetics

Sorption refers to the action of both adsorption and absorption. Adsorption occurs where the molecules of an adsorbate compound, through the consequence of surface energy, bond to the surface another compound, known as the adsorbent (Alley, 1994). Absorption is described as the uptake of the absorbate compound into the volume of the absorbent. Chemical analytical methods exist to quantify both adsorption and absorption separately; however, this research was concerned only with the cumulative effect, known as sorption. With respect to degradation, it was first necessary to quantify the rate and amount of sorption potential PG possesses. In order to accurately achieve quantification, both kinetic and isotherm experiments were conducted.

Sorption kinetic experiments determined the amount of time required for sorption to reach equilibrium. 100 mL AS was collected from the SBR and inactivated with heat at 80°C for 30 minutes. At this temperature, the ribosomes of bacteria denature (Lee and Kaletunc, 2002) but minimize changes in sludge features (Ren et al., 2007b). While other studies have used sodium azide (NaN_3) to inactivate metabolic activity (Yi and Harper, 2007) NaN_3 selectively inhibits cytochrome oxidase in gram-negative bacteria. Grampositive bacteria are resistant to the bacteriostatic effects of NaN_3 (Lichsterin and Soule, 1943) The heat-inactivated AS was distributed to vials in 10 mL samples, each containing 850 mg L^{-1} of TSS. PG was added to each AS sample to a final concentration of 50 mg L^{-1}, and the samples were mixed using a rotating disk. PG was extracted from both the liquid and solid phases of each sample at 0.5, 2, 4, 6, 10, 15, 20, 30 and 60 minutes. Additionally, there was a control sample of deionized water and PG. All measurements were conducted in duplicate.

Sorption Equilibrium Isotherm

360 mL of heat-inactivated AS biomass (80°C for 30 min) was placed in Erlenmyer flasks, each with a different concentration of TSS, namely 1125, 985.5, 807.5, 724.5, 591, 437, 268 and 151 mg L^{-1}. PG was added to each flask to a final concentration of 25 mg L^{-1}. The flasks were placed on stir plates for 15 min, the time at which sorption was considered complete according to the sorption kinetics experiment results. The PG was extracted from the liquid and solid phases of the biomass. All measurements were conducted in duplicate. The results were fitted to both the Freundlich and Langmuir sorption equilibrium isotherm models to see which model was best suited for this data.

Biodegradation

The batch tests were conducted in three Erlenmeyer flasks. Flasks, A, B, and C each contained identical concentrations of AS and feed proportional to the SBR feed. Flasks A and B were duplicates and contained 500 mg L^{-1} of PG, while flask C, a control sample, did not contain PG. Every hour, concentrations of chemical oxygen demand

(COD), ammonia, and nitrate were measured in the liquid phase of the AS in order to monitor the performance of the heterotrophic and nitrifying activity. PG from both the solid and liquid phases in the AS was also measured at these times.

Biodegradation with nitrification inhibition

In order to determine the extent to which nitrifying bacteria degraded PG, this experiment paralleled the previous biodegradation experiment, except that the nitrifying bacteria were inhibited by adding 86 μM (10 mg L^{-1}) allylthiourea (ATU) to the AS. ATU was initially added 12 hours prior to the beginning of the experiment to ensure adequate time for nitrification inhibition. An additional 10 mg L^{-1} ATU was added just prior to the test start time in order to ensure inhibition of nitrifying bacteria for the duration of the experiment. ATU is believed to bind with the copper of the AMO active site (Bédard and Knowles, 1989), and therefore selectively inhibits nitrification. While ATU can inhibit nitrifiers at concentrations as low as 8 μM (Hoffman and Lees, 1953; Hooper and Terry, 1973; Sharma and Ahlert, 1977; Tomlinson et al., 1966), complete inhibition can be achieved at an ATU concentration of 86 μM (10 mg L^{-1}) without affecting other metabolic activities (Ginestet et al., 1998). All measurements were taken in duplicate. An additional control was used with simply deionized water and PG to account for abiotic effects such as volatilization and losses to glassware.

Other Analytical Methods

Concentrations of COD, NH_3-N, NO_3^--N, and NO_2^--N were measured using Hach methods 8000, 10031, 10020, and 8153, respectively. Total suspended solids (TSS) and volatile suspended solids (VSS) were measured using standard methods (APHA, AWWA, WEF, 1998). All measurements and tests were conducted in duplicate.

Results and Discussion

Sorption Kinetics and Equilibrium Isotherm

The results from the sorption kinetics experiment are given in Figure 2. Sorption equilibrium was reached at approximately 10 min, at a rate of 3.31 mg L^{-1} min^{-1}. Therefore, the sorption equilibrium isotherm experiment was conducted using a minimum target contact time of 10 min. To ensure sorption was complete, 15 minutes was used as the contact time for the sorption equilibrium isotherm experiment.

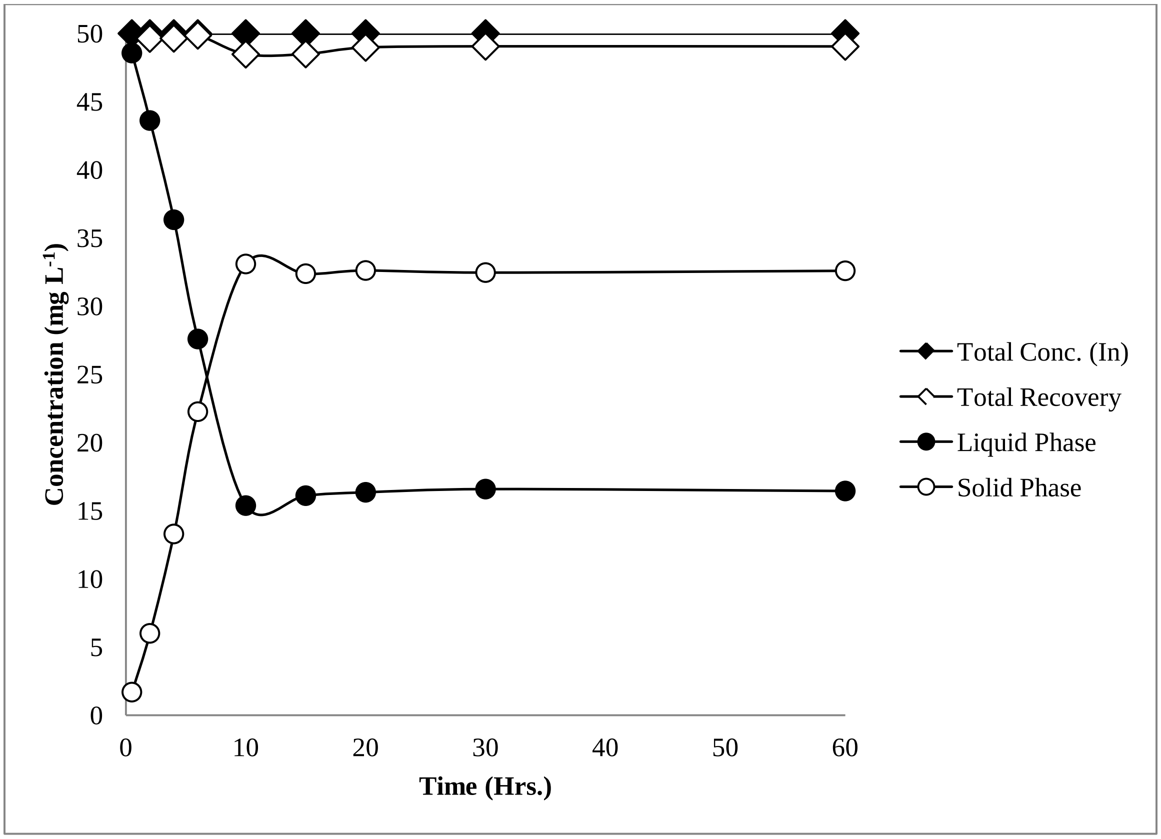

Figure 2. Propylene Glycol Sorption Kinetics: 50 mg L^{-1} heat-inactivated AS

The data was fitted to both the Freundlich and Langmuir sorption equilibrium isotherm models. The Freundlich model best fit the data with a solid-water distribution parameter coefficient (K_d) for PG of 1.56 L kg^{-1}. However, the Freundlich model under-predicts the actual sorbed amount by a factor of about two for degradations with nitrifiers active and inhibited (Figure 3). The uninhibited conditions exhibit similar results. One explanation for the poor ability of the sorption equilibrium isotherm to predict the actual sorbed amounts is that where there is biological activity, PG degradation in the liquid phase can create a concentration gradient in which sorbed PG may desorb and become available for degradation. Additionally, these results indicate that sorption characteristics for PG on a given biomass may change over time throughout a react period. Furthermore, sorption characteristics can also change among biomasses since PG characteristics, which can be important to sorption, can vary between different biomasses (Racz et al., 2012).

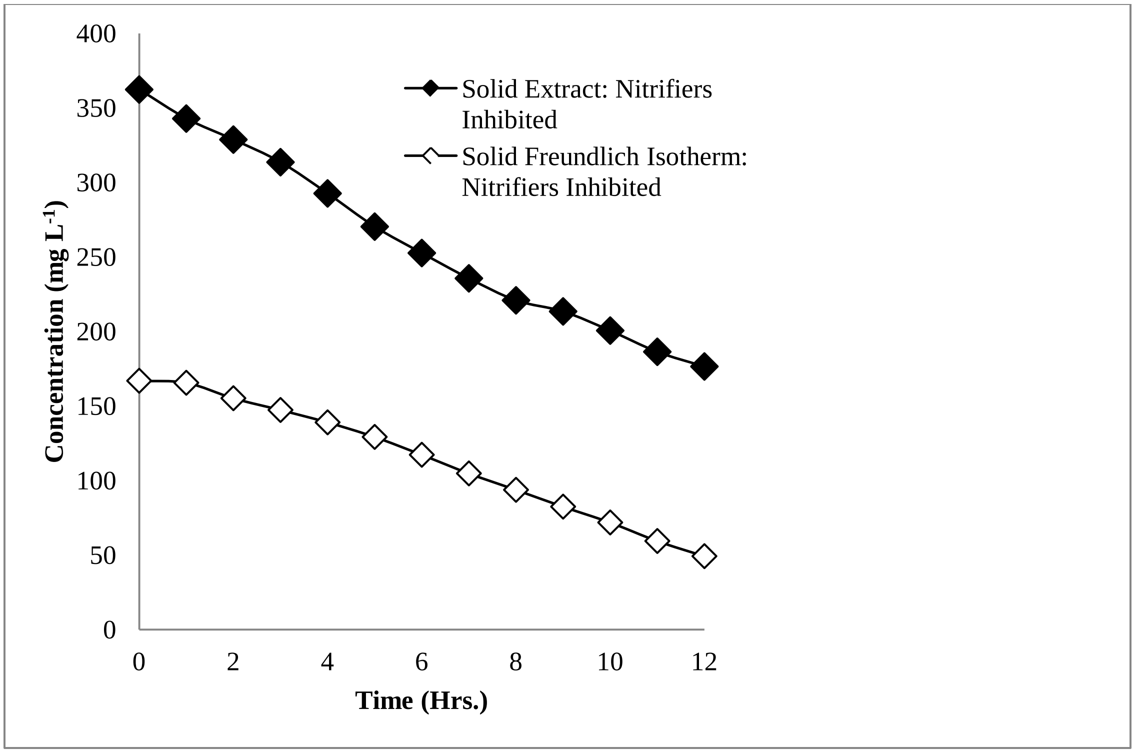

Figure 3. Actual and Predicted Sorption during degradation with nitrifiers inhibited

If the sorbed PG remains undegraded in a pre-treatment scheme using AS, there is the potential that the waste AS may require disposal as a hazardous waste. Nevertheless, the volume of waste AS ought to be much less than the volume of ADAF to be treated, and should not significantly negate the benefits of using an on-site biological pretreatment option.

Biodegradation of PG by Nitrifying AS

Figures 4 and 5 show COD concentrations observed during the degradation experiments where AS was active and inhibited with ATU. COD concentrations were out of the proper calibration curve range during the first several hours of the experiment in which nitrifiers were active. However, it is clear that COD oxidation readily occurred.

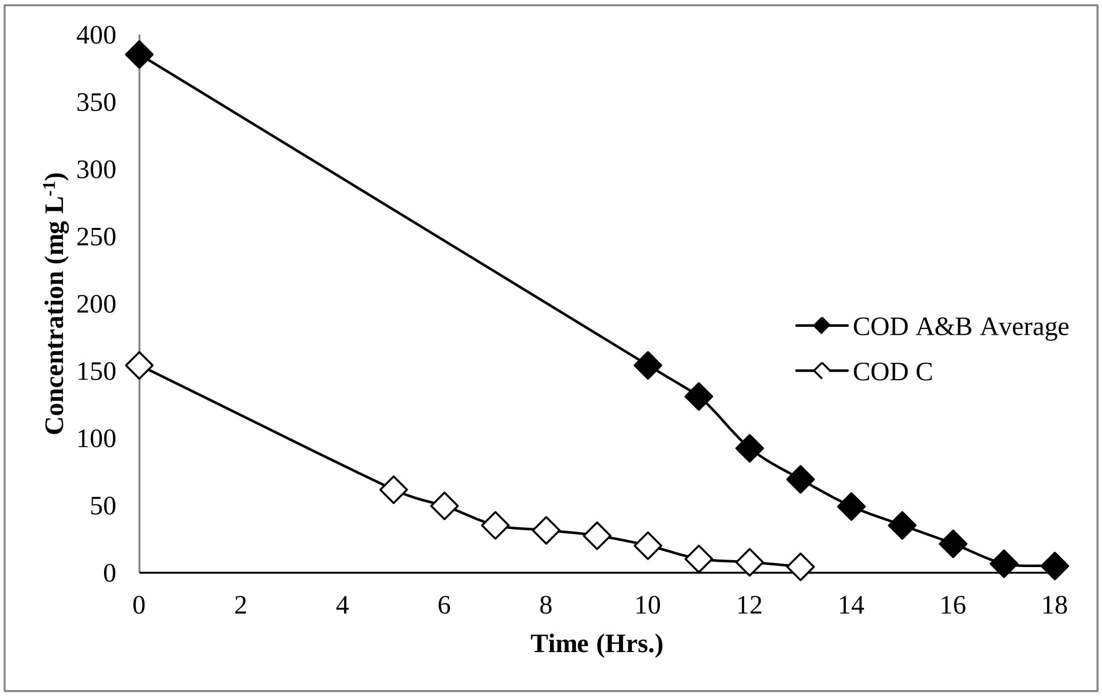

Figure 4. COD: 500 mg L^{-1} in activated sludge at 25° C with nitrifiers active

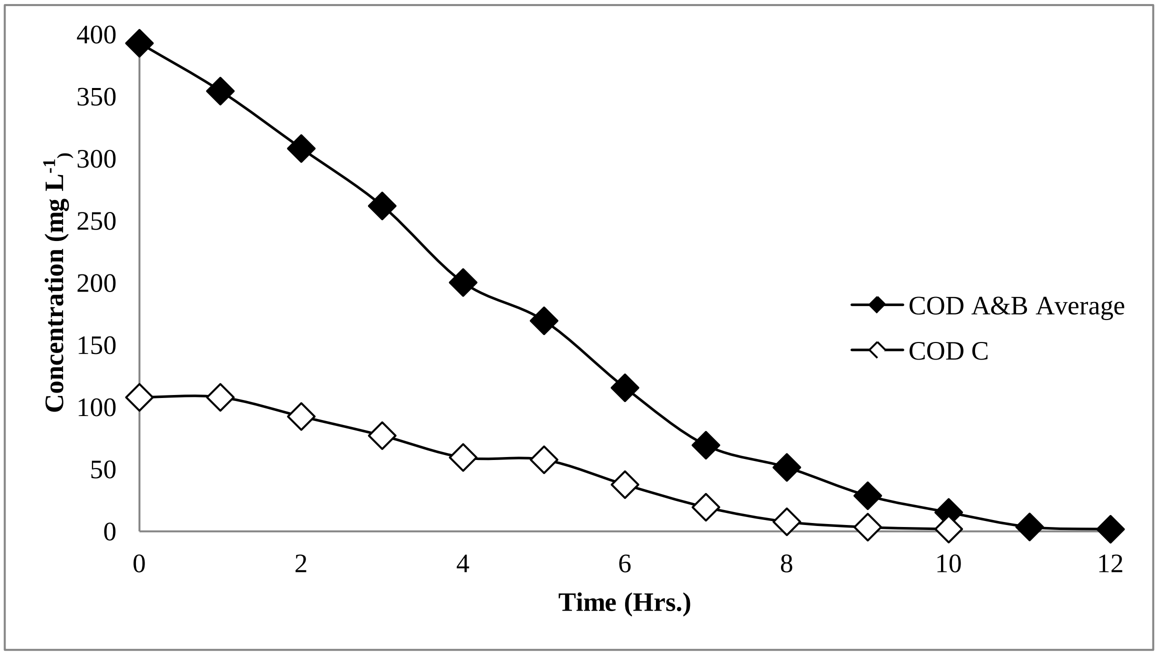

Figure 5. COD : 500 mg L^{-1} in activated sludge at 25° C with nitrifiers inhibited

The COD degradation rate where nitrifiers were active was 21.12 mg L^{-1} hr^{-1}, while COD control flask C decreased at a rate of 11.52 mg L^{-1} hr^{-1}. COD degradation followed first order kinetics with a rate constant of 35.0 mg COD mg VSS^{-1} h^{-1} with a degradation rate of 31.96 mg L^{-1} hr^{-1}, while COD control flask C decreased at a rate of 15.22 mg L^{-1} hr^{-1} where nitrifiers were inhibited. Therefore, PG addition to the AS did not impair COD oxidation. The experimental flasks contained 500 mg L^{-1} propylene glycol (PG), an organic carbon source that accounted for the higher initial COD concentration and more aggressive rate of COD decline. Similar results were observed during experiment in which the nitirifiers were inhibited. The NH_3-N and NO_3-N remained constant throughout the duration of the inhibited nitrifier degradation experiment, indicating that nitrifying activity was sufficiently suppressed. Figure 6 illustrates the actual PG concentrations in both the solid and liquid phases of the AS from the active nitrifier experiment and the inhibited nitrifier experiment. Total concentrations of the total PG fell from an average of 1050 mg L^{-1} to less than 350 mg L^{-1} over the duration of both experiments. TSS concentrations for degradation with nitirifiers ative and inhibited were 765.0 mg L^{-1} and 1257.5 mg L^{-1}, respectively. The 39.1% change in concentration is a result of biomass growth achieved during the two week break between active and inhibited experiments. The difference in TSS concentration accounts for the 33.33% decrease in time required for inhibited degradation.

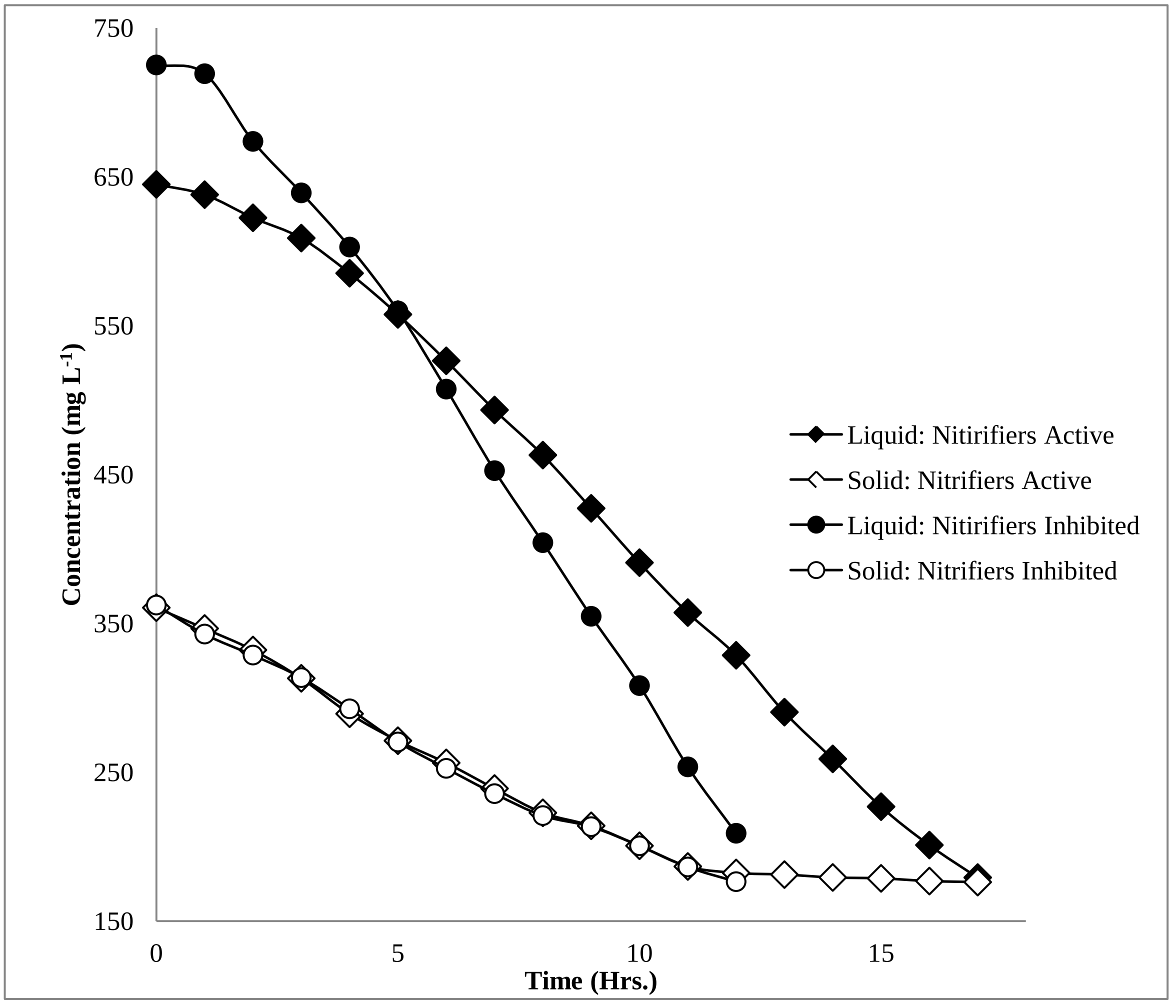

Figure 6. Solid and Liquid Phase PG Degradation: 500 mg L^{-1} activated sludge at 25° C with nitirifiers active and inhibited

These results suggest nitrifiers play an insignificant role in PG degradation, and heterotrophic bacteria are responsible for the majority of PG degradation. This observation is important because on-site treatment of PG can proceed without the need to care for nitrifying bacteria and consideration of their sensitivities to temperature and other potential upsets.

Conclusions

Degradation of propylene glycol (PG) occurs naturally and rapidly when introduced to aquatic environments. However its effects on aquatic environmental parameters, namely dissolved oxygen, make it of significant concern as a used aircraft deicer. We have demonstrated that PG is readily degradable by AS in a laboratory-scale sequence batch reactor. As the heterotrophic bacteria are responsible for the PG degradation, it is not necessary to ensure the strict conditions required for nitrifying bacteria performance. Therefore, AS may be a suitable bacterial consortium for on-site biological pre-treatment of PG.

III. Conclusions

Chapter Overview

The purpose of this chapter is twofold; it reviews the significant findings of the research as well as provide insight to future areas of investigation. It provides brief responses to the questions posed in Chapter 1 and highlights questions generated during the research process.

Review of Findings

Two research questions were identified for research in this thesis effort: 1) what is the effectiveness of municipal waste water treatment facility activated sludge (AS) in PG degradation, and 2) what is the role of sorption with respect to the fate of PG during degradation.

Sorption kinetics and sorption equilibrium isotherm experiments indicated that PG readily reaches sorption equilibrium in heat inactivated AS within in 15 minutes contact time. In addition, degradation kinetics experiments, with nitrifiers both uninhibited and inhibited, revealed significant and rapid degradation of PG. However, the Freundlich equilibrium isotherm model underpredicted the actual sorbed amount of PG by a factor of about 2. Once sorption reached saturation levels during the degradation experiments, 65% of initial concentration, it appears to return to the aqueous solution for degradation. This can be shown by examining the post degradation concentrations of the PG. For example, degradation during the nitrifiers inhibited experiment disposed of 70% of initial PG concentrations over 12 hr. Recalling sorption occurs in less than 15 minutes, the initial concentration of PG in solution, after sorption, can be assumed 35%.

Once the AS degrades a portion of that 35%, the PG sorbed to AS presumably returns to solution for degradation to account for a 70% reduction in PG concentration by 12 hr. This result, the sorption and desorption of a compound has also been shown by Racz, et al. (2012). These results indicate that used ADF may be a candidate for degradation by AS with the use of a SBR.

Significance of Research

While not the first to investigate degradation of propylene glycol (PG) as an aircraft deicer, this study investigated the PG degradation potential of municipal waste water treatment facility activated sludge (AS). Of major significance is the finding that heterotrophic bacteria readily consume PG, and nitrifying bacteria have little to no role in PG degradation. This study also took into account the role of sorption in the fate of PG in AS and found sorption to be a significant removal mechanism. However, sorption equilibrium isotherm models may not be the best predictor of sorption in a dynamic biological system where true equilibrium is elusive. This research should be considered a first step toward investigating the feasibility of fielding an operable, airfield used aircraft deicer (ADF) pre-treatment system.

Limitations

Common to lab based research, which intends to mimic field conditions, was the understanding that results obtained are merely indications, on which broad inferences can be made. It is generally impossible to accurately scale and represent field conditions, accounting for all variables that might impact an implemented, engineered system. This research focused, in part, on conducting a preliminary study that intended to only approximate field conditions for sorption equilibrium isotherm and degradation studies. More specifically, the intent of this study was to determine if pure PG is degradable by AS in an SBR rather than actual used ADF.

Another limitation of this research was the sensitive nature of the Gas Chromatography/Mass Spectrometry (GC/MS). The samples were typically diluted in order to measure the concentrations of PG within the range of the calibration curves. The implications of these constraints could be significant when trying to measure real-world used ADF concentrations of PG, which can reach 600,000 PPM.

Intuitively, laboratory experiments are subject to inaccuracies which can be attributed to unintended human error. Losses from sample transfer from apparatus to apparatus should not be ignored. Therefore, care was taken to account for these losses and to avoid contamination of laboratory equipment.

Used aircraft deicer (ADF) is, by its nature, inconsistent in composition. This inconsistency is due primarily to the fact that it comes in contact with airfield pavements and aircraft surfaces. Through overspray and drippage, ADF may trap or solubilize *in situ* salts, petrochemicals, or other organic or inorganic compounds. While PG is generally the primary constituent in pre-use ADF, it may not be the most harmful compound in the mixture once it is used. Therefore, successful degradation of PG by SBR does not account for inconsistent types and quantities of unknown compounds found only in field conditions. At a minimum, any field deployable degradation unit should contain oil/water separation and grit chamber, to mitigate compounds that might upset or cause the AS consortium to fail. Further investigation may reveal more requirements as a used ADF profile is developed.

Future Research

Before considering investment in deployment of a pre-treatment system, several research avenues should be investigated in order to determine feasibility. Future research should include:

1. Design of a field model, focusing on realistic constraints. Consider power requirements, oil/water separation, grit settling and removal, space available, maintenance requirements, training, frangibility considerations for an airfield, optimizing feed of reactor for year round operation, and discharge to local treatment facility or receiving water body.

2. Develop a general used aircraft deicer (ADF) solution. This study focused entirely on propylene glycol (PG) as it was assumed to be the largest component, by percentage of used ADF. Investigation and identification of actual constituents in field collected used ADF should be undertaken to understand variability and identify apparatuses that may need to be added to an airfield unit in order to account for those constituents. This study should further define the feasibility of fielding a unit for use.

Explore other treatment and disposal options for used ADF. While anaerobic digestion of used ADF has been widely studied, and proven to be plausible, metered and diluted flow to receiving water bodies as well as municipal waste water treatment facilities remain largely uninvestigated. This topic may require an advanced understanding of National Pollutant Discharge Elimination System (NPDES) permitting and other Environmental Protection Agency (EPA) regulations regarding disposal of used ADF.

Summary

The purpose of this research was to provide a first step in analyzing a possible ADF pre-treatment alternative available to the Air Force in order to meet EPA NPDES permitting regulations. Currently, Wright-Patterson Air Force Base, used as the subject for this study, disposes of its used ADF under hazardous waste contracts, which can be seen as a misuse because used ADF is not classified as hazardous. A premium is paid for the disposal method while the Air Force is allowed to simply collect and forget about the waste as it becomes the contractor's responsibility to dispose of properly. In an effort to allow the Air Force to take some ownership of its waste and not be subject to high disposal costs, this research investigated the ability of AS to degrade PG as an ADF through use of an SBR. Although only a preliminary analysis of general, biochemical feasibility, this study can be a first step toward the Air Force pre-treating its own waste.

Appendix A. Calibration Curves

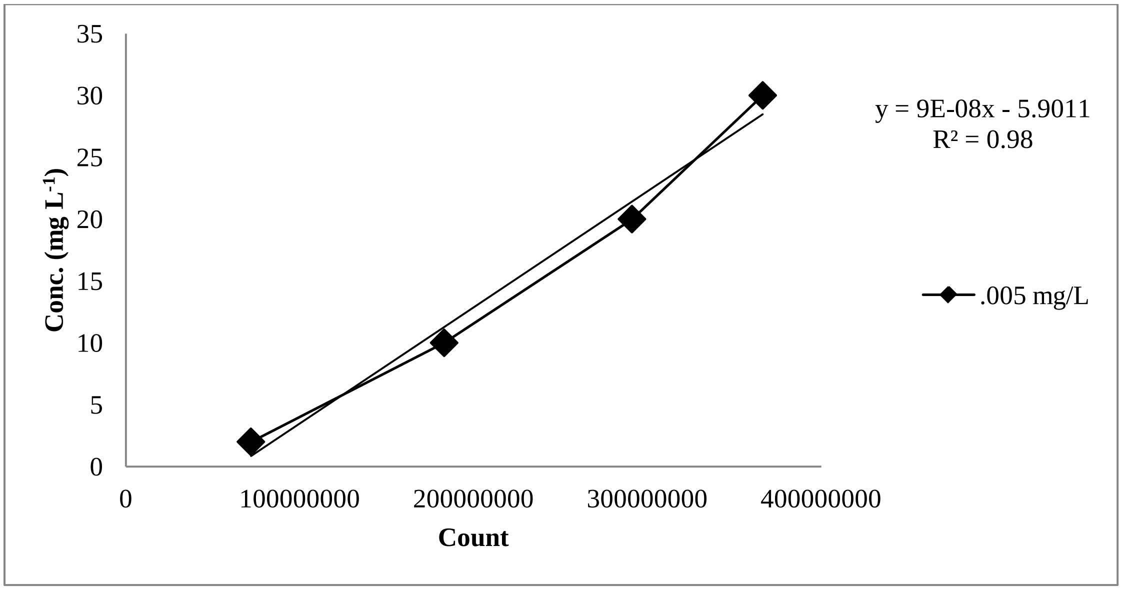

Figure 7. 5 µg L^{-1} Calibration Curve

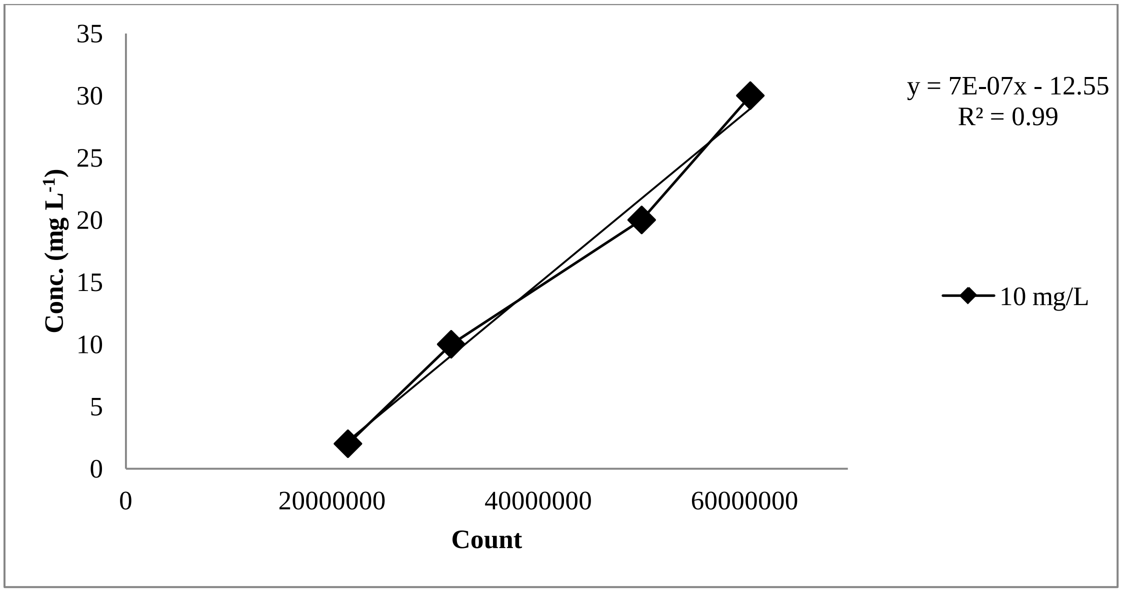

Figure 8. 10 mg L^{-1} Calibration Curve

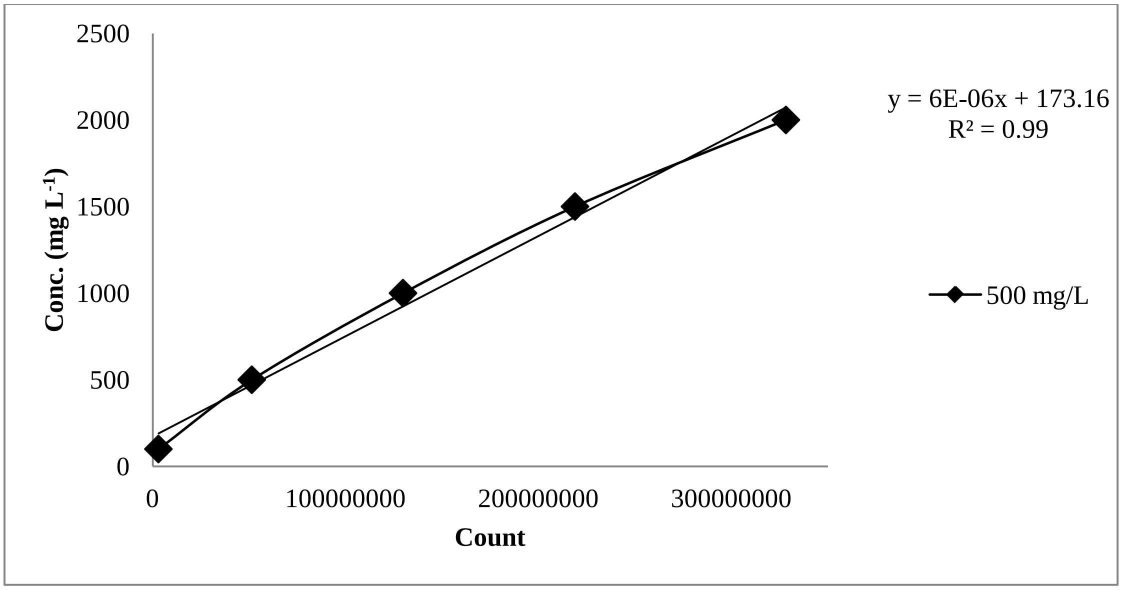

Figure 9. 500 mg L^{-1} Calibration Curve

Appendix B. Sorption Results

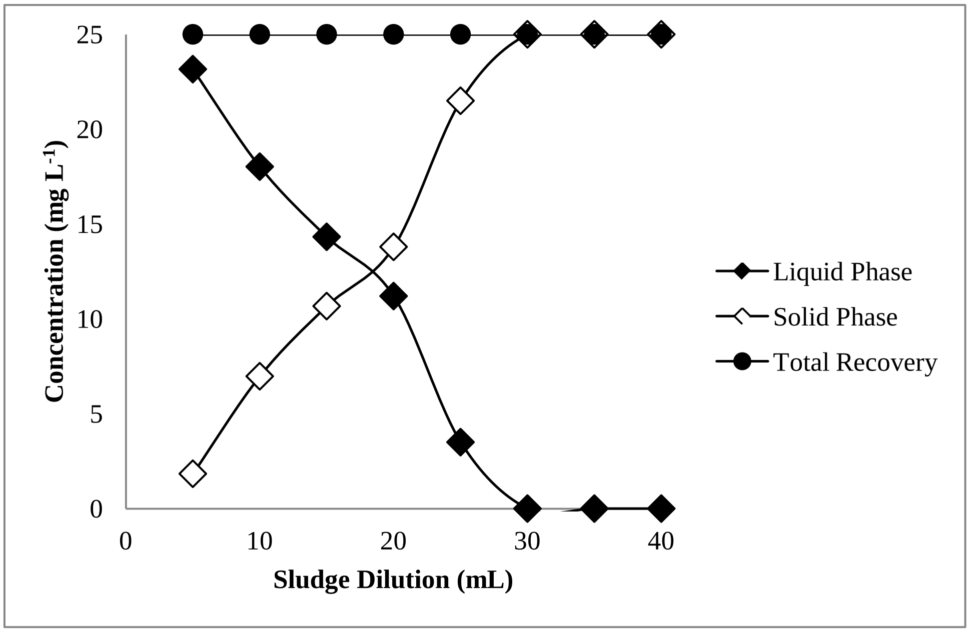

Figure 10. Sorption Kinetic Recoveries: 25 mg L^{-1}

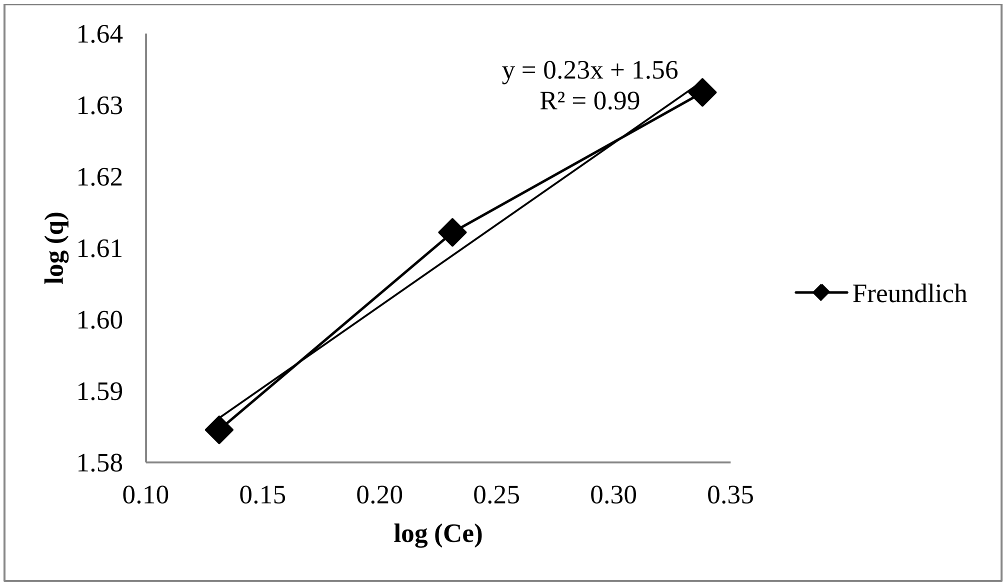

Figure 11. Freundlich Sorption Isotherm: 25 mg L^{-1}

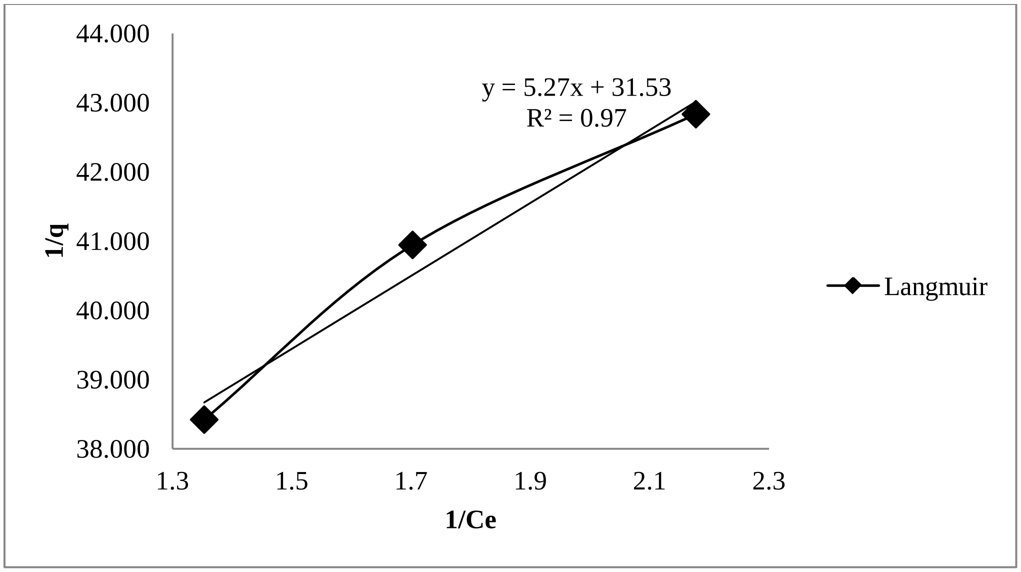

Figure 12. Langmuir Sorption Isotherm: 25 mg L^{-1}

Appendix C. Degradation Results

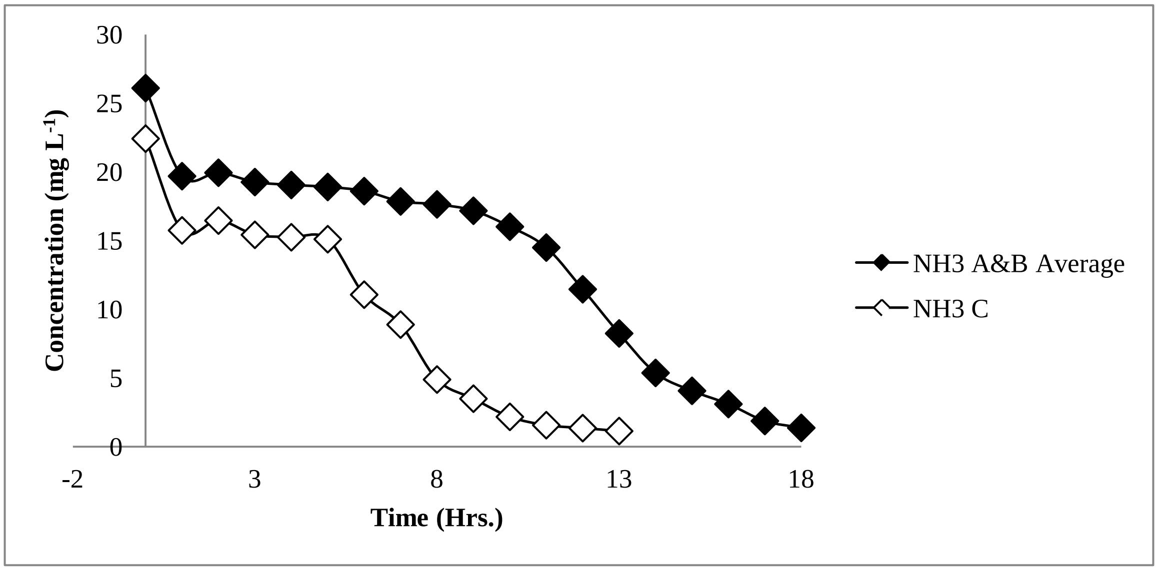

Figure 13. NH_3-N: 500 mg L^{-1} in activated sludge at 25° C with nitrifiers active

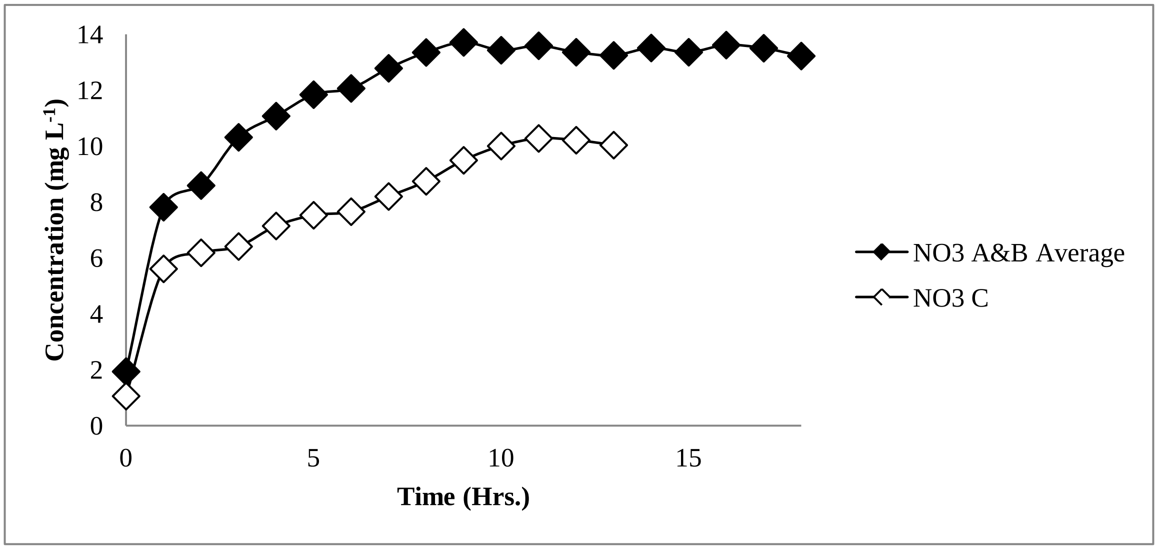

Figure 14. NO_3-N: 500 mg L^{-1} in activated sludge at 25° C with nitrifiers active

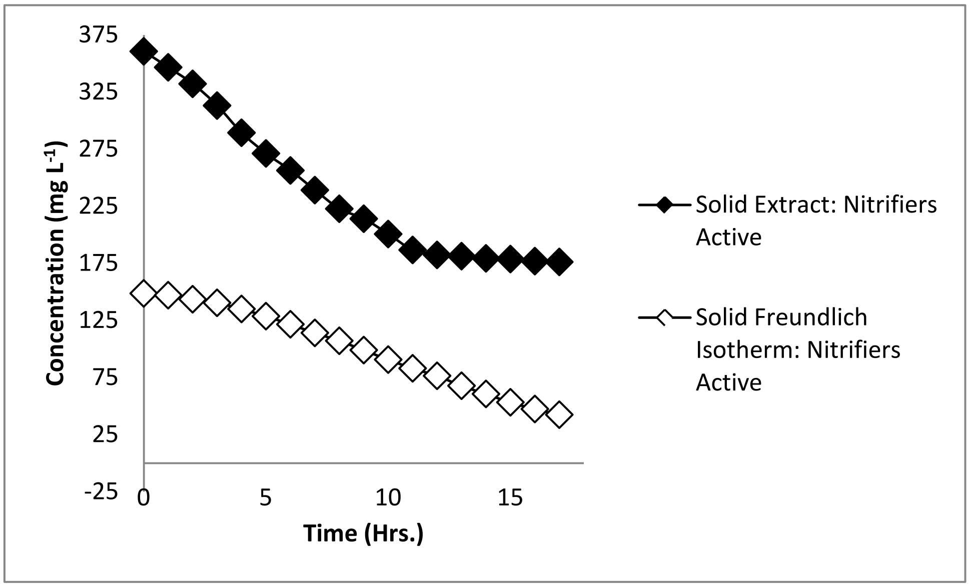

Figure 15. Freundlich Sorption Prediction/Degradation Sorption Results Comparison: nitrifiers active

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14. ABSTRACT
Aircraft deicing fluid used at airport facilities is often collected for treatment or disposal in order to prevent serious ecological threats to nearby surface waters. This study investigated lab scale degradation of propylene glycol (PG), the active ingredient in a common aircraft deicing fluid, by way of a laboratory-scale sequencing batch reactor containing municipal waste water treatment facility activated sludge (AS) performing simultaneous organic carbon oxidation and nitrification. The ability of AS to remove PG was evaluated by studying the biodegradation and sorption characteristics of PG in an AS medium. The results indicate sorption may play a role in the fate of PG in AS, and the heterotrophic bacteria readily degrade this compound. Therefore, a field deployable SBR may be appropriate for use in flight line applications.

15. SUBJECT TERMS
Aircraft Deicer, Activated Sludge, Biodegradation, Sorption, Wastewater Treatment

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